ECSS-E-HB-32-20 Part 5A
20 March 2011

EUROPEAN COOPERATION
ECSS
FOR SPACE STANDARDIZATION

Space engineering

Structural materials handbook - Part 5: New advanced materials, advanced metallic materials, general design aspects and load transfer and design of joints

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ESA-ESTEC
Requirements & Standards Division
Noordwijk, The Netherlands

Foreword

This Handbook is one document of the series of ECSS Documents intended to be used as supporting material for ECSS Standards in space projects and applications. ECSS is a cooperative effort of the European Space Agency, national space agencies and European industry associations for the purpose of developing and maintaining common standards.

This handbook has been prepared by the ECSS-E-HB-32-30 Working Group, reviewed by the ECSS Executive Secretariat and approved by the ECSS Technical Authority.

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Published by: ESA Requirements and Standards Division
ESTEC, P.O. Box 299,
2200 AG Noordwijk
The Netherlands

Change log

ECSS-E-HB-32-20 Part 5A 20 March 2011	First issue

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A glossary of terms, definitions and abbreviated terms for these handbooks is contained in Part 8.

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46 Aluminium alloys and their composites

46.1 Introduction

46.1.1 General

Aluminium alloys are established in aerospace, with many years of application and service experience.

Alloy developments are described that have aimed at improving the mechanical characteristics of basic aluminium alloys and the limitations on service temperature.

The ability to improve dimensional stability by combining alloys with low CTE materials is an advantage for space use.

The materials described are divided into the main groups:

- Conventional aluminium alloys.
- New aluminium alloys.
- MMC – metal matrix composites.
- FML – fibre metal laminates

46.1.2 Conventional aluminium alloys

In recent years it has become clear that many of the problems associated with conventional aluminium alloys, e.g. inconsistent fracture properties, were associated with the nature, size, morphology and distribution of intermetallic particles, both intended (as the strengthening phase) and unintended (from tramp elements). Attention has therefore focussed on improving both alloy chemistry and process technology to give more desirable structures in the finished material. In addition to alloy modifications, this has resulted in the introduction of modified thermo-mechanical treatments (combinations of heat treatments and hot or cold working) with new temper designations, which are expansions of the basic tempers, [See: 46.2].

Specific data on conventional aluminium alloys are not given in this handbook, [See: MMPDS-01 and PMP], Ref. [46-71], [46-72].

46.1.3 New aluminium alloys

These can be grouped as:

- Aluminium-lithium (Al-Li) alloys. [See: 46.4]
- Powder metallurgy (P/M) alloys:

- oxide dispersion strengthened alloys (ODS), having additions of small, stable particles, [See: 46.10].
- rapidly solidified powder (RSP) powder atomised materials which, due to rapid cooling, have different alloying mechanisms, [See: 46.11].

46.1.4 MMC - metal matrix composites

Various MMC material combinations are described, with emphasis on their typical mechanical properties and how these are affected by elevated temperatures. These materials can be classed as composites having:

- discontinuous reinforcement phases (particles or short fibres), [See: 46.12],
- continuous fibre reinforcement, [See: 46.14].

46.1.5 FML - fibre metal laminates

FMLs are laminated sheet materials containing either aramid fibres (ARALL), glass fibres (GLARE) or the newer derivatives with carbon fibres (CARE), usually between thin sheets of aluminium alloy.

Originally developed for aircraft skin structures, the materials and characteristics of interest for space use are described, [See: Chapter 100].

NOTE Many of the materials described are development products; some are more advanced commercially than others. All of the property data quoted is typical values.

46.1.6 Material availability

After a boom in the development of advanced aluminium-based materials, there have been some notable withdrawals of previously commercially-available products, Ref. [46-47]. Information on alternative materials is presented in the handbook, where possible.

Some organisations that have withdrawn products or ceased trading are:

- Cedegur Pechiney has been taken over by Alcan.
- Reynolds Metals have been taken over by Alcoa.

  NOTE Alcan and Alcoa are the remaining major suppliers for aluminium-lithium alloys.

- BP Metal Composites Ltd. (Farnborough, UK) has closed their site and no longer manufacture particulate reinforced aluminium alloys. BP continues with SIGMA fibres for titanium composites. The Farnborough site is now operated by AMC Ltd. who offer advanced alloys and MMC's produced by powder metallurgy.
- AMS Ltd. (previously Cray Advanced Materials) have ceased trading. Previously they were exponents of the use of LPF - liquid metal pressure forming for manufacturing continuous fibre and preform reinforced composite components. Similar process techniques are in use in the USA, [See: 46.14].
- Cospray Ltd. (part of Alcan) has closed. Previously they used the Osprey process to produce particulate reinforced aluminium alloys. However, a German Osprey licensee, PEAK Werkstoff (part of Erbslöh Gruppe, D) produces a range of aluminium alloys and MMC's.

- Alcan does not actively market Duralcan™ particulate reinforced MMC's, but the casting alloys are available to order.

Similarly, whilst a very large number of aluminium alloys, including a number of Al-Li alloys, have been registered with the Aluminum Association (USA), Ref [46-46], [46-59], only a limited number of alloys are of commercial significance and readily available. Likewise, further developments of alloy compositions, tempers and process technologies continue to show improvements in properties.

It is therefore imperative that the designer consults with the prospective material suppliers before making any commitment to the use of any particular material.

46.2 Conventional aluminium alloys

46.2.1 General

Aluminium alloys are established aerospace materials world-wide. Their performance and limitations, which are known for a wide range of environments, are based on over 40-years accumulated research, development, application and service experience.

The European Aluminium Association (EAA) provides details on aluminium alloys, markets and links to material suppliers in various market sectors, including aerospace.

This topic serves as a reference for those conventional aluminium alloys now finding use as matrix materials for the various metal matrix composites, Ref. [46-1], [46-2], [46-3], [46-71].

[See: ECSS-Q-70-71 for details of aluminium alloys for space use]

For design data, see MMPDS-01, Ref [46-71] which has superseded MIL-HDBK-5, Ref. [46-3].

46.2.2 Chemical composition

46.2.2.1 General

46.2.1 summarises the basis for classifying aluminium alloy composition under the International system, Ref. [46-60].

Alloy group	Wrought Alloys	Alloy group	Cast Alloys
	Major alloying elements		**Major alloying elements**
1XXX	99.00 percent minimum aluminium	**1XX.0**	99.00 percent minimum aluminium
2XXX	Copper	**2XX.0**	Copper
3XXX	Manganese	**3XX.0**	Silicon with added copper and/or magnesium
4XXX	Silicon	**4XX.0**	Silicon
5XXX	Magnesium	**5XX.0**	Magnesium
6XXX	Magnesium and Silicon	**6XX.0**	Unused Series
7XXX	Zinc	**7XX.0**	Zinc
8XXX	Other Elements	**8XX.0**	Tin
9XXX	Unused Series	**9XX.0**	Other Elements

For both cast and wrought alloys, the first digit indicates the main alloying element(s). For cast alloys only the product form is indicated by the digit after the point; 0 = castings, 1 and 2 = ingot.

⇩ ⇩

Wrought alloys: the second digit, initially 0, indicates minor modifications to the basic alloy composition.

Cast alloys: modifications to the original alloy are indicated by a serial letter added as a prefix, starting with A but omitting I, O, Q and X.

⇩

Condition (Temper) is indicated by a suffix letter separated by a hyphen. The basic temper can be followed by a further alpha-numeric code (optional)

Basic temper designations			
F	As fabricated. Products for which there are no special thermal or strain hardening processes.	H	Strain hardened. For wrought products which are strengthened by working, with or without thermal treatments. The H is always followed by one or more further digits.
O	Annealed. Used for cast products to improve ductility or dimensional stability and for wrought products to give lowest strength.	T	Thermally treated to stable temper other than F, O or H. Used for products thermally treated with or without strain hardening. The T is always followed by one or more further digits.
W	Solution heat treated. Unstable temper, used only for alloys which spontaneously age harden at room temperature.		**NOTE**: The letter P can be used, after the temper designation, to indicate variations to H, T or O tempers agreed between supplier and purchaser.

Figure 46.2-1 – Aluminium alloys: Chemical composition and temper designation

Specifications and standards exist for aerospace grade aluminium alloys within each country, e.g. DIN, ISO, DTD, and an International numbering system, based on the American Aluminium Association (AA) system, is widely-used for wrought alloys, Ref [46-59].

The International system has largely replaced the nationally-based alloy designations within Europe.

Russian wrought alloy designations, although using a 4-digit code, are different to the AA international system.

46.2.2.2 Cross referencing national standards

Table 46.2.1 and Table 46.2.2 enable comparison of some national specifications for wrought and casting alloy designation numbers respectively, although this is not a definitive list, Ref. [46-1].

In addition the UNS system for numbering metals and alloys covers aluminium alloys, with code numbers from A00001 to A99999, with the last four digits reflecting the ANSI code for the alloy, Ref. [46-61]. Conventional alloy specifications, plus supplier product codes, are provided in Ref. [46-47].

Variations in alloy chemical composition can exist within different specification systems for so-called 'equivalent' alloys. Care is needed when comparing alloys across different standards systems.

Table 46.2-1 - Aluminium alloys: Comparison of national specifications for wrought alloys

International	**Alloy**	**UK**	**France**	**Germany**		**Italy**		**Sweden**	**Spain**	**Switzerland**	**CIS**	**EUROPE**
AA	Type (1)	Old BS	Old NF	Werkstoff	DIN	Old UNI	New UNI	SIS	UNE			CEN (2)
1050A	Al99.5	1B	A5	3.0255	Al99.5	-	9001/2	4007	L-3051	Al99.5	-	AW-1050A
1080A	Al99.8	1A	A8	-	Al99.8	-	9001/4	4004	L-3081	-	-	AW-1080A
1199	-	1	A9	-	-	-	-	-	-	-	-	AW-1199
1200	Al99	1C, 6L16, 6L17, 4L34	A4	3.0205	Al99	3567	9001/1	4010	L-3001	Al99.0	A0	AW-1200
1350	[Al99.5]	1E, G1E	A5L A5B	3.0257	E-Al	-	9001/5	-	-	E-Al99.5	-	AW-1350
2011	Al Cu6 Bi Pb	FC1	A-U5 Pb Bi	3.1655	Al Cu Pb Bi	6362	9002/5	4355	L-3191	Al Cu6 Pb Bi	-	AW-2011
2014A	Al Cu4 Si Mg	H15, L-grades; DTD.	A-U4 S G	3.1255	Al Cu Si Mg	3581	9002/3	4338	L-3130	Al Cu4 Si Mg	-	AW-2014A P-2014A
2017A	Al Cu4 Mg Si	L93, L94	A-U4 G	3.1325	Al Cu Mg1	-		-	-	-	-	AW-2017A P-2017A
2024	Al Cu4 Mg1	2L97, 2L98 DTD-5090, -5100A, (AMD2433)	A-U4 G1	3.1355	Al Cu Mg2	3583	9002/4		L-3140	Al Cu4 Mg1.5	D16 1160	AW-2024 P-2024
2030	[AlCuPbMg]	-	A-U4Pb	3.1645	AlCuMgPb	-	-	-	-	-	-	AW-2030
2031	[AlCu2Ni1 MgFeSi]	H12	A-U2 N	-	-	-	-	-	L-3160	-	-	-
2117	Al Cu2 Mg	3L 86	A-U2 G	3.1305	Al Cu Mg0.5	3577	9002/1	-	L-3180	-	D18	- P-14
2214	[AlCu4SiMg]	-	Air-9048-610, -620.	-	AlCuSiMn	-	-	-	-	-	-	P-2214
2218	{AlCuNi]	6L25	A-U4N	-	-	-	-	-	L-315	-	-	-
2524	[AlCu4Mg]	-	-	-	-	7250	-	-	-	-	1163	-
2618A	-	H16, DTD	A-U2 G N, Air-9048-640	3.1924		3578	9002/6	-	L-3171	-	AK4-2	AW-2618A P-2618A
3103	Al Mn1	N3, NS3	A-M1	3.0515	Al Mn	3568	9003/3	4054	L-3811	Al Mn	1400	AW-3130
3105	-	N31, NS31	A-MG05	3.0505	AlMn0.5Mg0.5	3103	9003/5	-	L-3831	-	-	AW-3150
4043	[AlSi5]	N21	A-S5	3.2245	-	-	-	-	-	-	-	-
4047	[AlSi12]	N2	A-S12	-	AlSi12	-	-	-	-	-	-	-
5005	Al Mg1	N41	A-G0.6	3.3315	AlMg1	5764	9005/1	4106	L-3350	-	1510	AW-5005
5056	Al Mg5	N6, 2L58, 2L59	A-G5, A-G5M	3.3555	Al Mg5	-	-	4146	L-3320	-	1550	AW-5056 P-32
5083	Al Mg4.5 Mn	N8	A-G4.5M C	3.3547	Al Mg4.5 Mn	7790	9005/5	4140	L-3321	Al Mg4.5Mn		AW-5083
5086	Al Mg4Mn	-	-	-	AlMg4Mn	5452	9005/4	-	-	Al Mg4Mn	-	AW-5086 P-5086

5154A	Al Mg3.5(A)	N5	A-G3	3.3535	Al Mg3	3574	9005/8	-	L-3392	-	AMG3	AW-5154A
5251	Al Mg2	N4	A-G2 M	3.3525	Al Mg2 Mn0.3	-	-	-	L-3361	-	-	AW-5251
5454	Al Mg3.6	N51	A-G2.5M C	3.3537	Al Mg2.7 Mn	7789	9005/3	-	L-3391	AlMg2.7 Mn	-	AW-5454
5554	AlMg3Mn(A)	N52	-	-	-	-	-	-	-	-	-	-
5556A	AlMg5.2MnCr	N61	-	-	-	-	-	-	-	-	-	-
5754	[AlMg3]	-	A-G3 M	3.3535	Al Mg3	3575	-	4125	L-3390	Al Mg3	-	AW-5754
6060	AlMgSi	-	A-GS	3.3206	Al MgSi0.5	3569	9006/1	4103	L-3442	Al MgSi0.5	-	AW-6060
6061	Al Mg1 Si Cu	H20	A-GS U C	3.3211	Al MgSi1Cu	6170	9006/2	-	L-3420	-	AD3	AW-6061 P-6061
6063	Al Mg0.5 Si	H9	-	-	-	3569	-	4104	L-3441	-	AD31	AW-6063
6082	Al Si1 Mg Mn	H30	A-SG M0.7	3.2315	Al Mg Si1	3571	9006/4	4212	L-3453	Al Mg Si1 Mn		AW-6082 P-21, P-6082
6101A	E-AlMgSi(A)	91E	-	-	-	-	9006/3	4102	L-3431	-	-	-
6463	AlMgSi	E6, BT R6	A-85GS	3.2307	E-AlMgSi	3570	-	4102	-	-	-	-
7010	AlZn6MgCu	DTD5130A, DTD5120	-	3.4394	-	-	-	-	-	-	-	AW-7010 P-7010
7014	-	DTD5104A	-	-	-	-	-	-	-	-	-	-
7020	Al Zn4.5 Mg	H17	A-Z5 G	3.4335	Al Zn 4.5Mg1	7791	9007/1	4425	L-3741	Al Zn4.5 Mg1	-	AW-7020 P-7020
7049A	Al Zn8MgCu	-	A-Z8GU	-	-	-	-	-	-	-	-	AW-7049A
7075	Al Zn6 Mg Cu1.5	2L95, L160, L161, L162	A-Z5 G U Air-9048	3.4365	Al Zn Mg Cu1.5	3735	9007/2	-	L-3710	Al Zn6 Mg Cu1.5	V95	AW-7075, P-7075, P-42
8011A	AlFeSi	-	A-4L, A-FeS	3.0915	-	8011	-	-	L-3611	-		AW-8011A

Key: (1) Old ISO number; [CEN EN 573]

(2) EN573: AW prefix - engineering alloys. AL P prefix: AECMA aerospace alloy

Table 46.2-2 - Aluminium alloys: Comparison of national specifications for casting alloys

USA AA	SAE	**ISO**	**UK** BS/DTD	**France**	**Germany**			**Italy**	**Sweden** SIS	**Switzerland**	**CIS**	**Europe** CEN (2)
					Werkstoff	DIN	VDS	UNI				
150.1	-	Al99.5	LM0	A5	-	-		-	14 4022	G-Al99.5	-	-
170.1	-	Al99.7	-	A7	-	-		-	-	-	-	-
222.1 (1)	34	Al Cu10 Si12 Mg	LM12	-	-	-		3041	-	-	AL18V	-
242.2	39	Al Cu4 Ni2 Mg2	4L35	A-U4 N T	-	-		3045	-	-	-	-
295.1, .2	38	Al Cu4	2L91, 2L92	A-U5 G T	3.1841	G-Al Cu4 Ti		7256	-	G-Al Cu4 Ti	-	-
319.2	326	Al Si5 Cu3	LM4	A-S5 U	3.2151	G-Al Si6 Cu4	225	-	-	-	AL6	AC-45200 / AC-45000
333.0	-	Al Si8Cu3Fe	LM24	A-S10 U4	3.2161	AlSi8Cu3	226	-	-	-	-	-
336.1	321	Al Si11 Mg Cu	LM13	A-S11 UNG	-	-		3050 / 6250-28	-	-	AL30	-
355.1	322	Al Si5 Cu1 Mg	LM16	-	-	-		3600	14 4231	-	AL5	AC-45300 / AC-AlSi5Cu1Mg
356.1	323	Al Si7 Mg	LM25	A-S7 G	3.2371	G-Al Si7 Mg		3599	14 4244	G-AlSi7 Mg	AL9	AC-42000 / AC-AlSi7Mg
A356.2	336	Al Si7 Mg	2L99	A-S7 G0.3	3.2371	G-Al Si7 Mg		7257	-	-	-	
A360.2	309	Al Si12 Mg	LM9	A-S10 G	3.2381	G-Al Si10 Mg	233	3049	14 4253	G-AlSi10 Mg	AL4	AC-43200 / AC-AlSi10Mg(Cu)
A380.1	306	Al Si8 Cu3 Fe	LM24	A-S9 U3 Y4	3.2161	G-Al Si8 Cu3		5075	14			-
384.1	303	Al Si10 Cu2 Fe	LM2	A-S9 U3 Y4	-	-		5076	-	-	-	-
390.0	-	Al Si17 Cu4 Mg	LM30	-	-	-		-	-	-	-	-
A413.1	305	Al Si12 Cu Fe	LM20 / LM2	A-S12, A-S12U	3.2582	G-Al Si12 (Cu)	231	5079	14 4260	-	AL2	AC-47000 / AC-AlSi12(Cu)
A413.2	-	Al Si12	LM6	A-S13	3.2581	G-Al Si12	230	4514	14 4261	-	-	-
A443.1	35	Al Si5	LM18	-	-	-		5077	-	-	-	-
514.1	320	Al Mg5	LM5	A-G6	3.3561	G-Al Mg5	244	3058	-	-	AL28	AC-51300 / AC-AlMg5
520.0	324	Al Mg10	LM10	A-G10, A-G10Y4	3.3591	G-Al Mg10		3056	-	-	AL8, AL27	-
712	310	AlZn5Mg / Al Zn5 Mg Cr	LM31, DTD5008B	A-Z5G	-	-	-	3650 / 3602	14 4438	-	-	AC-71000 / AC-AlZn5Mg
-	-	Al Si6 Cu4 Zn	LM21	A-S5 U Z	3.2151	G-Al Si6 Cu4	225	-	14 4230	-	AL16V	AC-45000 / AC-AlSi6Cu4-
-	-	Al Si6 Cu3 Mn	LM22	A-S5 U	-	-	225	3052	-	-	AL6	AC-45400 / AC-AlSi5Cu3
-	-	Al Si9 Cu3 Mg	LM26	-	-	-		3050	-	-	-	-
-	-	Al Si7 Mg	LM27	-	-	-		-	14 4230	-	-	AC-46600 / AC-AlSi7Cu2
-	-	Al Si19 Cu Mg Ni	LM28	-	-	-		6251	-	-	-	-
-	-	Al Si23 Cu Mg Ni	LM29	-	-	-		-	-	-	AL26	-
-	-	Al Si2 Cu Ni Fe Mg	3L51	A-S2 U	-	-		-	-	-	-	-
-	-	Al Cu2 Ni Si Fe Mg	3L52	-	-	-		3046	-	-	-	-
-	-	Al Si5 Mg	DTD:716B, 722B 727B, 735B	A-S4 G	3.2341	G-Al Si5 Mg	235	3054	-	-	-	- -
-	-	Al Mg8 Zn	DTD5018A	-	-	-	349	-	-	-	-	AC-51200 / AC-AlMg9

Key: (1) inactive. (2) EN1706: AC prefix – aluminium cast alloys.

46.2.3 Aerospace alloys

46.2.3.1 General

The prime groups of alloys used are the 2XXX, 6XXX and 7XXX (wrought) and Al-Si casting alloys. These materials, after specific conditioning, achieve high strengths.

46.2.3.2 AECMA EN standards

European standards and specifications (EN) are being developed and adopted. These are progressively superseding the various National standards in member states, Ref. [46-47].

Aerospace EN specification designations are controlled by AECMA and apply to a particular alloy, condition and form, e.g.

EN 2092 Aerospace series: Aluminium alloy Al-P7075-T6 or T62:

clad sheet and strip between 0.4mm and 6mm.

For information on AECMA standards, [See: http://www.aecma-stan.org]

46.2.3.3 SAE AMS standards

These are widely-used aerospace standards, published by the Aerospace Division of SAE International, as Aerospace Materials Specifications (AMS). They cover items such as manufacturing and assembly processes, heat treatments and protection systems, so are in addition to chemical compositions standards.

[See: http://www.aerospace.sae.org]

46.2.4 Properties

46.2.4.1 Elevated temperatures

Depending on the precise alloy composition and conditioning, mechanical properties decrease with increasing temperature above about 100°C.

Certain conventional wrought alloys, such as 2014A, 2031 and 2618A, have been developed to retain usable properties to 200°C and 300°C, but these are the exception, Ref. [46-1].

46.2.4.2 Low temperatures

In general, the strength, ductility and toughness properties of aluminium increase with decreasing temperature, Ref. [46-48]. There is no transition temperature below which brittleness occurs, Ref. [46-1].

Of the various conventional alloy compositions available, only a few are considered for low-temperature engineering applications, Ref. [46-48]:

- CP - pure aluminium, which has high conductivity, e.g. used for electrical applications.

- Al-Cu, which has reduced notched toughness at low temperatures, so not widely used.
- Al-Mn, which has moderate strength, e.g. tube, plates in heat exchangers applications.
- Al-Mg, which is weldable. Cold work impairs ductility, e.g. storage and transportation tanks.
- Al-Mg-Si, which has moderate strength, is weldable with post-weld treatment, e.g. mainly aerospace applications.
- Al-Zn-Mg, which has a severe loss of notch toughness below about 77K, so is not used.

46.3 New aluminium alloys

46.3.1 Developments

The main developments in aluminium alloys can be grouped as:

- Al-Li - aluminium-lithium alloys, [See: 46.4].
- ODS - oxide-dispersion-strengthened systems, [See: 46.10].
- MA - mechanically alloyed systems, which are applied to Al-Li and ODS alloys.
- RSP - rapidly solidified powder systems, [See: 46.11].

All these materials offer weight-savings through increased specific properties or greater thermal stability than conventional alloys.

46.3.2 Aluminium-scandium alloys

There is also interest in aluminium-scandium alloys, seen by some as the next generation of aluminium alloys.

Work on scandium additions in Al-alloys began in the 70’s in Russia, with some US patents issued around the same time. In the 80's, Sc-additions in several alloy systems were investigated in Russia, which resulted in a series of Russian Al-alloys with a minor Sc content.

The effect of the Sc-addition depends on the type and composition of the alloy, but the advantages claimed include:

- Increased strength from Al_3Sc precipitates.
- Grain refinement during casting or welding.
- Increased resistance to recrystallization and enhanced superplastic properties, which result from the grain boundary pinning by Al_3Sc particles.

ICAA conferences have seen increasing numbers of papers on Al-Sc alloys over the past 10-years. Currently, the majority of openly-published information relates to metallurgical studies and evaluation, Ref. [46-86].

Application examples come mainly from the sports and leisure equipment industry, but aerospace organisations are also investigating Al-Sc alloys, e.g. used on the MiG-29.

46.4 Al-Li - Aluminium-lithium alloys

46.4.1 Development

46.4.1.1 Chemical composition

The two main groups of aluminium-lithium alloy compositions are:

- Without copper, such as Al-Mg, e.g. Russian alloys including 1420.
- Copper-containing, e.g. 2XXX and 8XXX series alloys.

Only the copper-containing alloys have so far achieved commercial application, so discussion is limited to these.

Irrespective of their group, the low fracture properties of early Al-Li alloys was linked to the presence of tramp elements, i.e. Na, K, Ca, H and S, which can now be controlled by the use of high-purity Li metals and appropriate manufacturing processes.

The current generation of Al-Li alloys limit some elements within compositions to, Ref. [46-52]:

- <0.002wt% Na.
- <0.2wt% Fe and <0.1wt% Si, typically: Fe and Si form coarse constituent particles in age-hardening alloys.

Higher silicon contents have been linked to an increased susceptibility to SCC stress corrosion cracking.

46.4.1.2 Effect of lithium additions

The addition of lithium to an aluminium alloy reduces the density and increases the stiffness. As a guide, each 1% of Lithium decreases density by approximately 3% and gives a 6% modulus increase (for additions up to ~4%).

Aluminium-lithium alloy development had to overcome many production difficulties and uncertainties regarding the long-life suitability, in terms of transverse fracture sensitivity. The anisotropy, mainly resulting from the textures developed during processing, still remains one of the major obstacles to the wider use of these alloys and much of the current R&D activity is focussed on overcoming this problem.

46.4.2 Processing

The majority of initial development centred on ingot metallurgy for producing wrought products. This was followed by:

- forging grades,
- weldable alloys,
- powder metallurgy,
- particulate reinforced composites,
- superplastic forming.

46.4.3 Applications

Aluminium-lithium alloys aim to supersede selected 2XXX and 7XXX series conventional alloys in aerospace structures, in particular the conventional alloys used for specific characteristics, i.e.:

- Damage tolerant: 2024-T3, 2204-T3
- Medium strength: 2014-T6, 2214-T6
- High strength: 7075-T6, 7050-T6
- Corrosion resistant: 7075-T73
- Weldable alloy: 2219

A number of comprehensive reviews have been undertaken on aluminium-lithium alloys, Ref. [46-6], [46-14], [46-15], [46-49], [46-50]. These studies considered the characteristics of Al-Li alloys, along with information on potential applications.

46.4.4 Producers

Table 46.4.1 summarises the commercial sources of primary alloy and product forms, Ref. [46-56], [46-59], [46-62].

Table 46.4-1 - Al-Li alloys: Commercial sources and products

Alloy	**Supplier**	**Composition (a)**							**Forms**	**Tempers**	**Target replacements**
		Cu	Li	Mg	Zr	Ag	Zn	Mn			
Standard alloys											
2090	Alcoa	2.4-3.0	1.9-2.6	0.25	0.08-0.15	-	0.10	0.05	sheet; 3-10mm	T83	2024-T3, 7075-T6, 7475-T6
2098	Alcan	3.2-3.8	0.8-1.3	0.25-0.80	0.04-0.18	0.25-0.6	0.35	0.35	sheet; 6.4-7.7mm	T82P (b)	2024-T62
2x98	Alcan	recent modification to 2098 to give enhanced damage tolerance							sheet	T82P (b)	2024-T62
2099	Alcoa	2.4-3.0	1.6-2.0	0.10-0.50	0.07-0.13	-	0.4-1.0	0.10-0.50	extrusions 1.2-75 mm	T8E65, T8E67	7075-T6511, 7050-T76511 2024-T3511, 2026-T3511
2195	Alcan	3.7-4.3	0.8-1.2	0.25-0.80	0.08-0.16	0.25-0.6	0.25	0.25	plate 6.4-50mm	T8R78	2219-T87
2196	Alcan	2.5-3.3	1.4-2.1	0.25-0.80	Ti+Zr 0.25	0.25-0.6	0.35	0.35	extrusions 1.6-25mm	T8511	7075-T76511
2297	Alcan	2.5-3.1	0.8-1.3	0.10-0.50	0.04-0.18	-	0.05	0.35	plate 35-150mm	T87	2124-T851
8090	Dolgarrog, Otto Fuchs (c)	1.0-1.6	2.2-2.7	0.6-1.3	0.04-0.16	-	0.25	0.10	sheet; extrusions/ forgings	T3, T34	-
1441	VIAM	1.6	1.7	0.95	0.08	-	-	-	Plate/sheet, extrusions	T1, T11	2024, 2524
Special order alloys											
2050	Alcan	3.2-3.9	0.7-1.3	0.20-0.6	0.06-0.14	0.20-0.7	0.25	0.20-0.50	-	-	-
2094	Alcan	4.4-5.2	0.7-1.4	0.25-0.80	0.04-0.18	0.25-0.6	0.25	0.25	-	-	-
2095 (d)	Alcan	3.9-4.6	0.7-1.5	0.25-0.80	0.04-0.18	0.25-0.6	0.25	0.25	-	-	-
2097 (e)	Alcoa	2.5-3.1	1.2-1.8	0.35	0.08-0.16	-	0.35	0.10-0.60	-	-	-
AMC500	AMC	(f)							Forgings	T1	-

Key:		
	(a)	A single figure denotes maximum content, except for 1441 where figures are nominal
	(b)	Supplied on 'O' temper for subsequent heat treatment
	(c)	Dolgarrog produce sheet; Otto Fuchs produce extrusions and forgings
	(d)	Similar to 2195 but produced for super-plastic forming (SPF)
	(e)	Alcoa alloy similar to 2297
	(f)	Dispersion hardened Al-Li alloy made by proprietary powder metallurgy process

46.4.5 Manufacturing processes

The various processing routes used for Al-Li alloys can be summarised as:

- Inert atmosphere ingot casting, which is the primary source.
- Rolling into sheet or plate, which produces a higher degree of anisotropy compared with conventional alloys.
- Extrusions, where, again, higher degree of anisotropy achieved. Close tolerances on long sections can be difficult to achieve.
- Forgings, which are limited to simple shapes as Al-Li alloys rely on cold working prior to ageing to acquire strength. 8090 is well suited for hand forging and 2091 for precision forging.
- Near-net shape, covering development of forging and spin-forming techniques, Ref. [46-50].
- Thermo-mechanical treatment: Al-Li can be solution-treated using most established techniques. Complex new tempers have been developed to improve toughness by under ageing. These are designated by the letter 'X', e.g. T8X or by the letter ‘P’ where this has been negotiated between the manufacturer and purchaser, e.g. T82P.
- Welding, e.g. 2195, developing techniques, such as Variable Polarity Plasma Arc (VPPA), gas tungsten arc, laser-based and Friction-Stir welding, Ref. [46-50].
- Superplasticity, where superplastic grades of 8090, 2090 and 2095 are available.
- RSP - rapid solidification processes, such as Liquid Dynamic Compaction (LDC).
- Osprey ‘Spray Deposition’, used for particulate-reinforced 8090 alloys, called COSPRAY by Alcan and now carried by PEAK Werkstoff.
- Planar Flow Casting, to enhance specific attributes, i.e. high strength or corrosion resistance, elevated temperature performance or lower density by increased lithium content. Such materials are more expensive than those produced by the ingot route.
- Mechanical alloyed materials, such as AMC500, which offer improvements in thermal stability and better stress corrosion cracking resistance than ingot Al-Li products.

Mechanical alloying or ‘high energy milling’ is used for dispersions added to alloys, giving a discontinuously-reinforced metal-matrix composite, [See also: 46.13 - for properties of SiC reinforced alloys].

46.5 Al-Li alloys: Characteristics

46.5.1 General

Table 46.5.1 gives some typical characteristics of Al-Li alloys. Their use is seen as desirable because of a reduced density and increased stiffness, enabling mass-saving.

Table 46.5-1 - Al-Li alloys: Typical properties compared with 7075

Properties	**Alloy**								
	2090	2098	2099	2195	2196	2297	8090	AMC500	7075
Ultimate tensile strength (MPa) (1)	441-531	503-510	510-600	510-615	520-540	414-441	370-480	400-500	400-586
Yield stress (MPa) (1)	386-483	470-476	430-550	470-580	470-490	379-400	265-435	300-420	303-462
Tensile modulus (GPa)	79.4	76	78	76	77.6	75.2	77	77	71.7
Density (kg/m3)	2590	2700	2620	2710	2630	2650	2540	2580	2810
Coefficient of thermal expansion (×10–6/K)	23.6	-	-	-	-	-	21.4	-	23.6
Heat capacity (J/kg/K)	1203	-	-	-	-	-	930	-	960
Thermal conductivity (W/cm°C)	88	-	-	-	-	-	95.3	-	130
Electrical conductivity (% IACS)	17-19	-	-	-	-	-	-	19	33
Key: (1) Data from Table 46.6.1 or Ref [46-3], and cover a range of forms and tempers									

To successfully replace accepted 2XXX and 7XXX alloys, other properties need to be matched or improved, these include:

- Strength,
- Toughness, and
- Fatigue resistance, coupled with,
- Acceptable corrosion resistance.
-

Significant alloy development was needed to reach acceptance levels for these, and doubts have remained in some areas of particular sensitivity:

- Reduced ductility,
- Low transverse strengths, and
- Susceptibility to stress corrosion cracking.

Further studies have shown that a combination of a ‘moderate’ lithium content of between 0.8% to 1.9%Li, depending on the base alloy composition, combined with further alloying additions and process modifications, can improve the stress corrosion resistance and fracture characteristics, Ref. [46-50].

46.5.2 Microstructure

Characteristics specific to Al-Li alloys can be summarised as:

- Properties attained by Al-Li alloys are strongly dependent on their microstructure. This is affected by:
  - alloy chemistry,
  - processing route, and
  - thermo-mechanical treatments.
- Additions of copper and magnesium assist in the formation of fine precipitates, i.e. Al2CuMg and Al2CuLi.
- Grain refinement in Al-Li alloys is achieved by additions of zirconium, which also acts as a recrystallisation inhibitor.
- Most conventional aluminium alloys have an elongated "pancake" type of grain structure to provide superior mechanical properties in the longitudinal and long-transverse directions. However, this is deleterious to Al-Li alloys. So, as far as is possible, a recrystallised microstructure is sought, especially for damage-tolerant grades. This can be promoted by an under-aged temper, T8X. However, a recrystallised structure does not give the highest resistance to stress corrosion cracking.

A degree of optimisation and compromise is necessary to produce an Al-Li alloy with the necessary properties. The higher anisotropy in Al-Li alloys as compared to conventional alloys cannot be avoided.

Further studies have shown the importance of alloying and trace element control, Ref. [46-50]:

- Control of tramp elements (Na, K, Ca, H, S), which are known to reduce fracture toughness, Ref. [46-52].
- Control of Si and Fe; Si increases the susceptibility to stress corrosion cracking, Ref. [46-52].
- Control of the Li-to-Cu atomic ratio (to avoid formation of the δ′ phase) can produce good damage tolerance and durability (in X2096).
- Small Ag additions (0.25 to 0.60%, typically) to the basic Al-Cu-Li-Mg alloy, Ref. [46-51]:
  - • instigate the formation of fine precipitates, which improve fracture toughness.
  - • improve stress corrosion resistance.
- This work led to the development of the Weldalite™ series of Al-Cu-Li-Mg-Ag alloys, the most notable being 2195 which is now used for the External Tank for the NASA Space Shuttle.
- Mn additions to the base Al-Cu-Li system with a controlled Li-to-Cu atomic ratio can help reduce strength anisotropy.

46.5.3 Further development

Al-Li alloy and process development continues with the aim of optimising the material characteristics for supersonic civil transport. For these higher-temperature applications, one development alloy (RX818) had increased volume fraction of strengthening precipitates through higher levels of Cu and Mg and thermo-mechanical processing was used to develop an unrecrystallised microstructure, Ref. [46-63]. Although this alloy showed high strength levels, Ref. [46-64] it was later dropped from this study due to poor fracture toughness performance, Ref. [46-65].

Higher Cu- and Mg-levels when coupled with a Mn addition encouraged dispersoid formation and promoted the recrystallisation process (ML337 development alloy). This gave a good combination of thermal stability and mechanical properties (strength and fracture toughness) at temperatures up to 135°C, Ref. [46-64]. Initial work also indicated that ML337 exhibits more isotropic ductility in the three directions, so improving the sheet-forming ability, Ref. [46-51].

RX818 and ML337 are Reynolds Metals Company (now Alcoa) development alloys, based on the Weldalite™ system, for NASA. RX818 has undergone further development and is now available from Alcan, in a temper giving improved mechanical properties, as alloy 2098-T82P, Ref. [46-62].

46.6 Al-Li alloys: Properties

46.6.1 Data

Extensive, validated property data is increasing for these relatively recent alloys. Manufacturers' data sheets are a main source of comprehensive data.

As a result of anisotropy, the minimum strength properties in most Al-Li products occur at 60° to the working direction.

Tensile and fracture toughness data for the short-transverse (S-T) direction is scarce. This is a major deficiency as the S-T properties of Al-Li alloys are poor, especially the ductility and fracture toughness. The S-T fracture toughness can be as low as 50% of that of comparable conventional alloys. However, recent developments in the Weldalite™ family by Alcan (Pechiney) have resulted in alloy 2x98-T82P (based on 2098) which has similar strength but better fracture toughness than the conventional aerospace sheet alloy 2024-T62, Ref. [46-62].

46.6.2 Tensile properties

In general, the static strength levels of Al-Li alloys compare well with conventional medium and high strength alloys. The ductility is, however, usually lower.

Table 46.6.1 provides typical tensile properties for the various alloy types and product forms, Ref. [46-6], [46-56], [46-57], [46-58], [46-62].

Table 46.6-1 - Al-Li alloys: Mechanical properties

Alloy and temper	Form	Direction (1) (2)	UTS (MPa)	YS (MPa)	Elong. (%)
2090-T83	sheet	L	531	483	3
2090-T83	sheet	LT	503	455	5
2090-T83	sheet	45°	441	386	-
2098-T82P	sheet	LT	503	476	6
2x98-T82P	sheet	LT	510	470	6
2099-T8E65	extrusion	L	600	550	8
2099-T8E65	extrusion	LT	520	470	-
2099-T8E67	extrusion	L	580	520	9
2099-T8E67	extrusion	LT	510	430	-
2195-T8R78	plate, 38 - 50mm	L	555	530	9
2195-T8R78	plate, 38 - 50mm	LT	575	530	8
2195-T8R78	plate, 38 - 50mm	45°	560	505	9
2195-T8R78	plate, 38 - 50mm	ST	595	500	3.5
2195-T8R78	plate, 6.4 - 12.7mm	L	615	580	9
2195-T8R78	plate, 6.4 - 12.7mm	LT	600	556	11
2195-T8R78	plate, 6.4 - 12.7mm	45°	525	490	12
2195-T8	plate, 11.4mm	L	609	574	8.5
2195-T8	plate, 11.4mm	45°	526	490	12.7
2195-T8	plate, 11.4mm	55°	510	470	14.7
2195-T8	plate, 11.4mm	60°	527	472	14.9
2195-T8	plate, 11.4mm	65°	563	492	14.5
2195-T8	plate, 11.4mm	70°	567	503	9.2
2195-T8	plate, 11.4mm	LT	589	551	11.2
2196-T8511	extrusion, 1.2 - 6mm	L	520	470	6
2196-T8511	extrusion, 6 - 25mm	L	540	490	5
2297-T87	plate, 50mm	L	441	400	10
2297-T87	plate, 75mm	L	427	393	9
2297-T87	plate, 100mm	L	427	393	5
2297-T87	plate, 125mm	L	421	386	5
2297-T87	plate, 150mm	L	414	379	5
8090-T652	forging	L	430	350	4
8090-T852	forging	L	480	435	5
8090-T8151	plate	L	420	350	5
8090-T8151	plate	T	420	320	5
8090-T8151	plate	ST	370	265	2.5
8090-T81	sheet	L	420	360	8
8090-T81	sheet	T	415	290	11
1441-T1	sheet	L	415	315	16
1441-T1	sheet	T	430	325	14
1441-T1	sheet	45°	405	280	18
1441-T1	extrusion	L	450	360	9
1441-T1	extrusion	T	475	390	9
1441-T11	sheet	L	450	395	9.5

Alloy and temper	**Form**	**Direction (1) (2)**	**UTS (MPa)**	**YS (MPa)**	**Elong. (%)**
1441-T11	sheet	T	455	390	9
1441-T11	sheet	45°	440	380	8.5
AMC500F1-T1	Forgings, 10-50mm	L	400	300	8-10
AMC500sa-T1	Forgings, 10-50mm	L	500	420	7-9
Key (1) Direction is defined in ASTM E 1823-05 Annex 2; L - long; T – transverse; LT - long transverse; ST - short transverse; (2) Angle - in-plane relative to L direction.					

46.6.3 Fracture properties

A summary of the fracture properties for various Al-Li alloys and product forms is given in Table 46.6.2, Ref. [46-6], [46-49], [46-58], [46-62].

Reliable data is still sparse and fracture toughness remains a problem with the high strength Al-Li alloys, but the newer 2x98 alloy shows good promise.

Fracture toughness data for some sheet materials are provided in Figure 46.6.1, Ref. [46-6].

Table 46.6-2 - Al-Li alloys: Fracture properties

Alloy-Temper	Form	Direction (1)	K_Q MPa√m	K_{Ic} MPa√m	K_c MPa√m
2090-T83	sheet	L-T	-	-	43.9
2098-T82P	sheet (Pechiney)	LT	-	-	130
2x98-T82P	sheet (Pechiney)	LT	-	-	160
2099-T8E65	extrusion	L-T	-	30	-
2099-T8E65	extrusion	T-L	-	27	-
2099-T8E67	extrusion	L-T	-	66	-
2099-T8E67	extrusion	T-L	-	55	-
2195-T8R78	plate, 38 - 50mm	L	-	37	-
2195-T8R78	plate, 38 - 50mm	LT	-	35	-
2195-T8R78	plate, 6.4 - 12.7mm	L	-	40	-
2195-T8R78	plate, 6.4 - 12.7mm	LT	-	40	-
2195-T8R78	plate, 6.4 - 12.7mm	45	-	35	-
2297-T87	plate, 50mm	L-T	-	35.2	-
2297-T87	plate, 75mm	L-T	-	35.2	-
2297-T87	plate, 100mm	L-T	-	34.1	-
2297-T87	plate, 125mm	L-T	-	33	-
2297-T87	plate, 150mm	L-T	-	31.9	-
8090-T8771	plate	L	27	-	-
8090-T8771	plate	T	24	-	-
8090-T8771	plate	S-T	19	-	-
8090-T81551	extrusion	L	36	-	-
8090-T81551	extrusion	T	33	-	-
8090-T82551	extrusion	L	32	-	-
8090-T82551	extrusion	T	20	-	-
8090-T851	extrusion	L	30	-	-
8090-T851	extrusion	T	20	-	-
8090-T652	forging	L	23	-	-
8090-T652	forging	T	19	-	-
8090-T652	forging	S-T	14	-	-
8090-T852	forging	L	-	22	-
8090-T852	forging	T	-	20	-
8090-T8151	plate	L	35	-	-
8090-T8151	plate	T	30	-	-
8090-T8151	plate	S-T	18	-	-
8090-T81	sheet	L	-	-	160
8090-T81	sheet	T	-	-	122
1441-T1	sheet (a)	LT	-	76.5 / 99.2 / 124	-
1441-T1	sheet (a)	TL	-	73.0 / 98.5 / -	-
1441-T11	sheet (a)	LT	-	76.6 / 99.8 / -	-
1441-T11	sheet (a)	TL	-	76.8 / 102.0 / -	-

Key (1) direction is defined in ASTM E 1823-05 Annex 2;

(a) Sheet thickness 1.4mm to 1.8mm; widths 200mm / 400mm / 600mm

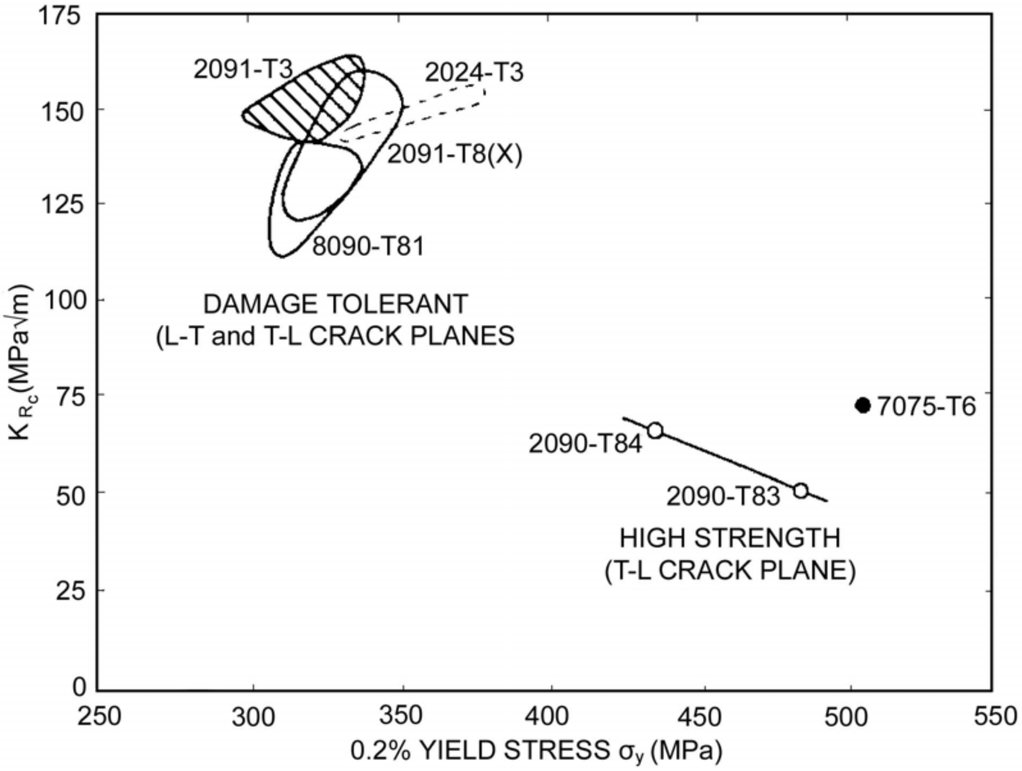


Figure 46.6-1 - Al-Li alloys: Fracture toughness versus yield strength for sheet materials

46.6.4 Fatigue properties

46.6.4.1 Crack growth

For sheet and thin plate, results to date indicate that the fatigue crack growth behaviour (growth rate v stress intensity factor) of Al-Li alloys is acceptable compared with that of conventional alloys.

Figure 46.6.2 and Figure 46.6.3 show evidence of this, although optimisation of heat treatment is necessary for each product form, Ref. [46-6].

Alloy 2091 shown in Figure 46.6.3 is not currently offered by Alcan (Pechiney) because alloys 2098 and 2x98 have largely superseded it. Since comparative data for these alloys is not published, the data for 2091 is included here for information only.

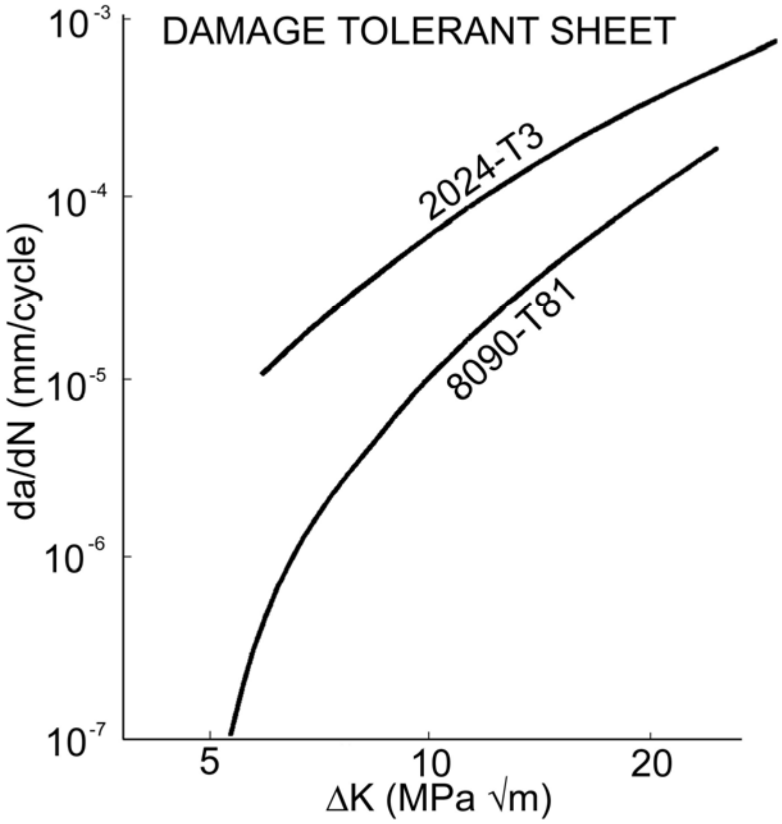


Figure 46.6-2 - Al-Li alloys: Comparison of fatigue crack growth behaviour for 2024-T3 and 8090-T81

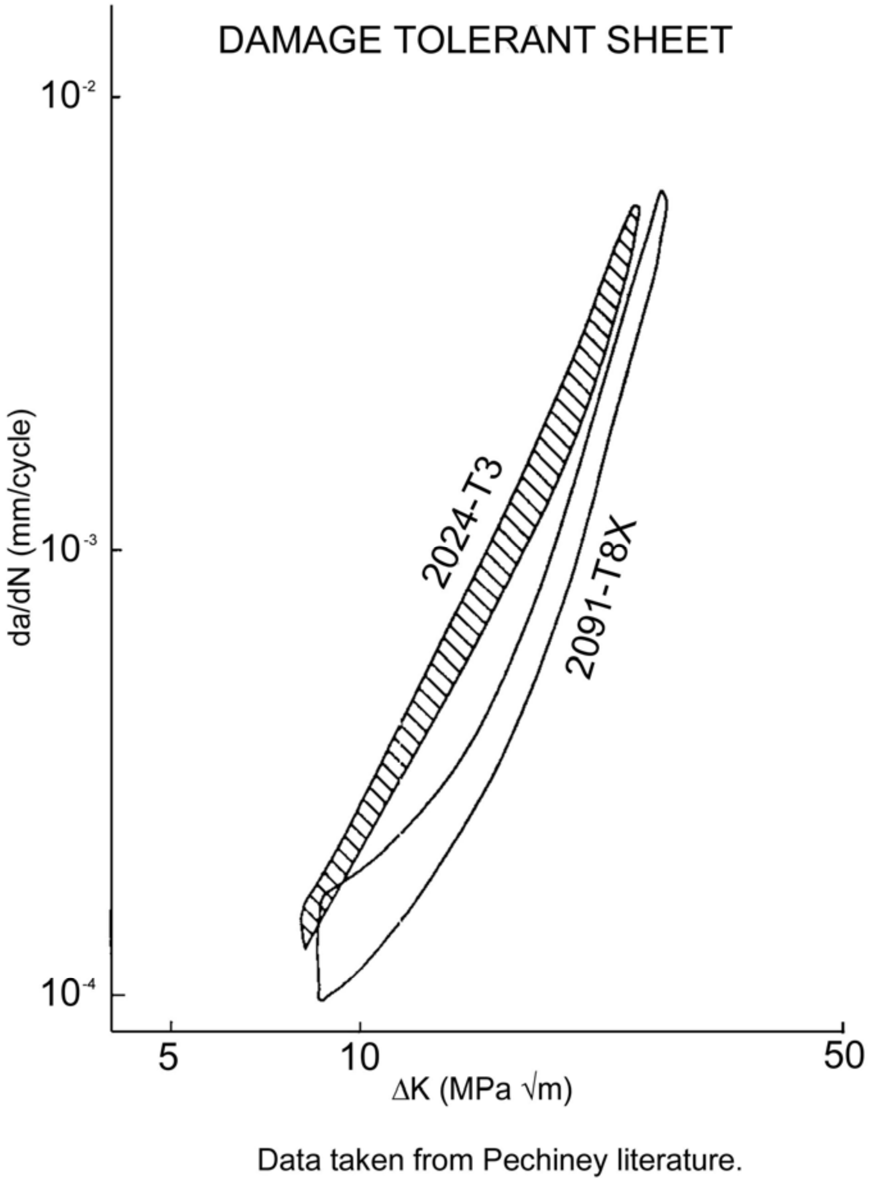


Figure 46.6-3 - Al-Li alloys: Comparison of fatigue crack growth behaviour for 2024-T3 and 2091-T8X

The Russian alloy 1441 is under evaluation by NASA as a fuselage sheet material and showed better fatigue crack growth resistance than the conventional fuselage sheet alloy 1163 Al (2524 alloy). The results are given in Table 46.6.3, Ref. [46-56].

Alloy 2524 is a variation of the 2024 alloy series, so these results can give an indication of properties compared with 2024.

Table 46.6-3 - Al-Li alloys: Fatigue crack growth rate of 1441 and 1163 sheet

Alloy and Temper (2)	**Direction (1)**	**ΔK MPa√m**	**$d(2a)/dN$, (mm/kcycle)**	
			average	range
1441-T1	LT	18.6	0.37	0.28 - 0.40
		31.0	2.00	1.26 - 3.17
	TL	18.6	0.29	0.14 - 0.51
		31.0	1.50	0.69 - 2.57
1441-T11	LT	18.6	0.79	0.42 - 1.21
		31.0	7.30	3.75 - 13.0
	TL	18.6	0.70	0.68 - 0.73
		31.0	3.40	2.56 - 4.14
1163-T3	LT	18.6	0.78	0.62 - 0.98
		31.0	3.85	3.30 - 4.40
	TL	18.6	0.92	0.74 - 1.14
		31.0	4.70	3.44 - 5.53
Test conditions:	Tested at a maximum fatigue stress of 100MPa and a frequency of 5Hz. The ratio of minimum fatigue stress to maximum fatigue stress (R) was 0. Tested on sheet 1.2mm to 2.0mm thick using centre-crack tension specimens from 300mm to 400mm wide.			
Key:	(1) direction is defined in ASTM E 1823-05 Annex 2; (2) 1163 is a Russian analog of AA2524			

The pronounced material anisotropy of thicker sections, such as in forgings, produces variations in fatigue crack growth behaviour. As shown in Figure 46.06.4, the short-transverse direction is noticeably poorer, Ref. [46-6].

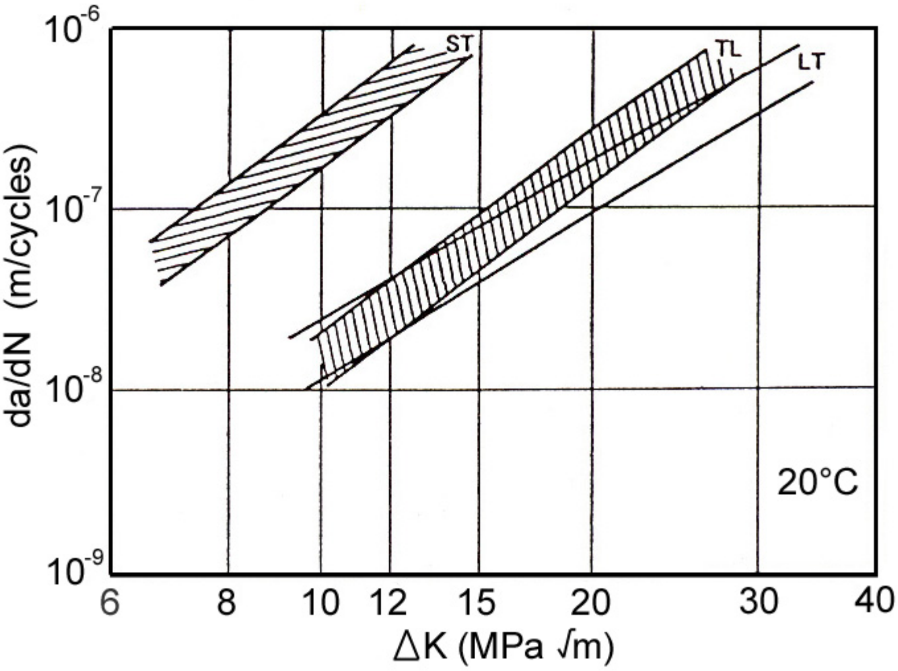


Figure 46.6-4 - Al-Li alloys: Comparison of fatigue crack growth behaviour LITAL A (8090) forgings at 20°C

46.6.4.2 Strength

It is now accepted that the fatigue strength (applied stress v cycles to failure) of Al-Li alloys can match that of the equivalent conventional alloys in most product forms. This is also valid for notched specimens. Published data on fatigue strengths can be confusing and depend on when the work was done, and whether specimens were notched or not. For dynamic mechanical applications, designers can use only that information on the most commercially developed ingots and their optimised heat treatments. Fatigue strengths in thicker sections have strong directionality.

46.6.5 Design values

46.6.5.1 General

Design values can only be stated for identifiable combinations of:

- alloy
- product form, and
- thermo-mechanical treatment

‘A’ and ‘B’ values are available from the suppliers for many of the other alloys referred to in this handbook, Ref. [46-62].

46.6.5.2 Extrusions

Table 46.6.4 gives an indication of data for extrusions that reflect the minimum guaranteed values which can be expected, Ref. [46-14].

Table 46.6-4 - Al-Li alloys: Design tensile strengths for extruded 8090 alloys

	8090-T8511		8090-T82	
	UTS (MPa)	**YS (MPa)**	**UTS (MPa)**	**YS (MPa)**
A-value(1)	505	434	515	441
B-value(1)	517	449	523	453
Average	532	468	534	468
Standard deviation	10.3	12.9	6.9	9.7
Key: (1) 'A' and 'B' values are available from the suppliers for many of the other alloys referred to in this handbook, Ref. [46-62].				

46.6.6 Further development alloys

Continued development of Al-Li alloys has centred on optimisation and overcoming the known property limitations of the first generation commercial alloys such that second, and now third, generation alloys have become available commercially and are covered in this handbook, [See also: 46.5].

Work continues on both alloy chemistry and process technology (including powder metallurgy techniques) to improve the isotropy and transverse fracture toughness properties.

Property data for many existing and newer Al-Li alloys is still under evaluation. 'A' and 'B' values are becoming available from alloy suppliers, who also provide other up-to-date information, Ref. [46-62].

Further data on alloy 2090-T83 sheet is published in MMPDS - Metallic Materials Properties Development and Standardization, which has replaced MIL-HDBK-5.

Additional data on alloy 2297-T8R85 plate is published in the PMP - Preliminary Material Properties Handbook, which is a precursor to inclusion in MMPDS, Ref. [46-71], [46-72].

46.7 Al-Li alloys: Stress corrosion cracking

46.7.1 General

For space applications, stress-corrosion cracking is the most critical form of degradation that demands examination because the SCC behaviour of earlier Al-Li alloys was poor. The situation has improved with modifications to alloy chemistry, tempering and ageing treatments.

[See also: ECSS-Q-ST-70-36: Material selection for controlling stress-corrosion cracking].

46.7.2 Test

The SCC performance of selected alloys is determined against ECSS-Q-ST-70-37 (ASTM G44 and G47) using a stressed specimen in a 3.5% sodium chloride (NaCl) solution.

Al-Li alloys are usually given a 'low resistance' (class 3) status, indicating that visual corrosion occurs after 30-days and specimen failures before 30-days are not uncommon.

The S-T short-transverse direction gives the lowest threshold stress for failure at levels as low as 50MPa.

ESA PSS-01-737 has been replaced by ECSS-Q-ST-70-37.

46.7.3 Stress corrosion cracking resistance

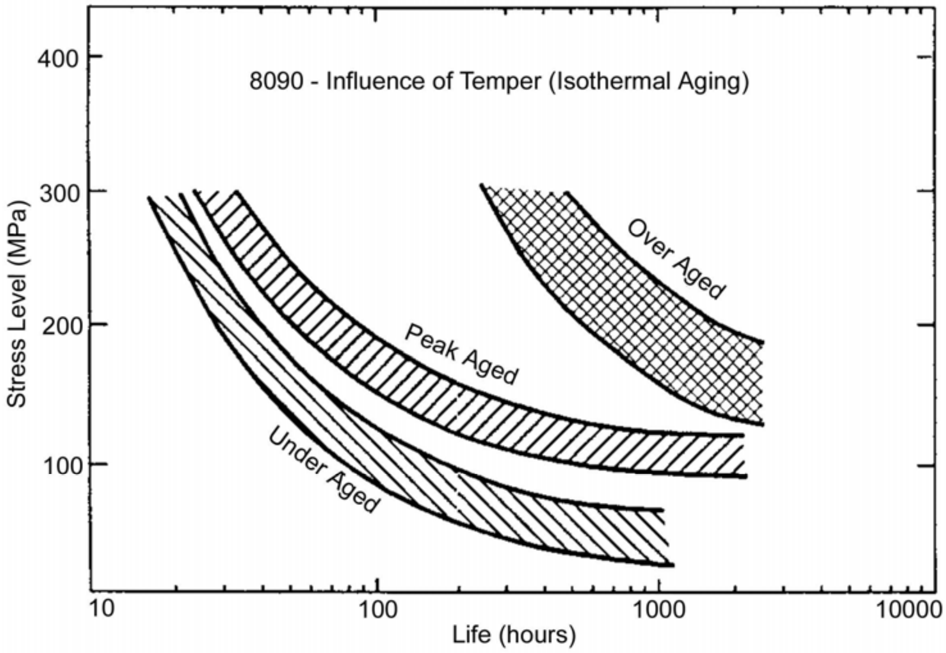
46.7.3.1 Alloy type and temper

For 8090-type alloys, the susceptibility to crack initiation is dependent on the copper content, particularly for alloys with low levels of magnesium. Cracks do not initiate in copper-free alloys. The initiation characteristics are also dependent on alloy temper. Overaged tempers give the best resistance to SCC initiation. Duplex ageing treatments can also assist in obtaining a balance between strength and SCC resistance. Where possible, the ageing temperature is reduced. Similar effects are noted in 2090 alloys, with peak-aged materials surviving longer.

The corrosion is influenced by the presence of Ti(Al2CuLi) precipitates at grain boundaries which are anodic to the matrix and preferentially dissolve causing intergranular cracking. Peak-ageing causes precipitation within the grains.

Small Ag-additions to Al-Cu-Li-Mg alloy systems have shown improvements in SSC resistance over non-Ag containing alloys, Ref. [46-51]. [See also: Recent alloys].

Figure 46.7.1 shows the effect of ageing on SCC behaviour, Ref. [46-17].



UA - 4 hours:190°C; PA - 16 hours:190°C; OA - 96 hours:190°C

Figure 46.7-1 - Al-Li Alloys: Influence of temper on stress corrosion cracking initiation for 8090 plates, S-T direction

Accumulated data on the SCC performance of 8090 Al-Li alloy for various product forms is given in, Ref. [46-15], [46-19], [46-18], [46-6]:

- Table 46.7.1, which gives the proposed classification of 8090 alloy in accordance with ECSS standards, along with the original ESA source.
- Table 46.7.2 gives tentative stress corrosion thresholds for 8090.
- Table 46.7.3 gives results of stress corrosion tests for 8090.
- Table 46.7.4 compares the SCC initiation behaviour of 8090 with conventional alloys.

Table 46.7-1 - Al-Li alloys: Alloy 8090 - Results of stress corrosion tests

ESA Metallurgy Report No.	Material type	Proposed classification(1) (2)
1338	8090-T651 (25 mm plate)	class 3
1474	8090-T8771 (90 mm plate)	class 3
1631	8090-T81 damage tolerant sheet (75% PS)	class 3
1632	8090-T81 damage tolerant sheet (50% PS)	class 3
1798	8090-T8 forging	class 3
Key	(1) Tests conducted to ESA PSS-01-737. This specification has been replaced by ECSS Q-ST-70-37; (2) See also: ECSS-Q-ST-70-36: Materials selection for controlling stress-corrosion cracking.	

Table 46.7-2 - Al-Li alloys: Tentative stress corrosion thresholds for 8090 alloy

Sheet	Temper	Alloy Category	LT SCC threshold, [MPa]
8090	T81	damage tolerant	200
8090	T6/T8	medium strength	> 350
Thin plate	**Temper**	**ST threshold stress, [MPa] (Al test 3.5% NaCl)**	
8090	T651	50-75	
8090	T8771	140	
Forging	**Temper**	**Threshold stress, [MPa]**	
8090	T652	200	

Table 46.7-3 - Al-Li alloys: Results of stress corrosion test on sheet material, as performed by NLR

Alloy	Nominal yield stress [MPa]	SCC test stress [MPa]	Lifetime [Days]	
			Initiation	Failure
8090-T8	450	200	>42	>42
		300	>42	>42
8090C-T3	214	200	>42	>42
		300	>42	>42
8090C-T81	341	200	1	>42
		300	2	>42

Table 46.7-4 - Al-Li Alloys: SCC initiation behaviour of 8090 alloy compared with that of conventional alloys

Alloy	Ageing Condition	S.T. Threshold Stress, [MPa]
8090	UA	60
	PA	115 (20 day)
	OA	230
8090	T651	<50 (20 day)
8090	UA	120 (2 day)
	PA	120 (6 day)
	OA	120 (29 day)
2024	T351	50 (20 day)
2014	T651	50 (20 day)
7070	T7651	150 (20 day)
7075	T7351	240 (20 day)

Key: UA = Under aged; PA = Peak aged; OA = Over aged.

46.7.3.2 Crack propagation

Crack propagation is assessed using a DCB double-cantilever beam specimen, which is notched and fatigue pre-cracked. Findings have been contradictory as to the relative merits of under- and over-ageing. Hydrogen embrittlement can also occur in saline environments. All investigations do show that for 2090 and 8090 alloys, the threshold stress intensity K_{1SCC} is reduced by over-ageing.

In general, the SCC behaviour of sheet and extrusion has improved during the alloy development programmes. However, problems are more acute with thicker-section plate and forgings.

46.7.4 Recent alloys

Alloy 2195, a member of the Weldalite™ family and commercially-available from Alcan, has undergone evaluation of its SCC and fracture characteristics as a replacement for 2219 in welded cryogenic fuel tank applications, Ref. [46-50], [46-51]. [See also: 46.9]

The other alloys offered commercially all show improved corrosion resistance, several having better properties than the conventional aerospace alloys 2024 and 7075.

Alloy 2297, whilst having lower strength level than some of the other newer Al-Li alloys, shows comparable SCC resistance to conventional 7XXX-series alloys, even in heavy plate sections up to 150 mm thick.

Table 46.7.5 provides a summary of SCC resistance and EXCO - exfoliation corrosion susceptibility data for currently-available plate, sheet and extrusions, Ref. [46-62].

Table 46.7-5 - Al-Li alloys: Current commercial alloys – summary of corrosion resistance

Alloy	Form	Direction (1)	SCC resistance (a)		EXCO(2) rating (b)
			MPa	Duration	
2098-T82P	sheet	LT	>240	30	-
2x98-T82P	sheet	LT	>240	30	-
2099-T8E65	extrusions	LT	330	-	P/EA
2099-T8E67	extrusions	LT	250	-	P/EA
2195-T8R78	plate	-	345	30	≥ EA
2196-T8511	extrusions	-	-	-	≥ EA
2297-T87	plate	ST	207	30	≥ EA

Key:
(1) Direction to ASTM E 1823
(2) EXCO – exfoliation corrosion susceptibility
(a) to ASTM G47
(b) to ASTM G34

46.8 Al-Li alloys: Manufacturing aspects

46.8.1 General

Special attention is given to health and safety, along with handling of Al-Li scrap to avoid contamination of that from conventional alloys. Therefore, the same processing equipment cannot be used for both conventional and Al-Li alloys.

46.8.2 Machining

Al-Li alloys have machining characteristics similar to those of other aluminium alloys, with small differences in cutting speeds and achievable surface finish. Aspects of machining can be summarised as:

- Chemically-active dust particles are generated. The presence of Lithium hydroxide can irritate the respiratory system if inhaled.
- Chemical milling generates more residue, so special equipment is needed for its efficient removal.
- Operations that generate molten metal, e.g. EDM electro-discharge machining, are best avoided because molten Al-Li alloy reacts violently in the presence of moisture.
- All scrap and swarf needs segregation from other recyclable aluminium alloys to avoid Li contamination and possible damage to furnaces not designed for Li-containing alloys.

Al-Li alloys probably need dedicated machining facilities.

46.8.3 Welding

Weldalite 049® was developed specifically for enhanced weldability. The subsequent developments in this family of alloys, and in particular alloy 2195, are candidates to replace the existing weldable alloy 2219, Ref. [46-50].

2195 behaves well at cryogenic temperatures, especially when given a modified two-step aging treatment, increasing its potential as a material for cryogenic fuel tanks, Ref. [46-67], [See also: 46.9]. The Li-content of 0.8 to 1.2% gives a modest mass-saving.

Other Al-Li alloys are weldable under suitable conditions and many of the newer alloys now commercially-available show excellent weldability:

- Surface layers on the alloy are removed by chemical or mechanical machining, to prevent porosity in the weld.
- TIG welding has been successfully applied to alloy 8090, using Al-5Mg filler metal. A post-weld ageing treatment improves the strength.
- For alloy 2090, welds have been achieved with 4047 and 4145 fillers. Post-weld solution-treatment and ageing can increase the weld strength to 80% of the base metal strength.
- Weldments in alloy 2195 made with the VPPA (variable polarity plasma arc) technique have been extensively examined, Ref. [46-50], [46-66].
- The newer technique of FSW - friction stir welding has also been examined with encouraging results, Ref. [46-66].

The welding of alloy 2195 has been extensively studied as part of the SLWT - super light weight tank development programme at NASA. The results of a study into the effects on fatigue crack growth rates are summarised in Table 46.8.1, Ref. [46-66].

The results indicate that both VPPA and FSW produced acceptable quality welds.

[See also: 46.6 – fatigue properties]

Table 46.8-1 – Al-Li alloys: 2195-T8 plate and weldments - summary of fatigue crack growth rate

Alloy + condition	t (mm) [3]	Orientation	R	Test temp.[3] (°C)	ΔK[3] (MPa√m) 6.6	11	22	Specimen ID
2195-T8 plate [1]	6.35, 12.7	L-T, T-L	0.1, 0.5	24	0.5-1.4	4.3- 7.8	33.7-78	All
				93	0.3-1.5	2.7-8.0	29.4-77.2	All
VPPAW 1	6.35, 12.7	L-T	0.1, 0.5	24	-	1.0-1.8	9.0-1131	All
FSW [1]	6.35, 12.7	L-T	0.5	−196	-	14.8	98.6-114.2	All
				24	-	5.6-11.6	34.3	All
				94	2.6-2.7	13.3-13.5	-	All
2195 [2]	6.35, 31.75	All	0.1, 0.5	−196	-	0.4-4.4	11-110	All
				24	0.07-16.5	0.2-55	-	All

Key: Orientation is defined in ASTM E1823-Annex 2.

Fatigue crack growth rate, *da/dN* (10^{-6} in/cycle).

VPPAW – variable polarity plasma arc welding.

FSW – friction stir welding.

Conversion from Imperial units: MATWEB http://www.matweb.com/tools/conversion.asp

1 – Ref. [46-66]

2 – Results from SLWT design allowables program: R.E. Reinmuller 'SO 89818 Al-Li Materials Database, Lockheed Martin Manned Space Systems, New Orleans, LA 70189

3 - Conversion from Imperial units: MATWEB http:/www.matweb.com/tools/conversion.asp

46.8.4 Cost implications

In general, the price of basic Al-Li product forms (sheet, plate, extrusions and forging grades) is higher than that of comparable conventional alloys.

Special demands during production increase costs further over conventional aluminium. Some of the contributory factors are:

- increase costs for scrap segregation and control,
- reduced scrap value,
- increased handling costs,
- increased tool wear.

As product prices are normally volume-related, the situation is likely to improve with the wider use of particular grades of Al-Li alloys, [See also: 46.9].

46.8.5 Applications

The costs indicate a distinct handicap for Al-Li alloys if one is seeking to replace established 2XXX and 7XXX series alloys.

The higher finished item cost can only be offset against mass-saving; there is no other justification for using Al-Li alloys. Such mass-savings have been shown for some aerospace structures, [See: 46.9]

46.8.6 Mass-saving

46.8.6.1 General

Whilst a direct material substitution approach is possible, the highest mass-savings are obtained from Al-Li alloys by optimising the design, [See also: 46.9].

46.8.6.2 Direct material substitution

For high Li-containing alloys (8090, 2090), a mass-saving of about 8% can be achieved.

Mass-savings in the range of 6% to 7% are probable for alloys with a moderate Li content, e.g. 2098, 2099, 2195, 2196 and 2297, Ref. [46-51].

46.8.6.3 Redesigned components

By redesigning to take account of the increased modulus, mass-savings of 15% to 18% can be possible, provided that strength criteria are met.

46.9 Al-Li alloys: Potential applications

46.9.1 General factors

Al-Li alloys appear attractive for space use, but the characterisation of stress corrosion cracking behaviour can present an obstacle, [See: 46.7]. Al-Li can be used if a contractor demonstrates that the possibility of SCC has been addressed for each individual application and the appropriate Fail-Safe or Safe-Life criteria are met.

[See: ECSS-Q-ST-70-36; ECSS-Q-ST-70-37]

Initially, appropriate components were those needing minimum machining, little or no welding having no fatigue loading. This implied sheet products, net-shape forgings and extruded sections for components such as brackets, panels, struts and adapter rings for satellite structures.

Single launch applications pose fewer problems than reusable, long-life structures. The recent weldable alloys, e.g. Weldalite™-series, 2095 and 2195 have been applied to cryogenic tanks.

[See: Super Lightweight Tank (SLWT)]

An example of the growing confidence in Al-Li alloys in long-life structures is their use in commercial aircraft applications. Traditionally, evaluation for use in space draws on the experience gained by contractors with materials used within aircraft.

[See: A380 - Floor beams]

46.9.2 Space Shuttle external tank

46.9.2.1 General

The ET external tank is the only major non-reusable component of the Space Shuttle system. The ET is the single largest element with dimensions of 46.94m (154 feet) long and 8.41m (27.6 feet) diameter.

During launch it acts as the structural 'backbone' of the Shuttle and contains the LH and LOX propellant for the Orbiters' 3 main engines. Early versions of the ET used aluminium, steel and titanium in their construction. The need to reduce mass and so enable heavier payloads to be carried by the Orbiter, especially for the construction of ISS international space station, resulted in modifications in the original design; as summarised in Table 46.09.1.

Table 46.9-1 – Al-Li alloys: Applications – mass savings in Space Shuttle external tank

ET - External Tank	Mass (kg)	Missions
SWT (Standard Weight Tank)	34246 (75 500 lbs)	STS-1 to STS-5 (1) STS-7
LWT (2) (Light Weight Tank)	29710 (65 500 lbs)	STS-6 STS-8 to STS-90
SLWT (3) (Super Lightweight Tank)	26308 (58 000 lbs)	STS-91 (June 1998)

Key: (1) ETs were painted white for missions STS-1 and STS-2. From STS-3 onwards, they were no longer painted to save weight and preparation costs.
(2) Materials and design changes, plus new fabrication techniques.
(3) Component redesign and use of 2195 aluminium-lithium alloy.

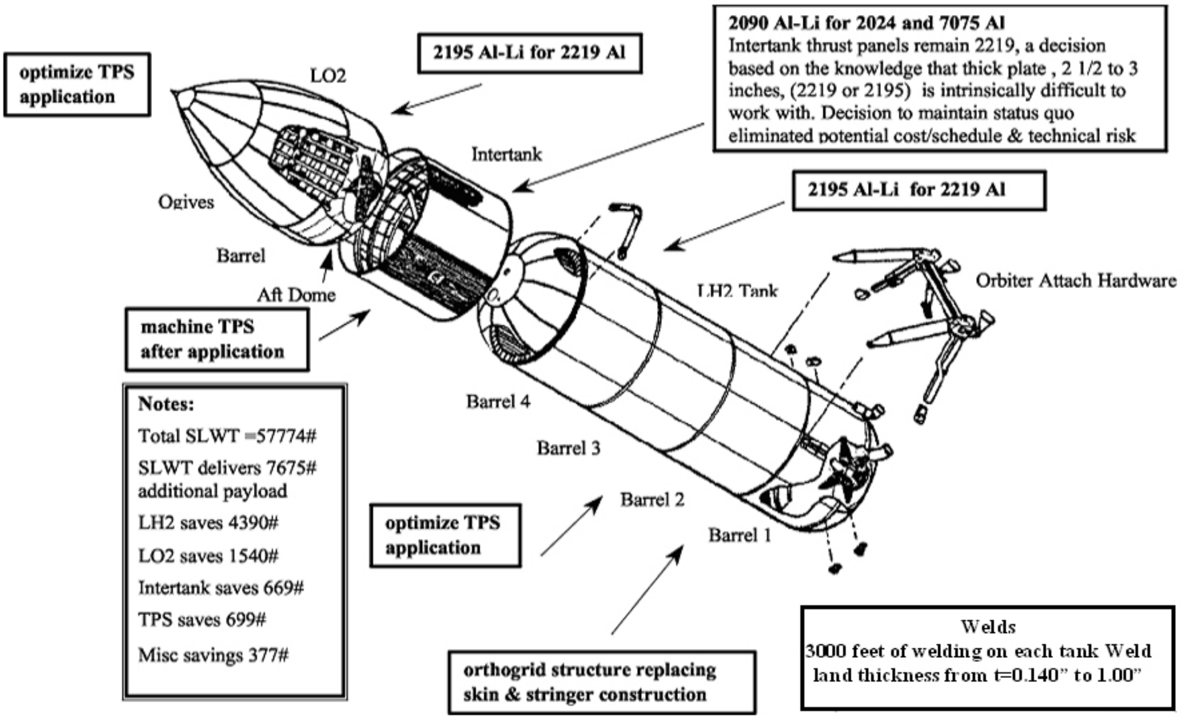
46.9.2.2 Super Lightweight Tank (SLWT)

The use of 2195 alloy in the construction of the SLWT is probably the largest use of an Al-Li alloy in current space applications. SLWT first flew in June 1998 on mission STS-91.

The weight-saving of about 3402kg over the previous LWT tank was achieved by component redesign and the use of an Al-Li alloy, which provides a 30% strength increase and 5% density reduction compared with the previous materials, Ref. [46-53].

Despite the modifications to the design and materials used in the ET, the overall concept remains the same.

Figure 46.9.1 shows the main ET tank components and the changes from the previous LWT, Ref. [46-53], [46-68].



Key: # = lbs.

Figure 46.9-1 - Al-Li alloys: Applications - Space Shuttle external tank, major changes from LWT

The main ET tank components are:

- LOX - liquid oxygen tank, which is an aluminium monocoque structure composed of preformed, chemically-milled gores, panels, machined fittings and ring chords which are assembled by fusion welding. The nose cone reduces drag and acts as a lightening rod. The main features are:
  - Dimensions: ~8.4m (331 inches) diameter × ~15.0m (592 inches) long.
  - Capacity: ~ 553 962 litres (19 563 cubic feet).
  - Operating pressure: ~145 kPa (20 to 22 psi)
- LH - liquid hydrogen tank is an aluminium semi-monocoque structure of fusion welded barrel sections; 5 major ring frames with forward and aft ellipsoidal domes. At the forward end of the LH tank is the ET/Orbiter forward attachment pod strut. At the aft end are 2 ET/Orbiter attachment ball fittings and the Solid Rocket Booster (SRB)-to-ET stabilising strut attachments. The main features are:
  - Dimensions (approximate): 8.4m (331 inches) diameter × 29.5m (1160 inches) long.
  - Capacity: ~ 1 515 461 litres (53 518 cubic feet).
  - • Operating pressure: ~228 kPa (32 to 34 psi)
- Intertank, which is a semi monocoque cylindrical structure with aluminium mechanically-joined skin, stringers and machined panels. Flanges on each end join the forward LOX tank and aft LH tank. It houses the ET instrumentation and provides an umbilical plate that interfaces

with the ground facility during pre-launch operations, such as purge, hazardous gas detection, H2 boil-off.

— Dimensions (approximate): 8.4m (331 inches) diameter × 6.9m (270 inches) long.

The ET external surface has a multilayer thermal protection coating (about 25 mm thick) which prevents ice forming on the tank structure and protects it from the thermal conditions during prelaunch, launch and flight.

46.9.3 A380 - Floor beams

46.9.3.1 General

The Airbus A380 represents the latest development in large, wide-bodied, passenger aircraft. The overall dimensions are:

- Wing span: 79.80 m
- Length: 73.00 m
- Height: 24.10 m
- Fuselage diameter: 7.14 m

The A380 family not only represents the largest civil aircraft built to date, but also provides a technology platform for future commercial aircraft development programmes.

46.9.3.2 Material selection

Weight-savings were of paramount importance in the selection of construction materials in order to provide lower fuel burn, reduced emissions into the atmosphere and lower operating costs.

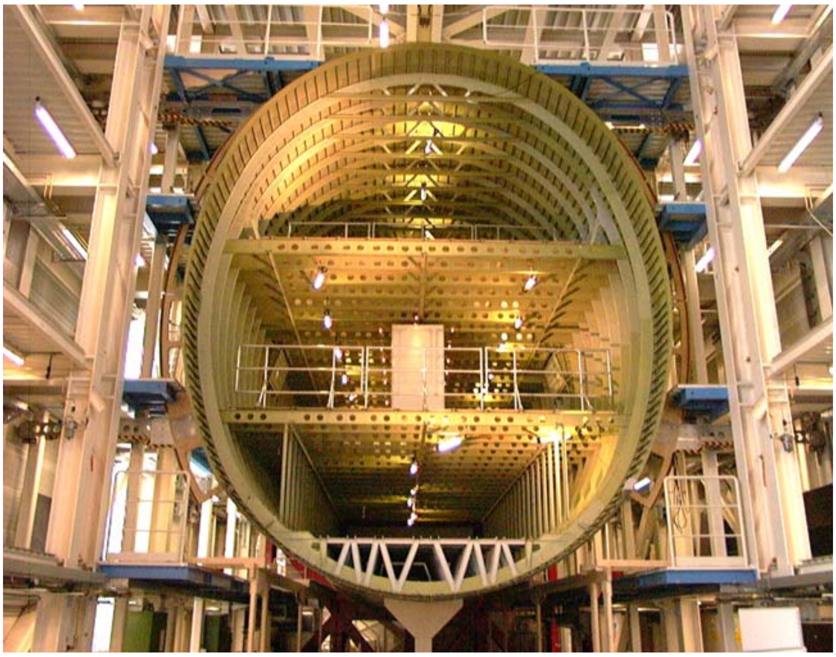
Although Airbus considered the use of Al-Li alloys for the A340, the first-generation alloys, such as 8090-T8511 and 2091-T851, were rejected over issues of thermal stability, anisotropy and crack deviation. These problems have been resolved with the availability of the third-generation Al-Li alloys.

Airbus has qualified alloys C460 (2099) from Alcoa and 2196 from Alcan in the form of heavy extrusions in the T8511 temper for the manufacture of floor beams; as shown in Figure 46.9.2.

Extruded Al-Li alloy profiles are used in the main deck floor beams (A380-800 sections 13 and 15), but are destined for use in both decks in the freighter version; adapted to suit local loads, Ref. [46-85].

Both alloys exhibit better or equal properties to conventional alloy 7175-T73511, with improved corrosion resistance, and provide substantial weight savings.

Based on current experience, Airbus considers Al-Li alloys as the main competitor to composite materials for aircraft construction. As a result, other applications for Al-Li alloys are under consideration, such as bottom wing stringers and fuselage skin, Ref. [46-69], [46-70].



Fuselage diameter: 7.14 m

Figure 46.9-2 - Al-Li alloys: Applications – Airbus A380 floor beams

Airbus also has a cooperative venture with Russia organisations, such as VIAM, to assess potential uses of Russian-origin Al-Li alloys. This programme considers a number of alloys with the aim of generating data to enable a direct comparison between the properties of Russian-origin materials with current specification western materials. The work includes 'prequalification' activities on a short-list of advanced materials, identified as having true potential, Ref. [46-84].

46.10 Oxide dispersion strengthened (ODS) alloys

46.10.1 Type and effect of dispersions

Dispersion strengthening relies on the distribution of many, very fine particles, usually a ceramic oxide, throughout a pure metal. These particles are of nanometre size range (2nm to 10nm), and interact with dislocations to give the strengthening effect as strain occurs in the metal, Ref. [46-8].

Cryomilling pure aluminium powder in liquid nitrogen results in dispersion strengthening by the formation of AlN - aluminium nitride particles. After subsequent compaction and degassing, this material can be extruded and then cold rolled to thin sheet, Ref. [46-55].

46.10.2 Processing

46.10.2.1 Powder

ODS alloys are prepared by a powder metallurgy route. Mechanical alloying (MA) is the main method of incorporating the oxide particles, e.g. 44μm air-atomised aluminium powder with 0.05μm alumina powder. Both are added to a high energy ball mill under liquid nitrogen (Raufoss A/S process). Nitrogen provides an atmosphere as the attritor breaks up the particles and consolidates them into the aluminium as oxy-nitrides. Particle content varies, but is under 10% and often nearer 3%. Alumina (oxy-nitride) is the popular strengthening medium, but other non-shearable, hard particles with high melting points can be used, e.g. Al_4C_3, TiO_2, ZrO_2 or Al_3Ti.

46.10.2.2 Consolidation

The powder is consolidated either by:

- hot isostatic pressing (HIP), or
- vacuum hot extrusion.

46.10.2.3 Product forming

The consolidated material can be worked further to a finished product by:

- forging,
- extrusion,
- swaging,
- rolling to sheet or plate material.

46.10.3 Cost factors

The alloys are expensive to produce and there are practical limits on the size of billet producible by the powder route.

46.10.4 Applications

ODS alloys are specialised products for applications needing aluminium materials with:

- higher thermal stability,
- greater wear resistance,
- hardness.

The high-temperature stability is of interest as a possible competitor to titanium in the temperature range 150°C to 450°C.

Aluminium nitride (AlN) dispersion strengthened materials have been considered for hypersonic aircraft structural elements, due to their, Ref. [46-55]:

- high strength up to 450°C,
- creep resistance,
- grain growth stability,
- corrosion resistance (pure aluminium matrix),
- high thermal conductivity (heat dissipation).

46.10.5 Properties

46.10.5.1 General

Emphasis is given here to ODS alloys with a 3% particle addition prepared by Raufoss A/S, (Norway), Ref. [46-9].

Aluminium-lithium alloy, AMC500, is also an ODS material produced by mechanical alloying, [See: 46.4, 46.5, 46.6].

46.10.5.2 Strength

ODS alloys are medium-strength materials, which offer usable properties to 450°C, e.g. proof stresses of around 120MPa at 400°C.

Figure 46.10.1 indicates the better strength retention of various mechanically alloyed systems above 200°C compared with a conventional higher temperature alloy, such as 2618, Ref. [46-9]. However, Figure 46.10.2 shows that the strain to failure is significantly reduced as temperature increases.

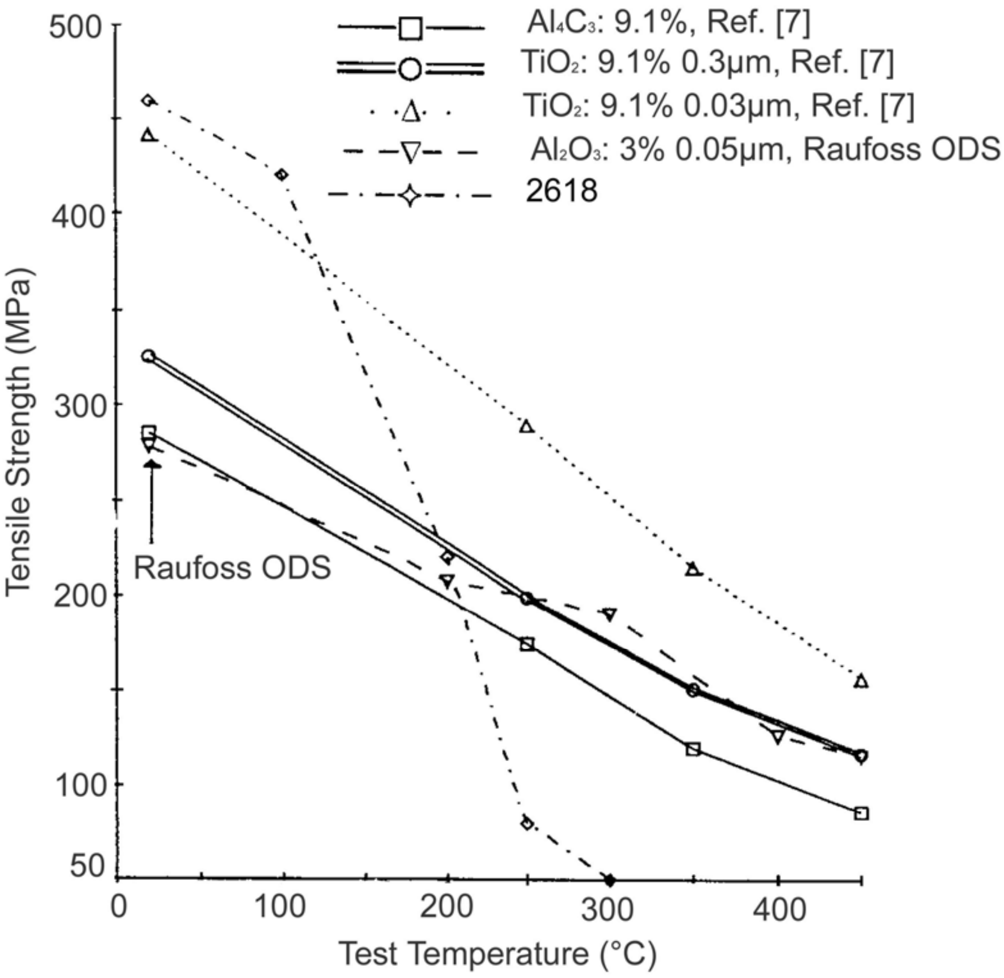


Figure 46.10-1 - Aluminium ODS alloys: Comparison of elevated temperature tensile strength for various mechanically alloyed materials with Al-2618

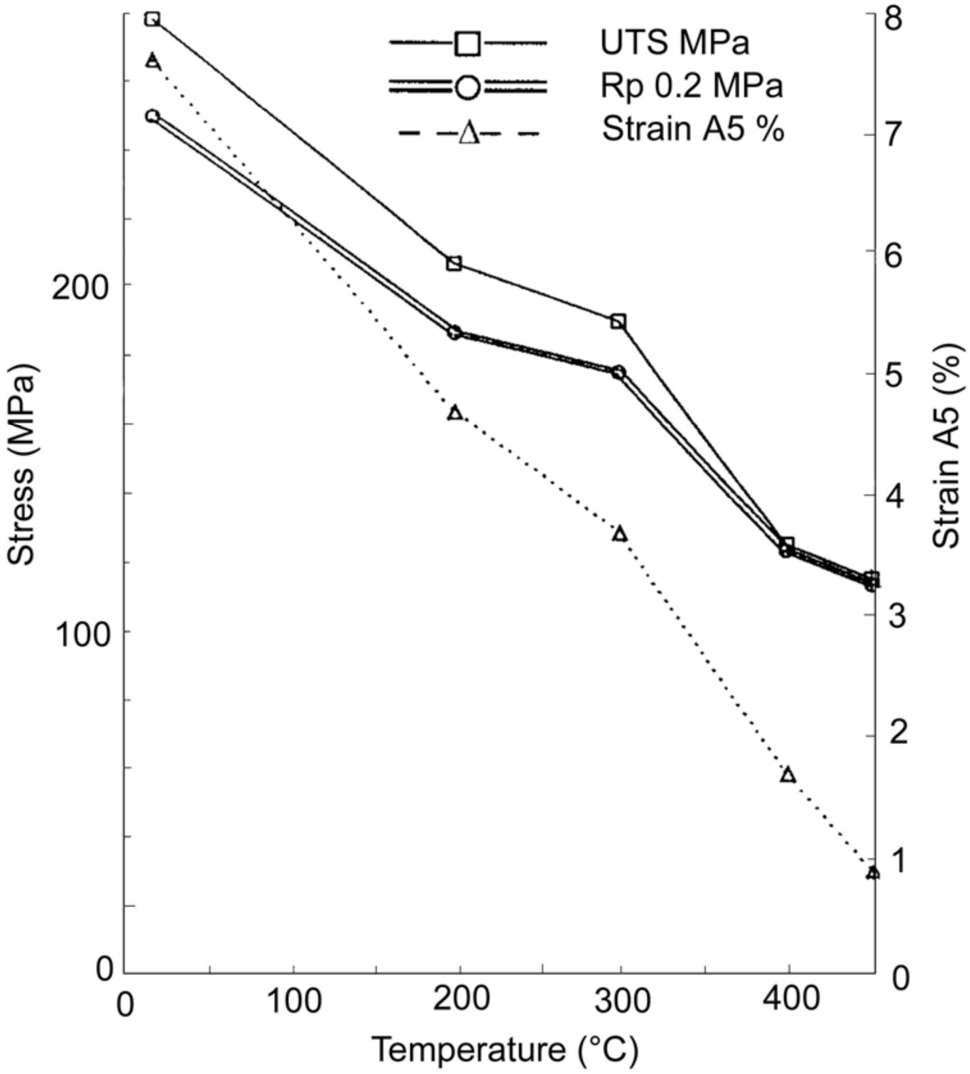


Figure 46.10-2 - Aluminium ODS alloys: Comparison of elevated temperature tensile strength, proof stress and ductility

The method of powder consolidation also influences mechanical properties, Ref. [46-9]:

- Proof stress, as shown in Figure 46.10.3.
- Ductility, as shown in Figure 46.10.4.

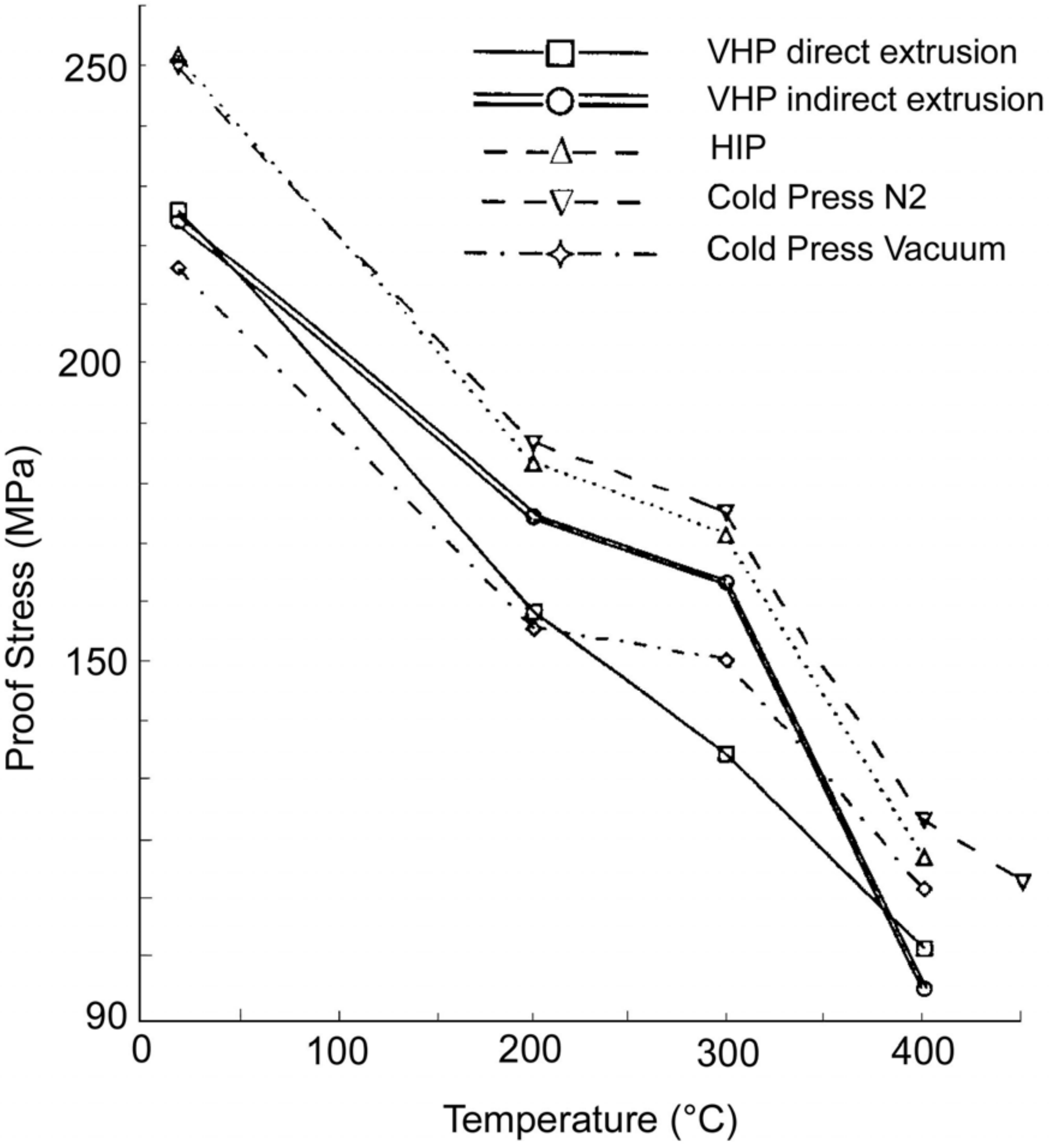


Figure 46.10-3 - Aluminium ODS alloys: Effect of consolidation method on proof stress

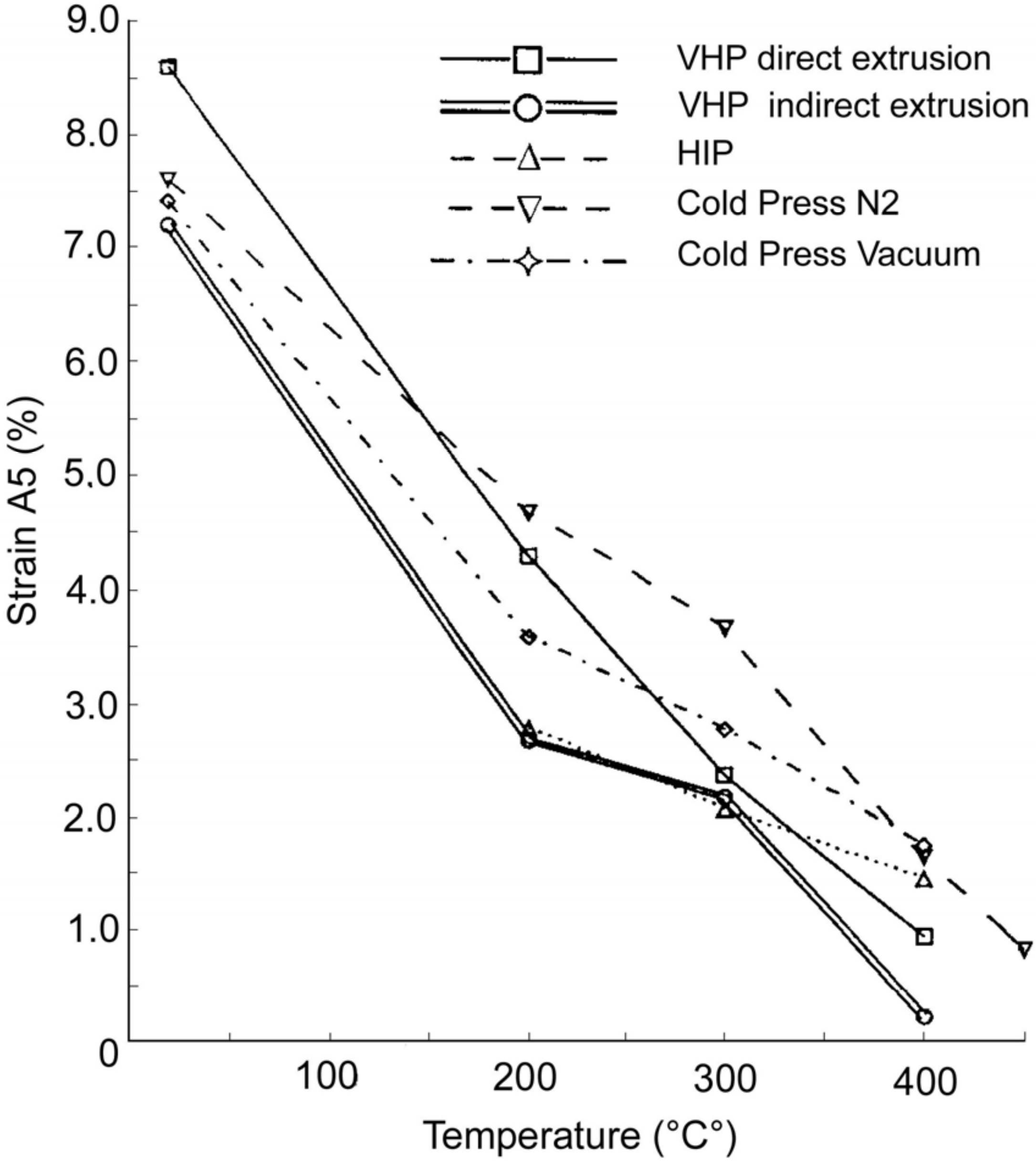


Figure 46.10-4 - Aluminium ODS alloys: Effect of consolidation method on ductility

46.10.5.3 Creep resistance

In view of the proposed use of ODS alloys at elevated temperatures, creep resistance is important.

Figure 46.10.5 shows that at 400°C life expectancy is reasonable if stresses are below 100MPa, although the ultimate limitation is the low failure strain (<1%), Ref. [46-9].

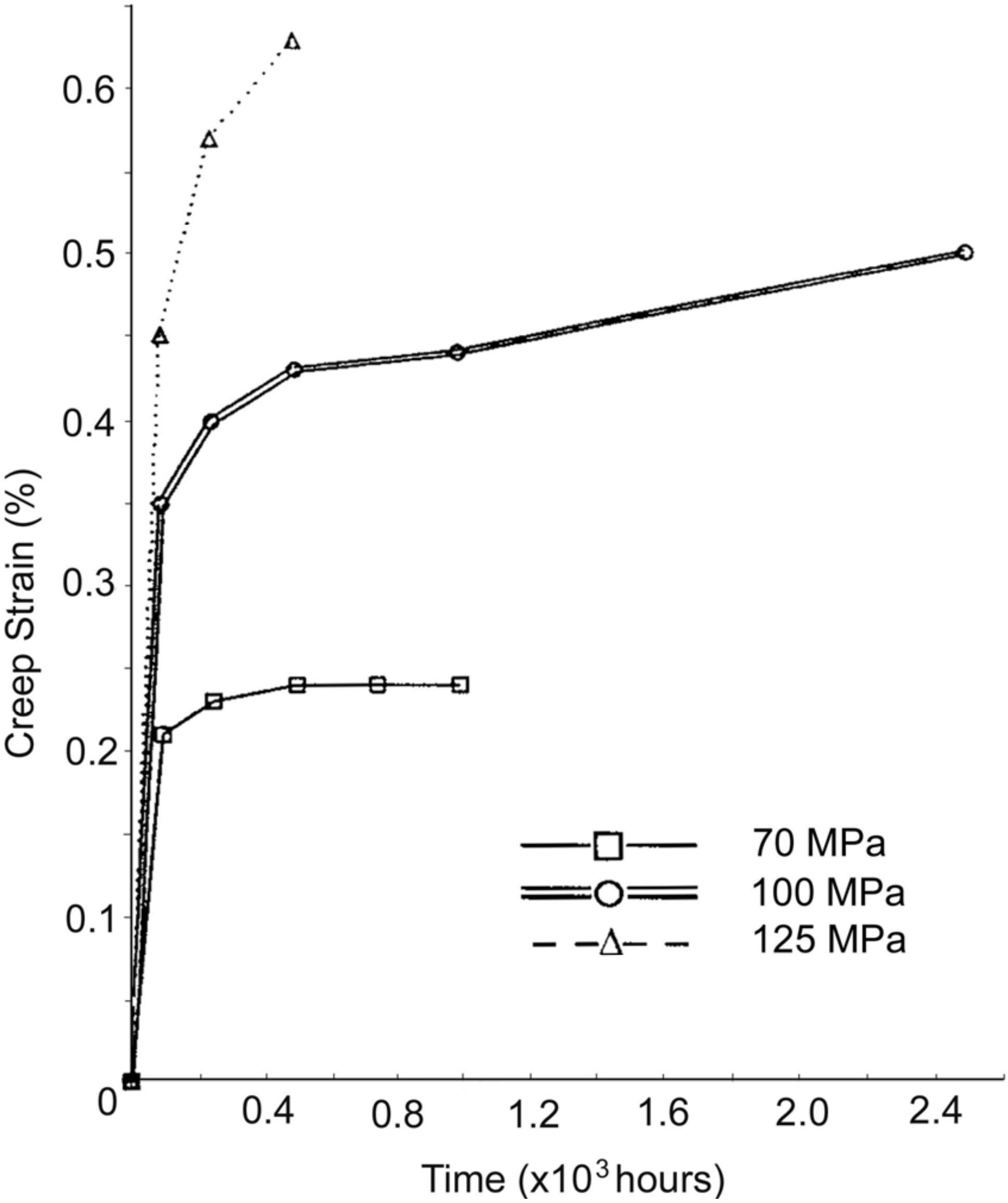
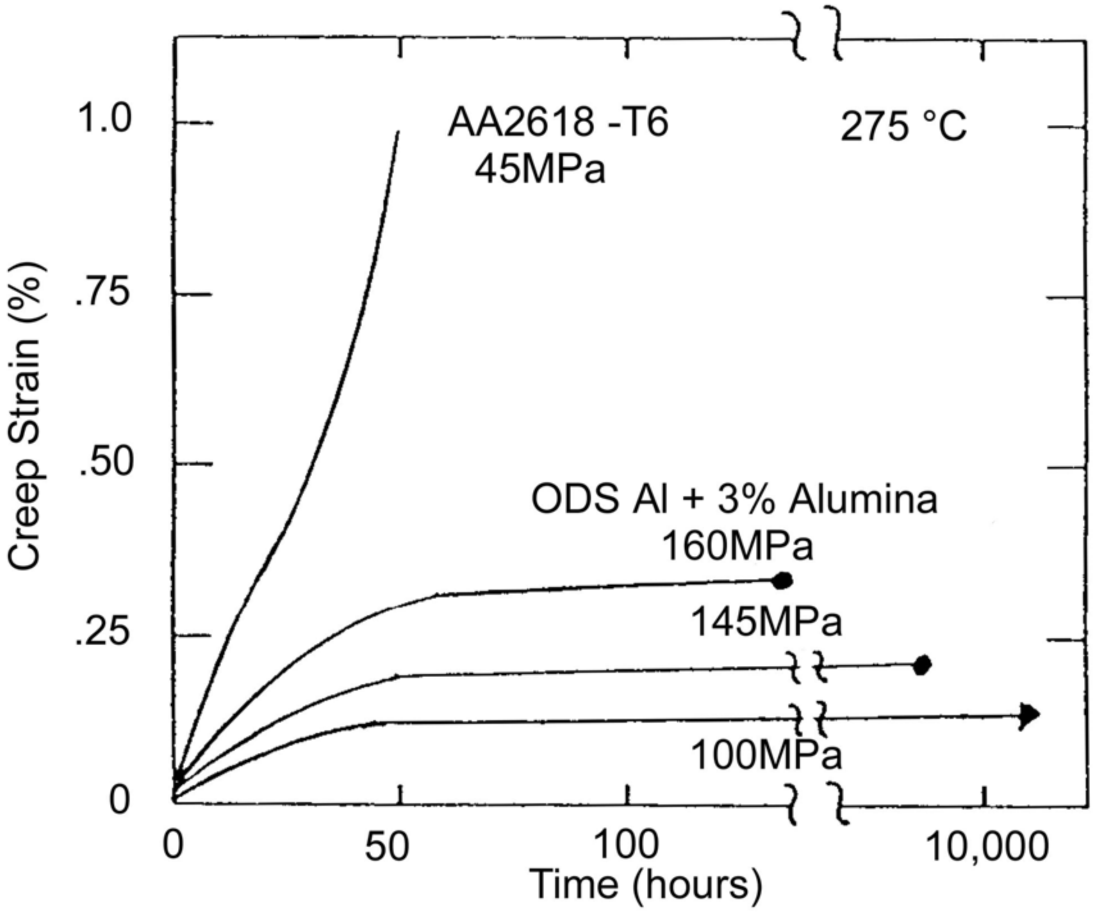


Figure 46.10-5 - Aluminium ODS alloys: Creep response at 400°C for 3 stress levels

Figure 46.10.6 provides creep data at 250°C which indicates more stable behaviour in the stress range 100MPa to 160MPa, Ref. [46-9].

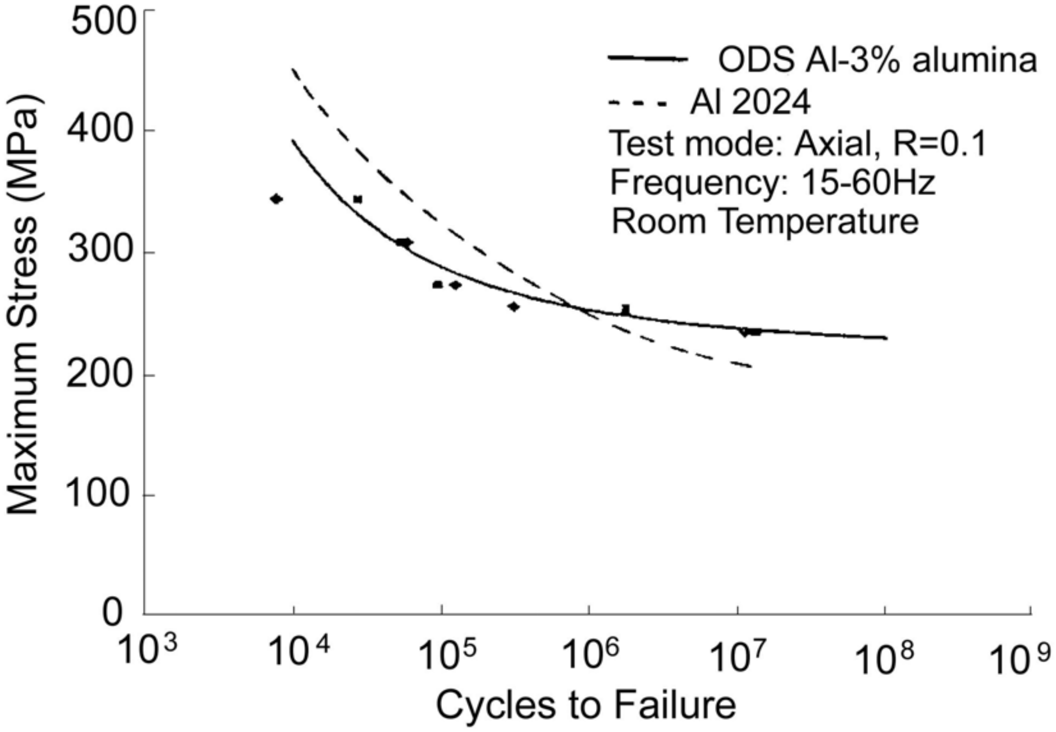


Dispersion content: 3%Al_2O_3

Figure 46.10-6 - Aluminium ODS alloys: Comparison of tensile creep curves at different stress levels with Al-2618

46.10.5.4 Fatigue

Figure 46.10.7 shows that the fatigue performance of the ODS 3% alumina alloy is initially hindered by a modest tensile strength, but a higher run-out stress is reached at high frequencies than for 2024 alloy. This suggests no fundamental deficiencies in the fatigue performance of ODS alloys, Ref. [46-9].



Dispersion content: 3%Al2O3

Figure 46.10-7 - Aluminium ODS alloys: Comparison of fatigue resistance with Al-2024

46.11 Rapidly solidified powder (RSP) alloys

46.11.1 Processing

RSP powders are made by breaking molten metal into small droplets which are solidified very rapidly. This can be achieved by:

- atomisation,
- splat cooling, or
- melt spinning.

As with ODS [See: 46.10], RSP materials avoid some of the limitations of melt ingot metallurgy, Ref. [46-2].

46.11.2 Microstructure

The RSP route produces a microstructural grain refinement. The smaller the mean free path between obstacles to dislocation movement (grain boundaries), the greater the strengthening. In addition, finer microstructural features are less apt to serve as fracture initiating flaws, thereby increasing toughness. Grain size is reduced because of the short time available for nucleation and growth during solidification.

In RSP processing, the normal alloying limits in aluminium can be exceeded as a result of increased super-saturation. This enables greater precipitation hardening without harmful segregation effects, which can arise in over-alloyed ingot metallurgy alloys. Moreover, elements that are essentially insoluble in the solid state, but have significant solubility in liquid aluminium, can be uniformly dispersed in particles undergoing very rapid solidification.

In this way novel alloy compositions and strengthening phases can be produced which are not achievable with conventional ingot metallurgy.

46.11.3 Development

The principal properties which are enhanced by rapid solidification processing are:

- high ambient-temperature strength,
- corrosion and stress-corrosion cracking resistance,
- elevated temperature properties.

46.11.4 Ambient temperature

46.11.4.1 Alloys

The most successful materials developed have been in the Al-Zn-Mg sub-system (7XXX alloys).

In more highly alloyed 7XXX alloy variants, dispersed transition-metal intermetallic phases were achieved. The most notable alloy developments have been:

- Cobalt-containing alloys: 7091 and 7090.
- Nickel and Zirconium-containing alloy: CW67, Ref. [46-11].

The alloy compositions are given in Table 46.11.1.

Table 46.11-1 - RSP aluminium alloys: Ambient temperature use - nominal alloy compositions

Alloy	Composition (wt%)									
	Zn	Mg	Cu	Co	Zr	Ni	Cr	Li	O	C
Rapid solidification										
7090	8.0	2.5	1.0	1.5	-	-	-	-	-	-
7091	6.5	2.5	1.5	0.4	-	-	-	-	-	-
CW67	9.0	2.5	1.5	-	0.14	0.1	-	-	-	-
7064	7.4	2.4	2.1	0.75	0.3	-	0.15	-	0.2	-
Mechanically alloyed										
Al-9052	-	4.0	-	-	-	-	-	-	0.5	1.1
AMC500 (1)	-	4.0	-	-	-	-	-	1.3	0.4 (2)	1.1 (2)
Key: Aluminium-Lithium alloy, AMC 500. [See also: 46.4]. Approximate values.										

46.11.4.2 Mechanical properties

Table 46.11.2 gives the ambient temperature mechanical properties of the various alloys.

Table 46.11-2 - RSP aluminium alloys: Ambient temperature use -tensile properties

Alloy	Temper	UTS (MPa)(1)	YS (MPa) (1)	Elongation (%)(1)
7091	TE192	640	600	13
	T7	595	545	11
7090	T6511	675	640	10
	T7	620	580	9
CW67	T7X1	614	580	12
7064	T6	683	635	12
	T7	650	621	9
Al-9052	F	450	380	13
	F	635	630	4
Key: (1) Longitudinal properties from experimental extrusions.				

46.11.4.3 Stress corrosion resistance

The SCC resistance of 7090 and 7091 is better than I/M 7XXX alloys. SCC resistance generally increases with cobalt contents between 0% and 1.6%, Ref. [46-12]. For ambient use, CW67 offers the best combination of strength and SCC resistance.

46.11.4.4 Fatigue

The effect of P/M processing on the fatigue behaviour of Al alloys is complex. In general, the resistance to fatigue crack initiation is improved, but resistance to fatigue crack propagation can be reduced.

A further alloy, 7064 (formerly PM-64) is in part strengthened by Zr, Cr and Co-containing dispersions. It also has good combinations of strength and SCC resistance, and has shown superplasticity.

46.11.5 Elevated temperature

46.11.5.1 Alloys

Most of the successful alloys developed contain iron, e.g. Al-Fe-Ce alloy compositions, such as CU78 and CZ42 from Alcoa.

Some further RS-P/M materials are Al-Fe-V-Si composition alloys, of which Allied Signal FVS-0812 and FVS-1212 are made by planar flow casting, Ref. [46-79], and AMC Calidus 350xq is made by atomising, Ref. [46-73].

46.11.5.2 Mechanical properties

The characteristics of each group of alloys can be summarised as:

- Al-Fe-Ce alloys, as shown in Table 46.11.3, CZ42 possess good strengths to 315°C, Ref. [46-13].
- Al-Fe-V-Si alloys, such as Calidus 350xq, FVS-0812 and FVS-1212, have usable strengths to 425°C; as shown in Table 46.11.4 and Table 46.11.5. Furthermore, they contain a large proportion of very fine silicides that increase the modulus and so offer potential mass-savings over Ti-alloys, for example; as shown in Table 46.11.6.

Table 46.11-3 - RSP aluminium alloys: Elevated temperature - modified property goals (minimum values) for shaped extrusions of P/M alloy CZ42

Temperature (1) (°C)	TS (MPa)	YS (MPa)	*E* (GPa)	Elongation (%)	Fracture Toughness, K_{1C} (MPa√m)
RT	448	379	78.6	5.0 †	L-T: 23, T-L: 18
166	365	345	68.9		
232	310	296	64.1		
260	283	262	62.1		
316	221	200	56.5		

Key: (1) Values at stated temperature; † At RT to 316°C.

Table 46.11-4 - RSP aluminium alloys: Room and elevated temperature tensile properties of planar flow cast alloy FVS-0812

Temperature (°C)	YS (MPa)	UTS (MPa)	Elongation (%)	*E* (GPa)
24	413	462	12.9	88.4
149	345	379	7.2	83.2
232	310	338	8.2	73.1
316	255	276	11.9	65.5
427	138	155	15.1	61.4

Table 46.11-5 - RSP aluminium alloys: Room and elevated temperature tensile properties of alloy FVS-1212

Temperature (°C)	UTS (MPa)	YS (MPa)	Elongation (%)	*E* (GPa)
24	559	531	7.2	95.5
150	469	455	4.2	-
230	407	393	6.0	-
315	303	297	6.8	-

Table 46.11-6 - RSP aluminium alloys: Elastic modulus, density and weight-saving parameters for thermally stable RS-P/M alloys

Alloy (1)	Composition	*E* (GPa)	ρ (kg/m³)	*E*/ρ (2) (MNm/kg)	$E^{1/3}/\rho$ (3) ($N^{1/3}m^{7/3}/kg$)
-	Al-5Cr-2Zr	80.8	2820	28.7	1.53
-	Al-5Cr-2Zr-1Mn	86.5	2860	30.2	1.55
CU78	Al-8.3Fe-4.0Ce	79.6	2950	27.0	1.46
CZ42	Al-7.0Fe-6.0Ce	80.0	3010	26.6	1.43
-	Al-8Fe-2Mo	86.2	2910	29.6	1.52
FVS-0812	Al-8.5Fe-1.3V-1.7Si	88.4	3020	29.3	1.48
FVS-1212	Al-2.4Fe-1.2V-2.3Si	95.5	3070	31.1	1.49
Calidus 350xq	Al-Fe-V-Si	80	2990	27.6	1.49
RAE 72	Al-7.5Cr-1.2Fe	89.0	2890	30.8	1.54
I/M 2219	Al-6.3Cu-0.3Mn-0.06Ti-0.1V-0.18Zr	73.0	2860	25.5	1.46

Key: (1) Sources: CU and CZ from Alcoa; FVS-series from Allied Signals Inc.; Calidus from AMC; others unknown;

(2) *E*/ρ - Specific modulus;

(3) $E^{1/3}/\rho$ - Buckling parameter.

46.12 Al-MMCs - Metal matrix composites

46.12.1 Introduction

There are many reasons for the interest in metal matrix composites. Initial developments were stimulated by applications which needed improved mechanical properties compared with the unreinforced matrix alloys, i.e.:

- Increased strength at room or elevated temperature.
- Increased stiffness.

Since the overall properties of the composite are largely determined by those of the reinforcing phase, this has lead to further applications that take advantage of the physical properties of the reinforcement, e.g.:

- Low CTE - coefficient of thermal expansion.
- High thermal conductivity.
- Good wear resistance.

Various MMC material combinations are described, with indications of their typical mechanical and physical properties. These materials can be classed as composites with either:

- discontinuous reinforcement phases (particles, short fibres or whiskers), [See: 46.13].
- continuous fibre reinforcement, [See: 46.15].

Just as with polymer matrix composites, most aluminium-matrix composites are part of a family of materials whose properties can be tailored by modifying the volume of reinforcing phase or the matrix alloy.

46.12.2 Manufacturing processes

A wide range of processes have been employed for the manufacture of MMC components, utilising solid, liquid and vapour-phase techniques. Several of these process technologies are suitable for both discontinuously and continuously reinforced materials.

An overview of the various processes is illustrated in Figure 46.12.1.

Further information on the processes used for commercially-available MMC is also provided.

[See: 46.13 for discontinuously reinforced aluminium-matrix composites; 46.15 for continuously reinforced materials]

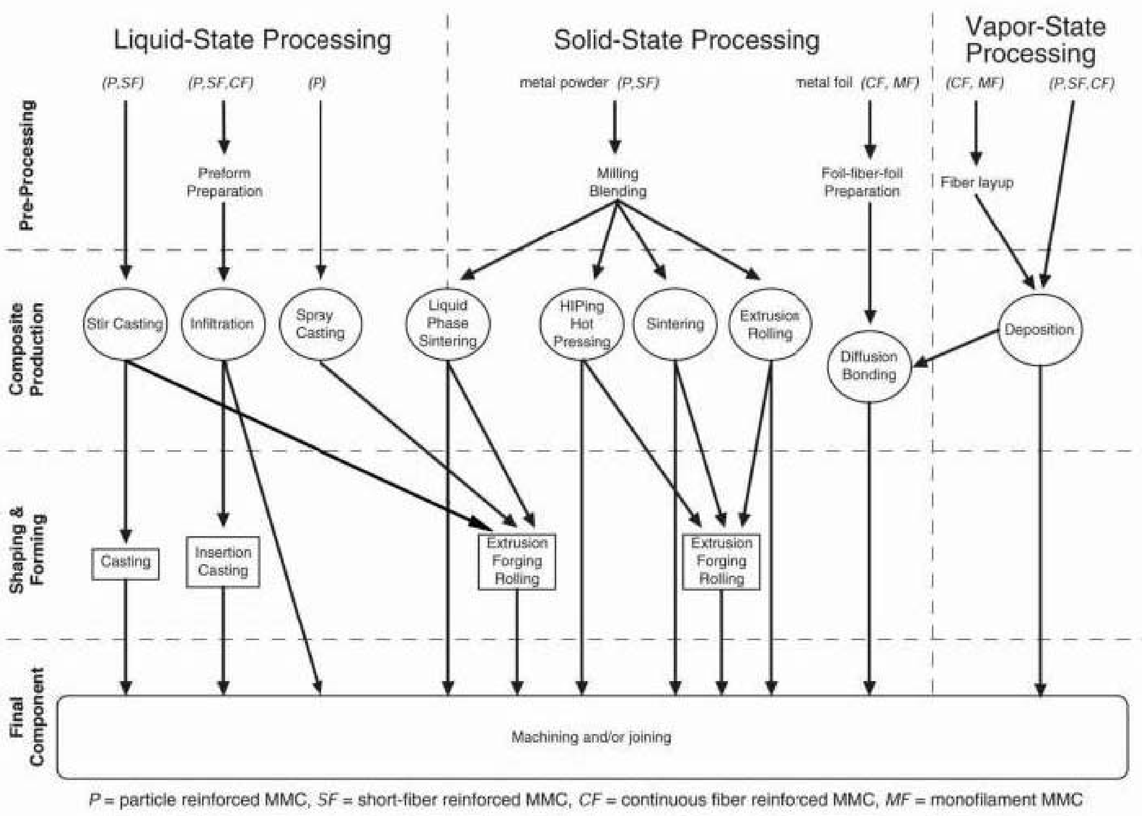


Figure 46.12-1 – Al-MMCs: Overview of manufacturing processes

46.12.3 Reinforcement materials

Information on the various materials used as the reinforcing phase is presented.

[See: 46.13 - discontinuously reinforced MMCs; 46.15 - continuously reinforced MMCs]

46.12.4 MMC nomenclature

A standardised nomenclature for aluminium-matrix composites has been established by the American National Standards Institute (ANSI) Committee H35 on Aluminium and Aluminium alloys under standard ANSI H35.5.

The nomenclature is best illustrated by an example, e.g.:

2009/SiC/15p-T4

where:

‘2009’	*indicates the matrix alloy and is the four-digit number registered with the Aluminum Association*
‘SiC’	*indicates the composition of the reinforcement material*
‘15’	*indicates the volume percentage of reinforcement*
‘p’	*code letter that indicates the form of the reinforcement, where p is particulate, w is whisker and f is fibre.*

NOTE ‘f’ is used for both continuous fibres and chopped fibres, i.e. a discontinuous reinforcement.

-T4’	*indicates the temper designation of the matrix alloy (suffix, where appropriate)*

46.12.5 Advantages of MMC's

Compared with polymer matrix composites, aluminium MMCs offer a number of advantages, including:

- Higher transverse stiffness and strength.
- Higher temperature capability.
- Reduced flammability risk.
- Higher thermal conductivities.
- Electrical conductivity.
- Better radiation resistance.
- Better resistance to fuels and solvents.
- No moisture absorption.
- No outgassing.
- Suitable for friction and wear resistant applications.
- Component manufacture from discontinuously-reinforced MMCs using conventional metalworking equipment.

46.12.6 Material availability

Whilst some aluminium-matrix composite materials are well established for some applications, such as brake discs, the industry is still relatively new and composed mainly of technology development companies. This inevitably leads to the introduction of new companies and closures of others. Identifying current suppliers of Al-MMC materials can therefore present difficulties.

Table 46.12.1 summarises the capabilities of the main suppliers (as of mid-2005), together with their geographic locations and their website addresses for further information and contact details.

Table 46.12-1 – Al-MMCs: Summary of suppliers and capabilities

Supplier (location)	Reinforcements	Matrix alloys	Process
AMC (UK)	SiC, p (a)	2124, 6061	powder metallurgy
CMT (UK)	Al2O3 , f	Al, Al-Cu2, ?	pressure infiltration
Electrovac (D)	SiC, p	AlSi7Mg	pressure infiltration
Sandvik-Osprey (UK)	Si	Al	spray forming
3M (US)	Al2O3 , f (a)	Al, Al-Cu2, ?(b)	melt infiltration
Ametek (US)	SiC, p	n.s (c)	pressure infiltration
CPS (US)	SiC, p	A356	melt infiltration
Duralcan (Canada)	SiC, p ; Al2O3 , f	3xx, 6061	melt stirring
DWA-DRA (US)	SiC, p	2009, 6069, ?	powder metallurgy
M Cubed (US)	SiC, p	Al, AlSi	melt infiltration
MC 21 (US)	SiC, p	3xx	melt stirring
Millenium Materials (US)	SiB6 , p	cast alloys ?	melt stirring
MMCC	C, f	AlSi	pressure infiltration
PCC-AFT (US)	SiC, p	cast alloys ?	pressure infiltration
PEAK (D)	SiC, p	wrought alloys	spray forming
Triton Systems (US)	SiC, p	cast alloys ?	pressure infiltration
TRL (US)	Al2O3 , f	Al	continuous melt infiltration
TTC (US)	SiC, p	Al, AlSi	melt infiltration

Key: (a): f = fibre, p = particulate; (b): ? = other alloys available; (c): n.s. = not specified

46.12.7 Sources of further information

Some further information sources include:

- MIL-HDBK-17-4, Ref. [46-74]: The American Department of Defense ‘Composite Materials Handbook’ has a volume on ‘Metal Matrix Composites’.

  NOTE Issue A only has limited information on aluminium MMCs.

- MMC-Assess, Ref. [46-75]: This was a European Brite Euram III thematic network project coordinated by the University of Vienna and run from 1998 to 2001 to exchange and assess information on MMCs. The website is still maintained and updated and contains a large amount of data on MMC materials and process technology and a list of potential suppliers.

  NOTE The list is updated with names of new suppliers but does not appear to be checked for those no longer trading.

- D.B.Miracle; 'Metal Matrix Composites for Space Systems: Current Uses and Future Opportunities', Ref [46-76]. The author is with the US Air Force Research Laboratories which sponsors much of the US (restricted) R&D on MMCs. However, a number of unrestricted publications are available for download from the site stated, Ref. [46-76].

46.13 Discontinuously reinforced Al-MMCs

46.13.1 Features

The discontinuous nature of the reinforcement means that these composites are ideally suited to applications needing multi-directional properties, i.e. in shaped components. This has resulted in the availability of materials that can be formed by casting or metal-working processes such as rolling, forging or extrusion, and subsequently machined. Components from most of the materials can also be joined using conventional welding, soldering or brazing techniques in addition to mechanical assembly.

46.13.2 Development

Many types of discontinuous reinforcements have been combined with aluminium alloys over the last 20 years. The objective is to improve both the mechanical and physical properties of the base alloy. Some are now established as commercial materials whilst further development continues.

Whilst initial interest was primarily in improved mechanical properties, there is now a significant growth in the development of aluminium-based MMCs as light-weight materials with high rigidity and good thermal conductivity, coupled with low thermal expansion. These are destined applications such as thermal management of high-power semiconductor devices and substrates for space mirrors.

46.13.3 Matrix alloys

The matrix alloys have been powder metallurgy, pure aluminium, wrought and casting alloys.

The wrought alloys tend to be from the 2XXX, 6XXX and 7XXX series and the cast alloys from the 3xx series or simpler 'cleaner' aluminium-silicon alloys.

46.13.4 Types of reinforcement

46.13.4.1 General

Discontinuous reinforcements are usually grouped as:

- Particulate, e.g. Silicon carbide
- Short or chopped fibre, e.g. Alumina or carbon.

- Whisker, e.g. Silicon carbide.

Whilst a variety of reinforcement materials and product forms have been studied only a limited number have, so far, proved technically or commercially viable. The most popular is particulate silicon carbide or chopped carbon fibres. Particulate silicon hexaboride (SiB6) also has a commercial presence.

There does not appear to be any commercial use of alumina or alumino-silicate particulates, mainly due to difficulties in achieving good bonding with the matrix, or whisker materials due to the high cost. These materials have therefore been excluded from this section.

An alternative material is the family of high-silicon Al-Si alloys processed by spray forming. Whilst strictly alloys, they are also described as ‘in-situ composites’ that contain a dispersion of silicon particles in an aluminium-silicon matrix, since the resulting product could not be made through conventional ingot casting techniques.

46.13.4.2 Silicon carbide

Particulate silicon carbide is widely available in a range of grades. Ultra-fine, FEPA 1000 or 1500 grits (micron sized) particles are preferred for high-strength MMCs, primarily manufactured by powder metallurgy routes.

Slightly coarser abrasive grit grades, FEPA 400 to 600 (from 10μm to 40μm, typically) are favoured for thermal management and wear resistant MMCs, which are generally produced via liquid metal techniques.

The properties of silicon carbide of particular interest are, Ref. [46-82]:

- Low density; 3210 kg/m^3.
- High elastic modulus; 430 GPa.
- High compressive strength; 2800 MPa.
- High hardness; 2480 Knoop.
- High thermal conductivity; 1320 W/mK.
- Low thermal expansion coefficient; 3.4 ppm/K.
- Good bonding with aluminium matrix.

[See also: 43.12 - silicon carbide technical ceramics]

46.13.4.3 Silicon hexaboride

An alternative particulate material has been put forward recently by Millenium Materials for some applications not demanding the high thermal conductivity of silicon carbide.

Silicon hexaboride (SiB_6) has similar strength and hardness to silicon carbide but its lower density, closer to that of molten aluminium alloys, means that it is more easily dispersed by the melt stirring process and remains in suspension facilitating shape casting techniques and recycling of runners. The main properties are listed in Table 46.13.1.

Table 46.13-1 – Al-MMCs: Typical properties of SiB6 silicon hexaboride particulate reinforcement – Hexon®

Appearance	Black Powder
Chemical formula	SiB_6
Density	2430 kg/m^3
Crystallographic structure	Orthorhombic
Hardness	2572 kg/m^2
Melting point	1950°C
Thermal coefficient of expansion	4.6×10^{-6}/C
Modulus of elasticity	290 GPa
Oxidation resistance	Stable in air to 1550°C
Electrical conductivity	6.5 to 200 ohm.cm (RT to 800°C)
Thermal conductivity	9 W/m/K
MOR (1) strength	225 MPa

Key: Suppliers' data
Hexon® SiB_6 is a registered tradename of Millennium Materials
(1) Modulus of Rupture

Carolite® is a proprietary MMC from Millennium Materials (USA) reinforced with silicon hexaboride.

[See also: 46.14 - properties of Carolite® composites]

46.13.4.4 Chopped carbon fibres

Some grades of pitch-based carbon fibres can be given a graphitising heat treatment. This results in extremely high thermal conductivity in the axial (longitudinal) direction. Coupled with very low (possibly negative) thermal expansion, low density and high modulus such reinforcements are of interest for thermal management composites.

The chopped fibres are obtained by milling the precursor resin fibres to around 300µm length before the carbonisation treatment. Typical properties are given in Table 46.13.2, Ref. [46-81].

[See also: 46.14 - properties of MetGraf™ Al/Cf composites]

Table 46.13-2 – Al-MMCs: Typical properties of constituents used for MMCC MetGraf™ Al/Cf composites

Material (1)	Young's modulus [GPa]		CTE [ppm/K]		Thermal Conductivity [W/mK]	Density [kg/m³]
	L(4)	T(5)	L(4)	T(5)		
Fibres: A and B (a) (2)	758	6.9	−1.45	10	550	2140
Fibres: C and D (b) (3)	931 to 965	6.9	−1.45	10	900 to1100	2150
Al-Si alloy	69	69	23	23	155	2660

Key (1) MMCC suppliers data; All are pitch-based products and are milled before carbonising;
(2) Milled fibres A and B are produced from the same resin as Cytec P-120;
(3) Milled fibres C and D are produced from the same resin as Cytec K1100;
(4) L - Longitudinal (listed as 'axial' in supplier's data);
(5) T - Transverse

46.13.5 Processing

46.13.5.1 General

Particulate reinforced aluminium alloys can be manufactured by numerous routes, [See: Figure 46.12.1].

46.13.5.2 Occupational health and safety

Many types of ceramic whiskers and polycrystalline fibres have been evaluated by the World Health Organisation's International Agency for Research on Cancer (Monograph 43, 1988) as possibly carcinogenic to humans, and are subject to occupational health and safety risk control measures in some jurisdictions.

Exposure to respirable dusts containing these materials should be avoided. Such dusts are not likely to be released from MMCs in their normal handling and use, but control measures need to be taken if the materials are machined, cut or subject to abrasion.

Refer to manufacturers' and suppliers' Safety Data Sheets for further information.

46.13.5.3 Powder metallurgy

Powder metallurgy processes start with fine constituent particles which are blended by high-energy milling before compacting to billets by vacuum hot pressing or hot isostatic pressing (HIPing), followed by thermo-mechanically processing to a finished product; similar to conventional alloys.

46.13.5.4 Liquid state

Liquid state processing methods include,

- melt stirring or stir casting,
- pressure casting or squeeze casting,
- infiltration,
- spray forming.

46.13.5.5 Stir casting

This is a well-established method in which a ceramic powder, usually particulate SiC, is mixed into a molten aluminium alloy under controlled conditions. The process has been used to produce the Duralcan® series of Al-based MMCs which are sold in ingot or billet form for subsequent fabrication by casting rolling or extrusion.

The nature of the process limits the amount of reinforcement that can be incorporated to usually a maximum of 20 volume percent. The usual matrix alloys are 3xx Al-Si alloys, which both assist manufacture and subsequent casting processes and also contribute to the mechanical properties of the composite.

An advantage of these materials is that they can be shaped using conventional gravity or pressure diecasting equipment. The main applications for these materials have been for wear-resistance, such as brake discs for motor sport and for high-speed trains.

An improved high-speed mixing process, recently announced by MC-21 (USA), claims the ability to incorporate up to 40 volume percent of low-cost SiC particulate in a short process cycle time. This is said to enable the manufacture of cast composite products at lower cost than alternative processes. The process can be used for casting components, directly after the stirring has been completed, or the molten composite can be cast into ingots for subsequent remelting and casting; as for Duralcan®-type materials.

46.13.5.6 Pressure-assisted or squeeze casting

This process utilises a preform of ceramic particles or fibres which is placed in the cavity of a conventional metal die before the matrix alloy is mechanically forced into the interstices under high pressure.

The advantages of the process include:

- High production speed,
- Ability to produce components that are selectively reinforced.

These advantages can reduce cost and enable the component to be machined or joined using conventional techniques. The main application area has therefore been in the automotive industry.

46.13.5.7 Infiltration

Infiltration techniques are now widely used for aluminium-based MMCs because they are capable of incorporating high volume loadings of reinforcement. There are a number of variations on the general principle, mainly depending on whether or not it is gas pressure-assisted and the degree of pressurisation.

Gas pressure infiltration utilises a preform (usually of SiC) which is cast or moulded to near net-shape before introduction into the composite production tooling. This process is also used for chopped fibre reinforced composites which for some, predominantly flat, applications are preformed with the fibre axes randomly aligned in one plane to give enhanced thermal properties.

A pressureless process, known as Primex™, was developed by the former Lanxide Corporation and is now operated by licensees (including M Cubed and TTC). This process uses matrix alloys containing magnesium, which reacts with nitrogen gas in the production tooling, to give spontaneously reduced pressure which draws the molten matrix into the preform. This enables loadings of up to 70 volume percent SiC reinforcement to be produced. In a variant of the process an infiltrated bed of SiC is dispersed into a further volume of matrix alloy to give composites with lower reinforcement loadings which can be cast by conventional techniques.

The lower pressures compared with pressure or squeeze casting mean that more complex geometries can be produced, there is less tendency for damage to the performs and lower cost tooling can be used, which makes the process more suitable for lower production rates.

46.13.5.8 Spray forming

Spray forming uses gas pressure to atomise molten metal into a stream of small droplets, which are then rapidly solidified on a continuously withdrawn substrate.

Powdered reinforcement particles can be introduced into the stream of molten metal to produce MMCs with fine matrix grain size. These composites are mainly used for wear resistant applications in the automotive industry.

Alternatively, high silicon-containing aluminium alloys can be spray formed to produce ‘in-situ’ composites which contain higher silicon contents than that possible by conventional processing techniques. These products are used primarily for their lower thermal expansion coefficients that are tailored according to the alloy composition.

46.14 Discontinuously reinforced Al-alloys: Properties

46.14.1 General

Owing to the differences in process methods and test conditions between products from different manufacturers, the data presented (from suppliers) is generally grouped according to material, i.e.:

- Powder metallurgy.
- Melt infiltration processes.
- Spray-formed materials.

The text attempts to draw comparisons between materials, where possible.

46.14.2 Powder metallurgy MMCs

46.14.2.1 General

Products made by PM powder metallurgical processes are aimed primarily at high-strength and elevated temperature applications. Data from suppliers of materials in this category, AMC and DWA, is presented.

Whilst most of PM materials are aimed at applications in thermal management, taking advantage of their high conductivity and low expansion, several materials suitable for structural applications are also produced this way.

46.14.2.2 AMC225xe and AMC640xa

These AMC materials are produced from:

- AMC225xe: 2124 alloy with 25 vol.% 2µm to 3µm SiC.
- AMC640xa: 6061 alloy with 40 vol.% 2µm to 3µm SiC.

The products are available as plate, extrusions or forgings and typical room temperature properties are given in Table 46.14.1.

Table 46.14-1 – Al-MMC's: Room temperature properties of AMC225xe and AMC640xa

Properties	AMC225xe *	AMC640xa *	
Matrix alloy	2124	6061	
Reinforcement	SiCp	SiCp	
Volume (%)	25	40	
Product form	plate	extrusion	extrusion
Heat treatment	T4	T6	T1
Orientation	L	L	L
Ultimate tensile strength (MPa)	650	570	560
Yield stress (MPa)	480	480	440
Fatigue Strength, 10^7 cycles, (MPa)	310	230	-
Elongation (%)	5	2.5	3
Young's modulus (GPa)	115	140	140
Density (kg/m^3)	2880	2900	
Thermal conductivity, (W/mK)	150	130	
Coefficient of thermal expansion, (ppm/K)	15.5	13.4	
Electrical conductivity (%IACS)	21	21	
* Suppliers' data			

The effects of temperature on the tensile properties of AMC225xe plate are given in Table 46.14.2, and on both tensile and fatigue properties of extruded material in Table 46.14.3, which also includes results for two Duralcan® materials tested under the same conditions. The good temperature resistance and stability of these materials makes them suitable for applications such as nozzle guide vanes and control valve blocks.

Table 46.14-2 – Al-MMC's: Elevated temperature properties of AMC225xe plate

Thermal Cycling	Temper	Temperature (°C)	UTS (MPa)	YS (MPa)
As heat treated	T4	150	616	474
		200	530	448
		260	194	128
		350	65	48
	T1	150	428	321
		200	358	276
		260	200	102
		350	65	48
After 200 thermal cycles, 50°C to 200°C	T4	150	442	369
		200	343	265
		260	193	125
		350	59	45
	T1	150	348	269
		200	265	187
		260	150	92
		350	56	46

Table 46.14-3 – Al-MMC's: Elevated temperature properties of extruded AMC225xe compared with Duralcan® MMC's

Material	Temp. (°C)	UTS (MPa)	YS (MPa)	E (GPa)	Fatigue strength, 10^7 cycles, (MPa)
225xe - T4 (1)	24	633	486	116.2	410
	150	616	474	110.9	330
	200	530	448	108.3	203
	250	194	128	106.6	100
225xe - T1 (1)	24	477	328	115.2	290
	150	428	321	111.1	200
	200	358	276	109.2	160
	250	200	102	107.3	105
W2F20A-T6 (2)	24	369	286	97.3	280
	150	345	267	92.1	195
	200	314	236	89.9	150
	250	228	213	87.3	110
F3S20S - T6 (3)	24	331	282	104.9	180
	150	264	225	99.8	110
	200	230	201	97.2	95
	250	150	122	94.6	70

Key (1) AMC225xe (2124 + 25% SiCp extruded bar);
(2) Duralcan® W2F20A - T6 (2618 + 20% Al_2O_3p extruded bar);
(3) Duralcan® F3S20S - T6 (A359 + 20% SiCp forged disc).

46.14.2.3 DWA 2009/SiC and 6092/SiC

DWA is one of the longest established suppliers of powder metallurgy based Al-MMC's to the aerospace industry. Most of their products utilise FEPA F1000 (measured around 6 μm) SiC particulates although the finer F1500 grade (around 2 μm) is being evaluated.

The most commonly used products are based on 2009 and 6092 aluminium alloys with reinforcement loadings up to 25%.

Table 46.14.4 gives room temperature properties of 2009/SiC/15.5 extrusion together with data for 6092/SiC extrusions with two different SiC contents and one material in plate form.

Table 46.14-4 – Al-MMC's: Typical room temperature properties of DWA 2009/SiCp and 6092/SiCp composites

Properties (1)		2009/SiC /15.5p	6092/SiC /17.5p	6092/SiC /17.5p	6092/SiC/ 25p
Form		extrusion	extrusion	sheet	extrusion
Temper		T-42	T-6	T-6	T-6
Thickness (mm)		95.3	2.3	2.5	18.8
Density (kg/m^3)		2823	2796	2796	2823
Tensile strength (MPa)	L	552	510	462	517
	LT	510		455	483
Compressive strength (MPa)	L	-	462	407	427
	LT	-	-	386	407
Shear strength (MPa)	L	-	303	290	310
	LT	-	-	290	290
Flexural strength (MPa)	L (E/d=1.5)	-	793	731	703
	L (E/d=2.0)	-	1000	958	945
	LT (E/d=1.5)	-	-	758	696
	LT (E/d=2.0)	-	-	958	910
Flexural yield strength (MPa)	L (E/d=1.5)	-	703	689	683
	L (E/d=2.0)	-	827	855	834
	LT (E/d=1.5)	-	-	696	683
	LT (E/d=2.0)	-	-	841	834
Yield stress (MPa)	L	372	448	393	421
	LT	345		365	400
Elongation (%)	L	7	7	8	5
	LT	6	-	7	4
Elastic modulus (GPa)	L	95	105	101	121
	LT	92	-	101	114
Compressive modulus (GPa)	L	-	105	100	121
	LT	-	-	100	113
CTE(ppm/K)	L	-	-	16.4	15.3
	LT	-	-	-	16.9

Key: (1) Supplier's data

Further data on 2009/SiC extrusions is given in Table 46.14.5, which shows the effects of variations in particle content and size, matrix temper and extrusion ratio.

Table 46.14-5 – Al-MMC's: Typical room temperature tensile properties of DWA 2009/SiCp extruded composites

Matrix alloy	SiCp (vol. %)	SiCp d50 Value (µm)	Temper	Extrusion ratio	Direction	YS (MPa)	UTS (MPa)	Elong-ation (%)	*E* (GPa)
2009	0	0	T4	20:1 (1)	L	255	358	10.0	71
2009	5	6.43	T4	496: 1 (2)	L	400	531	10.0	79
2009	15	6.43	T4	14:1 (3)	LT	348	483	5.2	94
2009	15	6.43	T6	14:1 (3)	L	383	530	8.5	100
2009	15	6.43	T4	496:1 (2)	L	424	594	9.8	105
2009	20	6.43	T4	20:1 (1)	L	424	608	3.7	-
2009	25	6.43	T4	14:1 (3)	LT	372	496	1.7	112
2009	25	1.92	T4	14:1 (3)	LT	421	545	1.8	114
2009	25	1.92	T4	14:1 + forge (4)	LT	427	586	1.8	117
2009	25	1.92	T4	14:1 + forge (4)	L	448	662	2.4	121
2009	25	6.43	T4	496:1 (2)	L	462	669	5.1	119
2009	25	1.92	T4	496:1 (2)	L	483	669	3.2	123
Key:	Supplier's data. SiCp d50 value measured by DWAAC using Coulter laser diffraction; Extruded materials sizes: (1) 12mm thick rectangular bar; (2)16mm diameter round bar; (3) 95mm diameter round bar; (4) 95mm diameter round bar forged to 25mm thick rectangular bar								

The effects of elevated temperature on tensile and fatigue properties of 2009/SiC with 15% and 25% particulate loadings are shown in Figure 46.14.1 and Figure 46.14.2 with comparative data for conventional aluminium alloys in each case.

The higher properties are obtained from composites based on finer (F1500) particulates. These materials have been used for aerospace applications needing stability and high-temperature resistance, such as control valve blocks and nozzle guide vanes.

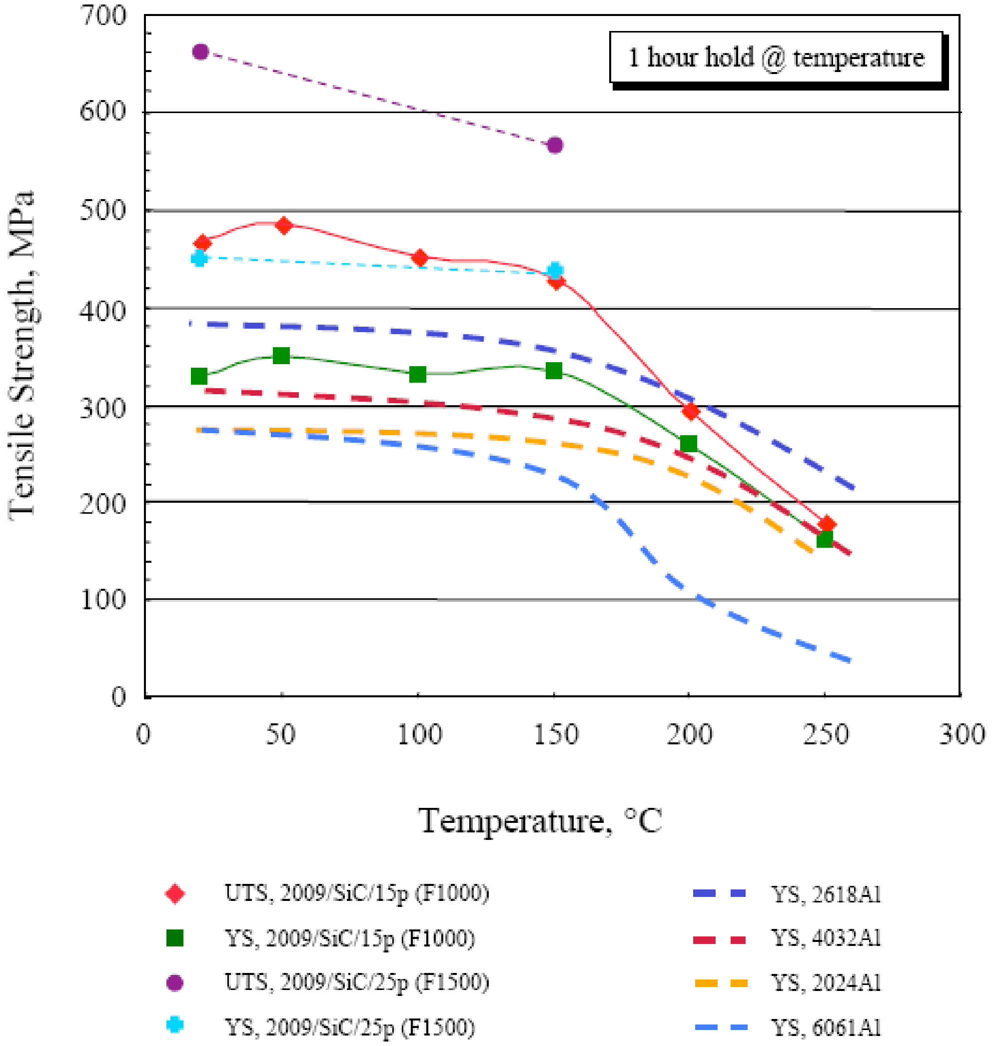


Figure 46.14-1 – Al-MMCs: Typical elevated temperature properties of 2009/SiC-T4 DRA compared with conventional wrought aluminium alloys

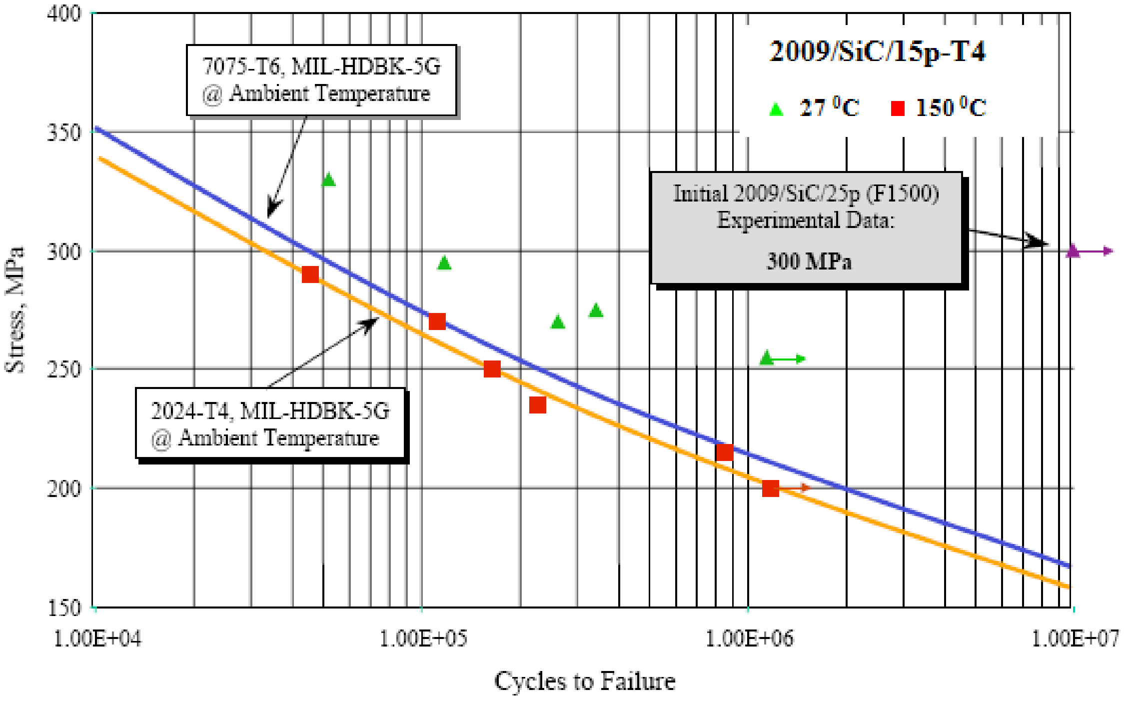


Figure 46.14-2 – Al-MMCs: Typical room and elevated temperature fatigue properties of 2009/SiC DRA compared with conventional wrought aluminium alloys

46.14.3 MMC's produced by melt infiltration processes

46.14.3.1 General

Current melt infiltration techniques are capable of producing aluminium-matrix composites with particulate loadings of up to 70 volume percent. By incorporating reinforcements with high conductivity and low expansion coefficient, these composites are finding wide use as lightweight materials for packaging of semiconductor devices for aerospace applications.

In addition, particularly at lower reinforcement loadings, many materials produced this way offer good combinations of mechanical and thermal properties and the ability to be cast to near net-shape, which makes them suited to structural space applications.

46.14.3.2 CPS AlSic-series materials

AlSic materials, from CPS - Ceramic Process Systems, are made using a gas pressure infiltration technique enabling SiC loadings up to 63 vol.%. The SiC preforms are moulded to near net-shape, which reduces the extent of subsequent machining necessary. Some typical properties for AlSic materials are given in Table 46.14.6.

Whilst both matrix and particulates contribute to the high thermal conductivity, which gradually increases with SiC content, the low expansion coefficient of SiC results in composites with significantly lower thermal expansion at higher particulate contents.

Table 46.14-6 – Al-MMC's: Typical properties of CPS Al/SiCp composites

Properties	AlSiC-9	AlSiC-10	AlSiC-12
Matrix Alloy A 356.2	37 vol.%	45 vol.%	63 vol.%
Reinforcement SiC (electronic grade)	63 vol.%	55 vol.%	37 vol.%
Strength (MPa) a-bar 4pt-bend	488	450	471
Young's Modulus (GPa)	188	167	167
Shear Modulus (GPa)	76	67	69
Density (kg/m3)	3010	2960	2890
Thermal Expansion, CTE, (ppm/°C):			
30°C to 100°C	8	9.77	10.9
30°C to 150°C	8.37	10.16	11.2
30°C to 200°C	8.75	10.56	11.7
Specific Heat (J/kgK) @ 25°C	741	786	808
Thermal Conductivity (W/mK) @25°C	200 typ. / 190 min	200 typ. / 190 min	180 typ. / 170 min
Electrical Resistance (μohm.cm)	20.7	20.7	20.7
Supplier's data.			

46.14.3.3 MCX-series Al/SiC materials

The Primex™ pressureless infiltration process developed by Lanxide is now used by Thermal Transfer Composites (TTC) to produce a range of thermal packaging materials.

The MCX-xxx series uses near net-shape SiC preforms to produce components with high contents of particulate to give low thermal expansion coupled with high thermal conductivity.

The MCX-xxxx series uses the PRIMEX CAST™ process in which a bed of infiltrated SiC particulates is diluted with molten matrix alloy to enable the (less viscous) composite to be cast using conventional techniques. Having lower SiC contents, these materials have intermediate values of thermal expansion coefficient, around half that of the unreinforced matrix alloy but, since they can be cast to near net-shape, they are suited to controlled expansion structural applications.

Typical properties of a number of MCX-xxx and MCX-xxxx materials are given in Table 46.14.7.

Whilst the actual SiC contents are not stated by the supplier, they can be estimated from the values given for density since SiC has a value of about 3.20kg/m^3 compared with about 2.70kg/m^3 for aluminium alloys.

Table 46.14-7 – Al-MMC's: Typical room temperature properties of TTC Al/SiCp composites

1: PRIMEX™

Properties	MCX-693	MCX-686	MCX-696	MCX-724	MCX-947
Flexural strength, 4pt-bend (MPa)	300	480	517	330	530
Young's modulus (GPa)	255	235	262	235	196
Poisson's ratio	0.24	0.22	0.25	0.23	0.25
Density (kg/m³)	2980	3000	3010	2940	2950
Coefficient of thermal expansion (ppm/K)	6.4	6.8	6.9	7.2	9.4
Specific heat (J/kg.K)	720-760	720-760	720-760	720-760	720-760
Thermal conductivity (W/mK)	180	175	192	165	179
Electrical resistivity (µohm.cm)	30 - 50	30 - 50	30 - 50	30 - 50	30 - 50
Supplier's data.					

2: PRIMEX CAST™

Properties	MCX-1195	MCX-1405	MCX-1605
Ultimate tensile strength (MPa)	226	239	295
Young's modulus (GPa)	151	125	106
Poisson's ratio	0.28	0.29	0.31
Density (kg/m³)	2870	2800	2770
Coefficient of thermal expansion (ppm/K)	11.9	14	16.2
Specific heat (J/kg.K)	763	830	890
Thermal conductivity (W/mK)	183	165	132
Supplier's data.			

46.14.3.4 ASC-xxx Al/SiC series materials

The Lanxide process is also used by M Cubed Technologies to produce a range of composites with SiC loadings from 30% to 70%, by volume. The properties of these ASC-xxx materials are given in Table 46.14.8 and, as expected from the similar process technology, are similar to those of the MCX-xxxx PRIMEX CAST™ materials from TTC. These materials are also of interest for both thermal management and structural applications.

Table 46.14-8 – Al-MMC's: Typical properties of composites from M Cubed Technologies

Properties	**Material designation**					
	ASC-301(1)	**ASC-303**	**ASC-401(1)**	**ASC-551(1)**	**ASC-701(1)**	**HSC-702E(2)**
Matrix	Al			Al-Si		
Particle Reinforcement	SiC	SiC	SiC	SiC	SiC	SiC
Content (% vol.)	30	30	40	55	70	75
Matrix (Heat Treatment)	Al-10Si-1Mg (T6)	Al AA359	Al-10Si-1Mg (T6)	Al-Si-Mg (F)	Al-Si-Mg (F)	Al-70Si
UTS, (MPa)	370	300	370	340	230	-
Flexural strength, (MPa)	-	-	-	-	-	270
Modulus, (GPa)	125	120	150	200	270	345
Poisson's ratio	0.29	0.29	0.28	0.24	0.22	0.19
Fatigue Limit, 10^7 cycles:						
R = 0.1 (MPa)	190					
R = –1 (MPa)	130					
Fracture Toughness (MPa√m)	15	-	-	11	10	5.5
Density, (kg/m^3)	2780	2780	2870	2950	3010	3040
CTE, 25°C to100°C, (ppm/K)	14	15	12	10	6.2	4.1
Thermal Conductivity (W/mK)	160	146	170	180	170	210
Specific heat (J/kg K)	820	-	750	-	730	700
Knoop hardness, 500g load (kg/mm^2)	165	-	-	343	647	1609

Key: Suppliers' data.
(1) ASC materials produced under Lanxide licenses;
(2) reactive infiltration technique of preform

The material designated HSC-702E is produced using a reactive infiltration technique in which a preform of SiC-containing free carbon is infiltrated with an Al-Si alloy.

The Si from the melt reacts with the free carbon to produce additional SiC, assisting the bonding of the final material, which can be considered as an aluminium-toughened SiC rather than an Al/SiC MMC. However, it is included in the Table, for comparison, where the higher hardness and lower expansion coefficient are apparent.

46.14.3.5 METSIC™ Al/SiC

Metal Matrix Cast Composites Inc (MMCC) has adapted rapid prototyping technology to the preparation of complex shaped reinforcement preforms directly from CAD files. These are then infiltrated with molten aluminium alloy using a proprietary pressure investment casting process.

The process is aimed at structural applications and typical properties of an Al/SiC/40$_p$ composite are given in Table 46.14.9, together with 6061 aluminium alloy and 1010 steel for comparison purposes.

Table 46.14-9 – Al-MMC's: Typical properties of MMCC METSIC™ Al/SiCp composite compared with aluminium and steel

Properties	Material		
	METSIC™	Al 6061-T6	1010 Steel
Matrix	Al	-	-
Reinforcement (%)	40 SiC	-	-
Ultimate tensile strength (MPa)	300-400	310	365
Young's modulus (GPa)	150	69	205
Density (kg/m^3)	3000	3000	8000
Thermal expansion (ppm/K)	10-12	23.6	12.2
Thermal conductivity (W/m.K)	185	167	49
Suppliers' data.			

46.14.3.6 Carolite® Al/SiB6 materials

As an alternative to SiC reinforcements, Millenium Materials has published limited information on Al/SiB$_6$ reinforced composites. It is claimed that whilst this reinforcement offers similar strength and stiffness enhancements to that obtained with SiC, its lower density makes it easier to disperse, and remain suspended, in molten aluminium alloys. This is said to make casting, using conventional techniques, more practicable and also enable the material to be recycled, so reducing costs. However, the low thermal conductivity of SiB$_6$ means the composites incorporating this material are aimed primarily at cast structural components.

Preliminary data for Carolite® composites is given in Table 46.14.10. Most of the data presented is calculated using the rule of mixtures for Al/SiC composites. Only the property values with grey background are actual data

Table 46.14-10 – Al-MMC's: Typical properties of Millenium Materials Carolite® SiB_6 particulate reinforced composites

Hexon® SiB_6 (vol.%)	Ultimate tensile strength (2) (MPa)	Yield stress (2) (MPa)	Fatigue strength(2) (MPa)	Elastic modulus(3) (GPa)	Thermal conductivity(3) (W/mK)	Thermal expansion(3) (ppm/K)
Matrix alloy A356A356						
0	**228**	**165**	**62**	**69**	**151**	**21.5**
10	259	221	131	97	146	15.5
15	345	310	138	103	120	14.9
20	352	324	145	117	110	14.3
30	372	345	159	145	100	12
40	386	359	172	154	95	9.7
50	407	379	186	193	85	8.9
60	427	400	200	214	75	8
70	448	421	207	241	65	7.1
Matrix alloy 6061-T6						
0	**310**	**276**	**62**	**69**	**201**	**23.5**
10	352	317	131	97	194	16.9
15	469	434	138	103	160	16.2
20	476	441	145	117	146	15.6
30	503	469	159	145	133	13.1
40	524	490	172	165	126	10.6
50	552	517	186	193	113	9.7
60	579	545	200	214	100	8.7
70	607	572	207	241	86	7.7

Key Suppliers' data.

(1) Values with grey background are actual data;

(2) Strength data estimated from data in literature for MMCs containing SiC. Due to the similarity of Hexon® SiB_6 and SiC, similar reinforcement effects are expected;

(3) Estimated from rule of mixtures or a fit to actual data.

46.14.3.7 MetGraf™ Al/Cf

In addition to high tensile strength and modulus, some grades of graphitised pitch-based carbon fibres have extremely high thermal conductivity (around 500 W/mK to 1000W/mK) in the axial direction. This is coupled with low density and low coefficient of thermal expansion, which in the transverse direction can be negative, although transverse thermal conductivity is low (around 2.4 W/mK).

By incorporating chopped fibres, randomly oriented in a 'felted' preform, Metal Matrix Cast Composites (MMCC) have produced aluminium-matrix composites with high thermal conductivity coupled with low expansion coefficient in the x-y directions and thermal properties reflecting those of the matrix material in the z-direction; as shown in Table 46.14.11.

Table 46.14-11 – Al-MMC's: Typical room temperature properties of MMCC MetGraf™ Al/Cf composites

Properties		MetGraf® 4-230	MetGraf® 7-200
Matrix alloy		Al/Si	Al/Si
Ultimate tensile strength (MPa):	In-plane (x-y)	103	93
	Thickness (z)	-	0
Ultimate compressive strength (MPa)		203	203
Flexural strength (MPa)		186	159
Yield stress, compression (MPa)		110	110
Young's modulus (GPa)		98	89
Density (kg/m^3)		2400	2500
Thermal expansion, average value of –55°C to +125°C (ppm/K):	In-plane (x-y)	4	7
	Thickness (z)	24	24
Thermal conductivity (W/mK):	In-plane (x-y)	230	200
	Thickness (z)	120	125
Electrical resistivity (µ.ohm.cm)		–	6.89
Hardness (Rockwell E)		–	60-80

Suppliers' data.

The special feature of these materials of interest for space applications is the very low density compared with conventional low expansion thermal packaging materials; given in Table 46.14.12.

The chopped fibre reinforcement also imparts good strength and modulus making these materials suited to applications needing a combination of good thermal management together with structural stiffness and dimensional stability, such as space mirrors.

Table 46.14-12 – Al-MMC's: Typical properties of MMCC MetGraf™ Al/Cf composites compared with other thermal packaging materials

	MetGraf® 7-200	**MetGraf® 4-230**	**Kovar**	**Al/SiC**	**CuMo 80-20**	**CuMo 85-15**	**CuW 90-10**	**CuW 85-15**
Thermal conductivity (W/mK)	200	230	17	180	160	140	160	175
Thermal expansion (ppm/K)	7.5	4.0	5.9	6.7	7.2	6.5	6.1	6.7
Density (kg/m^3)	2460	2400	8300	3200	9800	9900	1770	1630

Suppliers' data.

46.14.4 Spray-formed materials

46.14.4.1 Osprey CE alloys

The spray-forming process, developed by Osprey, was a bulk rapid solidification process for the manufacture of enhanced conventional alloys. The process was expanded to enable the incorporation of reinforcement particulates. The German licensee, Peak Werkstoff, is understood to be supplying wear-resistant Al-MMCs to the automotive industry.

Osprey are now concentrating on the manufacture of Al/Si low expansion materials. These are 'in-situ' composites in that the second phase material (in this case Si) is precipitated in fine form from a supersaturated high-temperature molten alloy by rapid solidification.

The process can be used for materials containing from zero to 70% Si which means the low expansion coefficient of silicon can be utilised to tailor the composite properties to any value between that of the base aluminium to around 8ppm/K for the 70% Si alloy.

The main advantages of these materials over alternative thermal packaging MMCs is their low density, because Si has lower density than SiC, and their ability to be machined using conventional equipment. Typical properties of the standard range of alloys are given in Table 46.14.13.

Table 46.14-13 – Al-MMC's: Properties of Osprey CE Al-Si 'in-situ composite' alloys

Properties	Osprey standard alloys					
	CE7	**CE9**	**CE11**	**CE13**	**CE17**	**CE17M**
Silicon content (%)	70	60	50	42	27	27
Density (kg/m^3)	2400	2450	2500	2550	2600	2600
Ultimate tensile strength (MPa)	100	134	138	176	236	380
Bend strength (MPa)	143	140	172	213	210	-
Yield stress (MPa)	100	134	125	155	183	-
Young's modulus (GPa)	129	124	121	107	92	92
Shear modulus (GPa)(1)	51	49	49	42	36	36
Poisson's ratio	0.26	0.25	0.25	0.27	0.28	0.28
Coefficient of thermal expansion (ppm/°C):						
–60°C to 200°C	7.6	-	11.6	-	-	-
25°C to 100°C	7.4	9.0	11.0	12.8	16.0	16.0
25°C to 200°C	8.3	9.9	12.7	13.6	17.0	17.0
25°C to 300°C	8.5	10.5	13.1	14.4	17.7	17.7
25°C to 400°C	8.2	10.8	13.7	15.0	17.5	17.5
25°C to 500°C	7.7	10.1	14.4	15.2	16.8	16.8
Thermal conductivity (W/mK):						
–100°C	180	-	-	-	-	-
–50°C	140	-	-	-	-	-
0°C	125	-	-	-	-	-
25°C	120	129	149	160	177	147
100°C	110	125	132	-	-	-
200°C	100	108	122	-	151	147

Key: Suppliers' data: Osprey (http://www.smt.sandvik.com/)
(1) Supplier quoted 'Rigidity modulus'

46.14.5 Further information

Owing to the manner in which discontinuously-reinforced materials are produced, there is scope for varying the properties to suite the specific needs of the user. The suppliers listed therefore tend to have additional information, which is published openly.

[See also: 46.12; Table 46.12.1 for supplier details]

46.15 Continuously Reinforced Al-Alloy MMC

46.15.1 General

Only those continuously reinforced aluminium composites produced by melt infiltration processes are described.

Materials produced mechanically by solid state bonding processes are described separately under FML - Fibre Metal Laminates, [See: Chapter 100].

46.15.2 Fibres

46.15.2.1 General

Continuous reinforcements studied for aluminium MMCs include, [See also: 42.6].

- Alumina fibres,
- Alumino-silicate fibres,
- Boron filament,
- Carbon fibres,
- Silicon carbide filaments and fibres,

Whilst boron and silicon carbide fibres received some attention, mainly for specialised military applications, these reinforcements have not been developed for wider spread use, so are not considered of current interest for space applications. Problems associated with these materials were both technical and economic.

Table 46.15.1 gives typical properties of those continuous reinforcement fibres which are of greatest interest for use with aluminium matrix alloys. Whilst activity continues on the development carbon fibre reinforced materials (much of the work is covered by US military restrictions), only Nextel 610 fibres have achieved significant commercial status, Ref.[46-79].

Table 46.15-1 – Al-MMC's: Typical properties of continuous reinforcing fibres

Fibre type(1)/Name	**Carbon HT**	**Carbon IM**	**Carbon HM**	**Al_20_3:SiO_2 Altex®**	**Al_20_3 Nextel® 610**
Composition	> 99% C	> 99% C	100% C	15% $Si0_2$	99% Al_2O_3
Density (kg/m^3)	1800	1800	1800 – 2200	3300	3900
Properties (2):					
Strength (MPa):					
L	4000-5000	5300-6400	1900-4400	1800	3000
Young's modulus (GPa):					
L	230-235	290-300	380-930	210	380
T	15	15	15	210	380
Thermal expansion (ppm/K):					
L	−0.1 to −0.4	−0.1 to −0.4	−1.2 to −1.5	6	7.9
T	n.a.	n.a.	9.5 to12.5	-	-
Thermal conductivity (W/mK):					
L	9 to 17	32 to 35	69 to 1050	-	<30
T	low	low	low	-	<30
Key:	(1) HT - high tenacity; IM - intermediate modulus; HM - high modulus (2) L longitudinal; T transverse Altex is a tradename of Sumitomo; Nextel® is a tradename of 3M				

46.15.2.2 Alumina Nextel™ 610

Nextel® 610 is a continuous alumina fibre, classed as high-tensile – high-modulus, from 3M and supplied in a roving form (fibre bundles). Fibres have a coating (size) that is removed at temperatures above 550°C, i.e. at melt infiltration temperatures. Typical properties for Nextel® 610 are summarised in Table 46.15.2.

Table 46.15-2 – Al-MMC's: Typical properties of 3M Nextel™ 610 alumina fibre

Nextel® 610 (1)	Properties
Composition, α-alumina, Al2O3 (%)	>99
Filament:	
Filament tensile strength, 25mm gauge (MPa)	3100
Filament tensile modulus of elasticity (GPa)	379
Roving:	
Sizing (%)(1)	2.0
Sized denier(2)	3000
Filament diameter (μm)	12
Filament count	750
Filament density (kg/m^3)	3.90
Surface area (m^2/gm)	<1
Roving tensile breaking load, 150mm gauge (N)	89
Creep rate (69MPa) at temperature:	
1000°C	2.0×10^{-9}/s
1100°C	1.8×10^{-7}/s
1200°C	1.7×10^{-5}/s
Coefficient of thermal expansion (ppm/K)	8.0
Dielectric constant (9375 MHz)	9.0
Key: (1) Suppliers' data. Nextel® is a tradename of 3M; (2) Percentage by mass of fibre coating; (3) Grams per 9000m of material with sizing (coating) applied.	

46.15.2.3 Carbon fibres

Carbon fibres are available in three main types:

- HM - high modulus, where fibres are either pitch-based or high-temperature treated PAN based.
- HT - high tenacity, which are low-temperature treated PAN based.
- IM - intermediate modulus, which are PAN-based, with a specific heat treatment.

Although the fibres used for continuous reinforcement of aluminium alloys are the same as those used for CFRP composites, only a limited number have been evaluated for MMCs, e.g. Thornel HM types P-100, P-120 and K-1100 from Cytec.

46.15.3 Matrix alloys

Many aluminium alloys have been considered for use as MMC matrix phases. Since variations of the melt infiltration process are used to incorporate the aluminium matrix, this influences the choice of alloy. The main considerations are:

- fluidity of the melt,
- fibre-matrix interface bonding,
- prevention of melt fibre interactions.

Owing to these factors, the most commonly used matrix material is commercially pure aluminium (99.85%). Other matrix materials used include Al-2%Cu, 3xx casting alloys and 6061 wrought alloy.

The use of 3xx (Al/Si) casting alloys is said to overcome the problems of aluminium carbide formation, which otherwise causes fibre degradation and poor fibre-to-matrix bonding, Ref. [46-81].

46.15.4 Characteristics

46.15.4.1 Carbon fibre reinforced composites

Initial work with carbon fibre reinforced aluminium composites was unsuccessful because of property degradation arising from the formation of aluminium carbide at fibre-matrix interfaces and surface tension problems resulting in incomplete penetration of the fibre bundle.

Such problems have been resolved by using silicon-containing alloys, which results in the formation of a barrier layer of SiC at the fibre-matrix interface. The solubility of carbon is also because of the alloy silicon content, Ref. [46-81]. A remaining problem with carbon fibre reinforced aluminium, which is limiting extended application, is the susceptibility to galvanic corrosion.

The densities of carbon fibres are around half that of alumina fibres, which makes carbon fibre-reinforced composites of particular interest where weight-saving is a prime consideration.

46.15.4.2 Alumina fibre reinforced composites

The addition of alumina fibres to aluminium is a natural combination because of the chemical compatibility and the freedom from galvanic corrosion; a known problem with carbon reinforcements. The most widely used, 3M Nextel 610, fibres have similar strength and modulus to many carbon fibres, [See: Table 46.15.1], and can also be used as preforms with complex shapes and tight radii. This makes them suitable for shaped components in addition to unidirectional reinforcements.

In addition to useful mechanical properties at elevated temperatures, this group of materials are perceived as having benefits over other MMCs in situations where corrosion can be a problem.

46.15.5 Processing

46.15.5.1 General

Processing routes fall into two broad categories:

- continuous lengths of materials (prepregs and shapes).
- discrete products, using preforms.

Both types of products are processed using liquid metal infiltration techniques.

46.15.5.2 Continuous infiltration

TRL - Touchstone Research Laboratory (USA) use a process similar to pultrusion of polymer composites, for the manufacture of their MetPreg™ continuously reinforced tapes. These are generally based on Nextel® 610 alumina fibres in a pure aluminium matrix, although the use of glass or carbon fibres has also been studied, Ref. [46-82].

As well as a basic thin tape, which is utilised as a prepreg material for lay-ups, filament winding or other fabrication techniques, the process is also suitable for producing continuous tubes, angles or channels, [See also: 46.16 - typical properties].

46.15.5.3 Preform infiltration

Preform infiltration processes used for continuous reinforcements are similar to those used for discontinuously reinforced composites, [See: 46.13].

Infiltration is achieved through applied gas pressure, usually with prior evacuation of the mould cavity. The preforms can consist of loose bundles of fibres, woven cloths or filament wound structures suitable for manufacture of cylindrical or tubular components.

A number of different processes are used, including pressure-assisted investment casting and gas pressure infiltration.

LPF - liquid pressure forming is a process developed by CMT (Composite Metal Technologies), which has similarities with the low pressure diecasting process used for aluminium alloys.

The preform is placed in a heated metal die which is evacuated before liquid aluminium is introduced by a two-step pressurisation process. After completion of the infiltration, the melt is consolidated by a higher pressure applied by hydraulic pistons.

46.16 Continuously reinforced Al-alloy MMC: Properties

46.16.1 Mechanical properties

46.16.1.1 General

Continuously reinforced composites, in particular unidirectionally reinforced materials, tend to be anisotropic in that the properties in the longitudinal direction are highly dependent upon those of the reinforcement whilst in the transverse direction the properties of the matrix alloy have a greater influence.

Since the properties of shaped composites are highly dependent upon the specific orientation of the reinforcement only data for unidirectionally reinforced materials is given here as guidance to the properties that can be expected.

Composites with bi-directional reinforcement, either from a woven, lay-up or filament wound fibre reinforcement, are available but there is no property data published openly.

An estimation of property values can be made using established techniques or by comparison with those for fibre-reinforced polymers.

Typical room temperature properties of a number of continuously reinforced aluminium-matrix composites are given in Table 46.16.1, Ref. [46-79].

46.16.1.2 Alumina fibre reinforced composites

The greatest activity on continuously reinforced aluminium-matrix composites has been in the development of Nextel® 610 alumina reinforced materials.

The fibres are readily available and the composites do not pose the risk of galvanic corrosion which is present with carbon fibre reinforced aluminium.

Table 46.16-1 – Al-MMC's: Typical properties of continuously reinforced MMCs

Fibre (1)	**Vol %**	**Matrix**	**Process (2)**	**Density (kg/m^3)**	**Direction (3)**	**UTS (MPa)**	**E (GPa)**	**CTE (ppm/K)**	
								50°C 150°C	**50°C 300°C**
Carbon (M40,Toray)	60	Al99.85	GPI	2200	L	1500	240	–0.2	0
Carbon (EHMS, Courtaulds)	60	Al99.85	GPI	2200	L	1000	230	0.6	0.2
					T	100	30	17.0	-
Alumino-silicate Al$_2$O$_3$:SiO$_2$ (Altex)	50	Al99.85	GPI	3000	L	1050	130	7.5	6.6
					T	130	115	14.0	17.0
Alumino-silicate Al$_2$O$_3$:SiO$_2$ (Altex)	50	AlZnMg	PAIC	3000	L	1000	135	-	7.3
					T	200	85	-	18.7
Alumina Al$_2$O$_3$ (Nextel 610)	50	AlZnMg	PAIC	3200	L	1200	240	-	-
Alumina Al$_2$O$_3$ (Nextel 610)	60	Al99.85	GPI	3300	L	2000	260	n. a.	-
Alumina Al$_2$O$_3$ (Nextel 610)	60	Al99.85	3M	3400	L	1600	240	-	7
					T	120	130	-	16

Key: (1) Reinforcement fibre (material, name/code, source);
(2) GPI - gas pressure infiltration; PAIC - pressure assisted investment casting;
(3) L – longitudinal; T – transverse.

46.16.1.3 Infiltrated composites

Typical room temperature properties of Nextel® reinforced pure aluminium and Al-2%Cu alloy are given in Table 46.16.2.

Table 46.16-2 – Al-MMC's: Typical properties of 3M unidirectional Al-Nextel□ composites

Properties $^{(3)}$	Matrix	
	Pure Al	**Al-2%Cu** $^{(1)}$
Fibre reinforcement	Nextel®	Nextel®
Fibre volume (%)	60	60
Ultimate tensile strength (MPa): L	1600	1500
Ultimate compressive strength (MPa): L	1700	3400
Shear strength, at 2% strain (MPa)	70	140
Transverse strength, at 1% strain (MPa): T	140	280
Young's Modulus (GPa):		
L	240	240
T	130	160
Shear Modulus $^{(2)}$ (GPa)	48-57	45-56
Density (kg/m^3)	3400	3400
Coefficient of thermal expansion, average value 25°C to 500°C (ppm/K):		
L	7	9
T	16	16

Key: Suppliers' data.
(1) weight percent;
(2) measured parallel and across fibres;
(3) L – longitudinal; T – transverse.

The influence of the stronger Al-2%Cu matrix can be seen in the transverse, compressive and shear properties.

The good elevated temperature resistance of alumina fibres provides enhanced elevated temperature tensile properties to the Al-Nextel® composites.

For the composite based on pure aluminium with 60 volume% Nextel® fibres, the properties at 3000C are:

- Longitudinal tensile strength: 1400 MPa (RT 1600 MPa),
- Longitudinal Young's modulus: 200 GPa (RT 240 GPa).

For many aerospace applications, good axial strength and stiffness coupled with light weight are of high importance. These properties of alumina fibre-reinforced aluminium, together with the good elevated temperature properties, have been exploited in push rods for motor sport engines.

Typical properties of the base material and of 226mm long × 9.5mm diameter push rods are given in Table 46.16.3. Data for 4130 steel is included for comparison purposes.

Table 46.16-3 – Al-MMC's: Typical properties of 3M MMC push rods

Material		
Properties	**Al/Nextel®**	**4130 Steel**
Stiffness (GPa)	221	205
Ultimate Compressive Strength (MPa)	2400	1500

Application: Push rods⁽¹⁾; 9.5mm diameter × 226mm long		
Properties	**Al/Nextel®**	**4130 Steel**
Bending stiffness (Nm2)	84	74
Compressive failure load (kN)	132	72
Critical buckling load (kN)	16.29	14.28
First bending resonance (Hz)	630 Hz	-
Key: Suppliers' data. Nextel® is a tradename of 3M Corp. (1) High-performance motor sport engine component		

46.16.1.4 Prepreg-based composites

Composite with unidirectional reinforcement, produced by filament winding or lay-up can also be produced from continuously infiltrated prepreg, such as MetPreg™ Al-alumina fibre material, [See: 46.15].

Typical properties for the basic tape material, 9.5mm wide × 0.5mm thick, are given in Table 46.16.4, Ref. [46-82].

The properties are close to those published by 3M for similar materials.

Table 46.16-4 – Al-MMC's: Typical properties of TRL MetPreg™ Al/Al_2O_3f continuous fibre composites

MetPreg™ alumina reinforced aluminium 'prepreg' tape	
Characteristics:	
Matrix	Pure Al
Reinforcement fibre	Nextel 610
Fibre content (Volume %)	50
Thickness (mm)	0.5
Width (mm)	9.5
Density (kg/m^3)	3300
Properties:	
Tensile strength, at RT (MPa)	1500
Tensile modulus, at RT (GPa)	215
Compressive strength, at RT (MPa)	2070
Elongation (%)	0.7
Maximum use temperature$^{(1)}$ (°C)	400
Thermal expansion (ppm/°C)	7
Thermal conductivity (W/mK)	115
Electrical resistivity (µohm.cm)	5

Key: MetPreg™ is a tradename of TRL – Touchstone Research Laboratory (USA).
Nextel® is a tradename of 3M Corp.
(1) 85% of the room temperature tensile strength.

46.16.1.5 Carbon fibre reinforced composites

Since carbon fibre reinforced aluminium is susceptible to galvanic corrosion, there has been less commercial activity on these materials.

Companies, including MMCC-Metal Matrix Cast Composites, have been working in this area, but publication of the results is restricted under US DoD and other security regulations. Through the use of silicon-containing alloys, MMCC claim to have overcome the melt-to-fibre interface reaction that resulted in aluminium carbide formation, which also posed problems in the consolidated composites. This approach has been used for producing discontinuously, chopped carbon fibre-reinforced aluminium composites, Ref [46-81]. [See: 46.14].

46.16.2 Physical properties

All the continuously reinforced aluminium-matrix composites have low densities, with carbon fibre-reinforced materials offering the greatest potential benefits. These materials also offer high thermal conductivities and low thermal expansion coefficients, properties of importance for long term dimensional stability and heat dissipation properties in aerospace applications.

As with the mechanical properties, the enhanced thermal properties resulting from the reinforcement are found mainly in the longitudinal direction.

Where available, physical properties are given for:

- Thermal expansion: Carbon (Toray M40), alumino-silicate (Altex) and alumina (Nextel) reinforced aluminium alloys, [See: Table 46.16.1; Table 46.16.2; Table 46.16.4].
- Electrical properties and thermal conductivity: MetPreg™ alumina reinforced aluminium, [See: Table 46.16.4].

46.17 Al-alloy MMC: Potential applications

46.17.1 Benefits of Aluminium-matrix composites

Traditionally aluminium alloys are the main group of materials used in aircraft and spacecraft construction for operational temperatures up to 150°C.

Whilst aluminium has been replaced by advanced polymer composites, e.g. CFRP, and fibre-laminate materials, e.g. GLARE™, advances in aluminium-based MMCs have resulted in a range of materials that offer substantial benefits compared with polymer matrix composites for specific applications in spacecraft and launch vehicles. These benefits can be summarised as:

- High specific strength,
- High specific stiffness,
- High thermal conductivity,
- Low thermal expansion
- Good long-term dimensional stability,
- Electrical conductivity,
- Better radiation resistance,
- No outgassing,
- Better resistance to fuels and solvents
- Reduced flammability risk.

As an example of the good specific properties of Al-MMCs, Figure 46.17.1 shows a property map of continuously-reinforced alumina fibre aluminium matrix composites together with the properties for competitive materials.

Some examples of applications-based uses include those demanding:

- High specific strength and temperature resistance.
- High specific stiffness and good thermal properties.

- High conductivity with low thermal expansion.
- High specific stiffness and dimensional stability.
- High specific strength and chemical resistance.

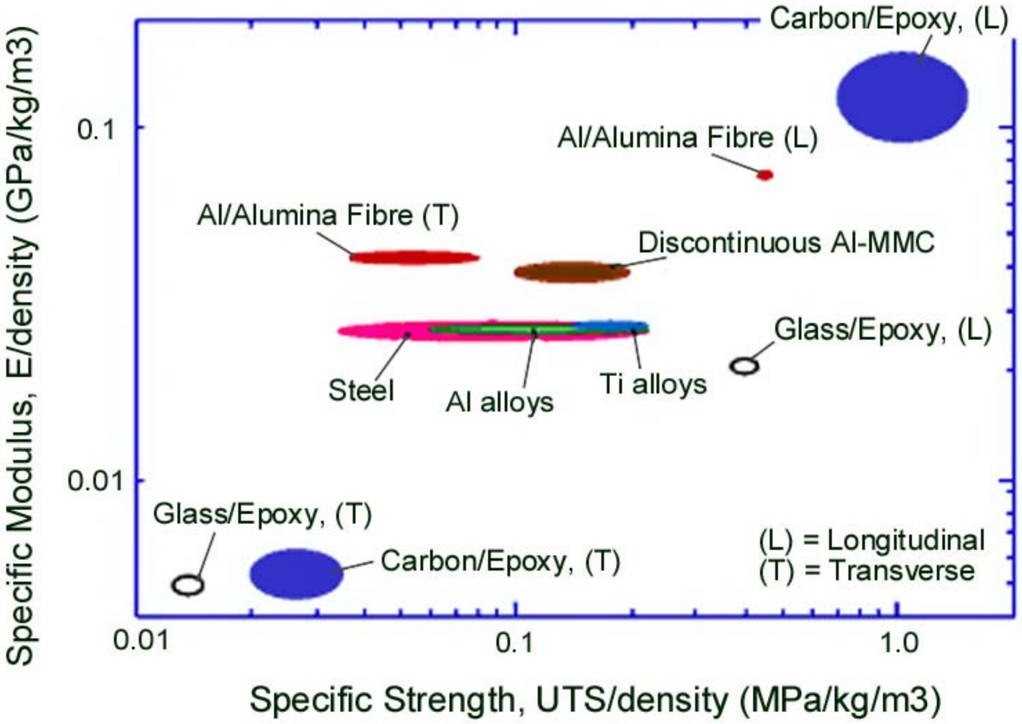


Figure 46.17-1 – Al-MMCs: Comparison between Al-continuously reinforced alumina fibre composites and other materials

Some examples of case histories are also available from:

- Suppliers' websites, [See: Table 46.12.1],
- MMC-Assess, Ref. [46-75].

An extensive review of the current and potential space applications for aluminium matrix composites is given in Ref. [46-76].

46.17.2 High specific strength and temperature resistance

Discontinuously reinforced Al/SiCp composites are being used for hydraulic control block for helicopters and nozzle guide vanes for gas turbine engines. This indicates potential applications for high-duty applications in launchers.

46.17.3 High specific stiffness and good thermal properties

The antenna waveguide for the Hubble Space Telescope was initially made from carbon fibre infiltrated with 6061 alloy. This was eventually replaced by discontinuously reinforced Al-MMC at lower cost, whilst still maintaining high stiffness combined with good heat dissipation and good dimensional stability resulting from the low thermal expansion coefficient. These properties have also been exploited in thermal radiator panels on other spacecraft.

46.17.4 High conductivity with low thermal expansion

Al/SiCp discontinuously reinforced composites and Al/Si CE alloys are being used for thermal management of semiconductor devices. The electrical conductivity of Al-MMCs also offer electronic and radiation shielding for sensitive components together with a significant weight-saving compared with traditional electronics packaging materials.

46.17.5 High specific stiffness and dimensional stability

Aluminium-based MMCs are being evaluated as substrates and carriers for space mirrors. In addition to light weight, this application needs high stiffness and excellent, uniform dimensional stability; properties which are facilitated by the low thermal expansion and high thermal conductivity offered by discontinuously reinforced aluminium-matrix composites.

46.17.6 High specific strength and chemical resistance

Propellant tanks are often made from aluminium alloys, but continuously reinforced aluminium composites offer further potential for weight reduction as a result of the higher specific strength.

Such components are candidates for filament wound or lay-up methods of construction using either liquid infiltration or aluminium prepreg materials.

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'Airbus-Russia Co-operation: Light alloys', Session LAT051.1.
AeroMat 2005, Orlando, Florida, June 2005

[46-85] 'Creating a Titan'
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Download from: www.home.no/al-sc/

[46-87] P.S. Gilman et al: Allied-Signal, Inc.
'Rapidly solidified aluminum-transition metal alloys for aerospace applications'
AIAA-1988-4444 : AHS, and ASEE, Aircraft Design, Systems and Operations Meeting, Atlanta, GA, Sept. 7-9, (1988)

46.18.2 Sources

46.18.2.1 Al-Li alloy suppliers

Alcan	www.alcan.com www.alcan-aerospace.com
Alcoa	www.alcoa.com www.millproducts.alcoa.com
AMC	www.amc-mmc.co.uk
Dolgarrog Aluminium Ltd	www.dolgarrog.com
Otto Fuchs	www.otto-fuchs.com
VIAM	www.viam.ru

46.18.2.2 Discontinuously reinforced aluminium suppliers

AMT – Aerospace Metal Composites (UK)	http://www.amc-mmc.co.uk/
DWA	http://www.dwa-dra.com/
CPS - Ceramic Process Systems	http://www.alsic.com/
TTC – Thermal Transfer Products	http://www.thermaltc.com/index.html
M Cubed Technologies (USA)	http://www.mmmt.com/
MMCC-Metal Matrix Cast Composites, (USA)	http://www.mmccinc.com/
Millennium Materials (USA)	http://www.millenmat.com/
Peak Werkstoff (D)	http://www.erbsloeh.de/deutsch/e_werkstoff/

46.18.2.3 Continuously reinforced aluminium suppliers

TRL – Touchstone Research Laboratory (USA)	http://www.trl.com/
MMCC-Metal Matrix Cast Composites, (USA)	http://www.mmccinc.com/
3M MMC (USA)	http://www.3m.com/market/industrial/mmc/
CMT – Composite Metal Technologies (UK)	http://www.cmt-plc.com/

46.18.3 ECSS documents

[See: ECSS website]

ECSS-Q-70-71	Data for the selection of space materials and processes; previously ESA PSS-01-701.
ECSS-Q-ST-70-36	Material selection for controlling stress-corrosion cracking; previously ESA PSS-01-736.
ECSS-Q-ST-70-37	Determination of the susceptibility of metals to stress-corrosion cracking; previously ESA PSS-01-737.

46.18.4 ASTM standards

[See: ASTM website]

ASTM E 527	Standard Practice for Numbering Metals and Alloys (UNS)
ASTM E 1823	Standard Terminology relating to Fatigue and Fracture Testing: Annex 2
ASTM G 34	<Title not stated>
ASTM G 44	<Title not stated>
ASTM G 47	<Title not stated>

46.18.5 Other standards

ANSI H35.1	American National Standard Alloy and Temper Designation Systems for Aluminum (2004)
MIL-HDBK-17-4A	Composite Materials Handbook – Volume 4, Metal Matrix Composites (June 2002)
MMPDS	Metallic Materials Properties Development and Standardization DOT/FAA/AR-MMPDS-01 (January 2003)
NOTE	Replaces MIL-HDBK-5
PMP	Preliminary Material Properties Handbook, Volume 2: SI units AFRL-ML-WP-TR-2001-4027 (July 2000)
NOTE	Destined for inclusion in MMPDS

47 Titanium alloys and their composites

47.1 Introduction

The main features of titanium alloys used in aerospace structures are described. The effects of alloying and processing on the various groups of alloys are also discussed.

Specific design data on conventional titanium alloys are not given in the handbook.

Superplasticity and the ability of titanium alloys to re-absorb oxide films at elevated temperatures have made them of interest for structures which can be superplastically formed and diffusion bonded in one process (SPF/DB), [See: 47.4; Chapter 72].

Manufacture of titanium matrix composites (Ti-alloy MMCs) has proved problematical, owing to the reactivity of the alloy when in contact with the reinforcement phase. As a result:

- Very few particulate reinforced composites have been produced with properties exceeding those of the more recent plain alloys, [See: 47.5].
- Suitable continuous reinforcements are limited; all are monofilaments rather than fibres, [See: 47.6].
- Processing methods are solid-state, rather than with a molten matrix phase, to limit reinforcement degradation. However, use at elevated temperatures also results in degradation.

Typical properties are given for various composites, [See: 47.7].

Use of titanium alloys in hydrogen environments needs very careful evaluation. They are prone to hydrogen embrittlement at all temperatures, except in the cryogenic range, [See: 47.8].

In oxygen atmospheres at temperature above 500°C, oxidation occurs and, if scuffed or impacted, ignition and burning may result, [See: 47.9].

Coatings are under development to reduce the effects of gaseous environments at operational temperatures, [See: 47.10].

Some potential applications for titanium alloys and MMCs are discussed in 47.11.

47.2 Conventional alloys

47.2.1 Material selection factors

The primary reasons for using titanium alloys stem from the:

- good corrosion resistance.
- useful combination of:

  - low density (4500 kg/cm^3),
  - high strength (0.2% yield stresses up to 1100MPa).
- useful properties up to 600°C.

[See: ECSS-Q-70-71: Data for the selection of space materials and processes, previously ESA PSS-01-701]

47.2.2 Microstructure

47.2.2.1 Ductile-to-brittle transition

Some titanium alloys, notably low-interstitial alpha (α-) alloys, do not exhibit a ductile to brittle transition, making them suitable for cryogenic applications.

47.2.2.2 Allotropy

An important characteristic of titanium-based materials is the reversible transformation (allotropy) of the crystal structure from an α-hexagonal close-packed (hcp) state to a β-body-centred cubic (bcc) state above a given temperature.

The allotropic transformation depends on the type and amount of alloy contents. It enables complex variations in microstructure and more diverse strengthening opportunities than those of other non-ferrous alloys, such as copper or aluminium.

47.2.2.3 Thermo-mechanical processing

The diversity of microstructure and properties depends not only on alloy additions but also on thermo-mechanical processing. By varying thermal or mechanical processing, or both, a broad range of properties can be produced.

47.2.3 Effect of alloy elements

The principal effect of an alloying element is its influence on the α→β transformation temperature.

- Vanadium is a β stabiliser, and is combined with Aluminium to give the α + β alloy Ti-6Al-4V.
- Aluminium increases tensile strength, creep resistance and the elastic moduli. Limited to 6%, as above this level embrittling aluminides (Ti_3Al-α_2) will form.
- Tin has extensive solid solubility in both α and β phases and is often used as a solid-solution strengthener in conjunction with aluminium to achieve higher strengths without embrittlement.
- Zirconium forms a continuous solid-solution with titanium and increases strength at low and intermediate temperatures.
- Molybdenum is an important β-stabiliser promoting hardenability and short time elevated temperature strength.
- Niobium is another β-stabiliser added to improve oxidation resistance at high temperatures.
- Iron tends to lower creep strength. The reduced iron content in alloy Ti-1100 is a means of improving creep strength.

- Carbon is an α-stabiliser that also widens the temperature difference between the α- and β-transus. Typically, β-stabilisers cause a widening or flattening between the α and β transus temperature. The lean β-content of the alloy IMI 829 gives a near-α alloy with a steep β-transus approach curve. In contrast, an alloy with additional β-stabiliser, such as Ti-6Al-4V results in an α-β alloy with a flattened approach curve. The use of carbon to flatten the approach curve whilst stabilising the α-phase is the basis for the near-α alloy IMI 843. Alloy IMI 834 is heat-treated high in the α-β region to give about 7.5 to 15 vol.% of primary α in a fine grain (0.1mm) matrix of transformed β. This combination of equiaxed α and transformed β provides a good combination of creep and fatigue resistance.

Table 47.2.1 summarises the effect of alloying elements on microstructure.

Table 47.2-1 - Titanium alloys: Effects of alloying elements on microstructure

Alloying element	**Range (approx. weight.%)**	**Effect on structure**
Aluminium (Al)	2 to 7	α - stabiliser
Tin (Sn)	2 to 6	α - stabiliser
Vanadium (V)	2 to 20	β - stabiliser
Molybdenum (Mo)	2 to 20	β - stabiliser
Chromium (Cr)	2 to 12	β - stabiliser
Copper (Cu)	2 to 6	β - stabiliser α and β strengthener
Zirconium (Zr)	2 to 8	[See: 47.2]
Silicon (Si)	0.05 to 1	Improves creep resistance

47.2.4 Alloy classes

47.2.4.1 General

Titanium alloys are classified as:

- Alpha, can include near-α
- Alpha-Beta, also near-α, super-α and lean-β
- Beta.

Titanium alloys are specified by nationally-based, e.g. DIN, NF, etc. and internationally-accepted standards, e.g. ASTM, CEN. They are also commonly denoted by their proprietary ‘product’ name, e.g. IMI and Timetal designations.

A comparison of Ti-alloys covered by various standards and product designations is provided in Ref. [47-26].

47.2.4.2 Near-a alloys

Table 47.2.2 shows how processing temperatures of near-α alloys can be influenced. This demonstrates the options available for microstructural variations and their relationship to property improvements.

Table 47.2-2 - Titanium alloys: Influence of processing temperatures on near-α alloys

Property	β - processed	α - β processed
Tensile strength	Moderate	Good
Creep strength	Good	Poor
Fatigue strength	Moderate	Good
Fracture toughness	Good	Poor
Crack growth rate	Good	Moderate
Grain size	Large	Small

47.2.5 Alloys for aerospace use

47.2.5.1 General

Of the titanium alloys appropriate to aerospace use, Ti-6Al-4V (α-β) has been the baseline material for many years. The principal product forms of interest are:

- Wrought forms for airframe use, and
- Forgings for turbine engine components.

Table 47.2 3 summarises information on relevant titanium alloys.

Table 47.2-3 - Titanium alloys for aerospace use: Characteristics

Alloy group or specification	Nominal composition (%)	Available product forms (Country)	General description	Typical aerospace applications
Commercially pure (CP), e.g. Timetal 35A to 100A; Code 12				
-	-	All wrought forms (UK)	Excellent corrosion resistance. Good weldability	Readily fabricated complex shapes requiring intermediate strength.
Near-α alloys				
Timetal 6-2-4-2 [Ti-6242S]	Ti-6Al-2Sn-4Zr-2Mo-0.08Si [Ti-6Al-4Zr-2Mo-0.1Si]	Plate, sheet, forgings, (UK & USA)	Silicon imparts additional creep resistance	Forgings and flat-rolled products in engines & airframes needing high strength & toughness. Excellent creep resistance & stability to 450°C
Timetal 685 [IMI 685]	Ti-6Al-5Zr-0.5Mo-0.25Si	Rod, bar, billet, extrusions, forgings (UK)	Weldable medium strength alloy.	Alloy for elevated temperature uses up to ~520°C. Weldable.
Timetal 829 [IMI 829]	Ti-5.6Al-3.5Sn-3Zr-1Nb-0.25Mo-0.3Si	Rod, bar, billet, extrusions, forgings & sheet (UK)	Weldable medium strength alloy with good thermal stability & high creep resistance to 600°C.	Elevated temperature alloy for service up to ~540°C. Weldable.
Timetal 834 [IMI 834]	Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si-0.06C	As for IMI 829 (UK)	Weldable high temperature alloy with improved fatigue performance over Timetal 829 & 685.	Maximum use temperature up to ~ 600°C. Weldable.

Alloy group or specification	Nominal composition (%)	Available product forms (Country)	General description	Typical aerospace applications
Timetal 1100 [Ti-1100]	Ti-6Al-2.7Sn-4Zr-0.4Mo-0.45Si	Billet, bar, sheet, welding wire, forgings, castings (USA & Europe)	High combined strength, creep, fatigue & fracture toughness.	Maximum use temperature up to ~600°C. Weldable.
α - β alloys				
Timetal 6-4 [IMI 318]	Ti-6Al-4V Also: ELI grade 0.1O2	All product forms (Universal alloy)	Useful creep resistance up to 300°C & excellent fatigue strength. Fair weldability.	Aircraft gas turbine disks & blades. Airframe structural components & fastener stocks (heat-treated to give 1100MPa tensile strength).
Corona -5	Ti-4.5Al-5Mo-1.5Cr	Researched for plate, forgings & SPF sheet (USA)	Improved fracture toughness over Ti-6Al-4V & easier to work	Not taken up replacement for Ti-6Al-4V
Timetal 550 & 551 [IMI 550 & 551]	Ti-4Al-4Mo-2Sn-0.5Si	Rod, bar, billet, extrusions, forgings (UK)	High strength alloy with Timetal 551 the highest (4Sn). 550 weldable; 551 not weldable.	For high strength applications requiring useful creep resistance to 400°C.
β - alloys				
Beta III	Ti-11.5Mo-6Zr-4.5Sn	No longer produced (USA)	Excellent forgeability & cold workable. Very good weldability.	Aircraft fasteners, sheet metal parts.
Timetal 15-3 [Ti-15-3]	Ti-15V-3Al-3Cr-3Sn	Sheet, strip, plate (USA)	Cold formable β alloy. Heat treatable to 1310MPa tensile strength. Weldable.	High strength aircraft & aerospace components to 300°C. Matrix alloy for composites.
Timetal 17 [Ti-17]	Ti-5Al-2Sn-2Zr-4Mo-4Cr	Forgings (USA)	Unlike other β alloys, offers good creep strength up to 430°C.	Forgings for turbine engine components where hardenability, strength, toughness & fatigue are important.
Timetal 21S [Beta 21S]	Ti-15Mo-3Nb-3Al	Sheet, strip, plate, foil (USA)	High strength, cold formable.	Honeycomb in engine structures (228 to 593°C), hydraulic tubes. Matrix alloy for composites.

47.2.5.2 Specifications

Within Europe, AECMA provide specifications for various aerospace titanium alloys and product forms, Ref. [47-26].

For example, CEN specification:

EN 2517PR Titanium alloy Ti P63 alloy: annealed – sheet, strip & plate,
a ≤100mm

AECMA use a different alloy reference compared with CEN, e.g. Ti P63 (CEN); Ti P64001 (AECMA) for nominal composition alloy Ti-6Al-4V.

47.2.6 Heat treatment

Titanium alloys are heat-treated with the aims of:

- Reducing residual stresses caused by fabrication (stress-relieving).
- Optimising combinations of ductility, machinability and dimensional stability (annealing).
- Increasing strength (solution treating and ageing)
- Optimising special properties such as fracture toughness, fatigue strength and high temperature creep strength.

The α and near-α alloys can be stress relieved and annealed. High strength cannot be developed in these alloys by any type of heat-treatment. The β alloys, with metastable β are strengthened by ageing, as the retained β decomposes. The β alloys can be age hardened, as the stability of their β phase gives large section hardenability. For β alloys, stress relieving and ageing treatments can be combined; annealing and solution treatment may be identical operations.

The α-β alloys exhibit heat-treatment characteristics between that of the α and β classes. They can be age hardened by the decomposition of beta, but these alloys do not exhibit the same section hardenability as the β alloys owing to the lower amount of retained β. Nonetheless, the α-β alloys are the most versatile in that certain microstructures can be enhanced by processing in either the α-β or the β-phase region, as indicated earlier for near-α alloys.

For creep strength, β processing of near-α alloys is useful. Near-α enables working or heat-treatment in the β-phase field without loss of room temperature ductility (possible with other alloys). Near-α alloys can be worked high in the α-β for an intermediate microstructure with a mixture of equiaxed and acicular α.

47.2.7 Mechanical properties

47.2.7.1 General

Table 47.2.4 presents a summary of properties, which should be viewed in conjunction with the heat-treatments applied, Ref. [47-4].

Table 47.2-4 - Titanium alloys: Indicative mechanical properties

Alloy	Form	Temp. (°C)	UTS (MPa)	0.2%PS (MPa)	El (%)	R of A (%)	Comments
Ti-6242S	Forging Stock	RT 480	895 620	825 485	10 15	25 30	Solution treated & aged.
IMI 685	Forging Stock ≤ 360mm ø	RT 520	950 610	880 480	6 9	15 20	As manufactured, surface cleaned & etched. 1050°C/≥ ½hr/OQ+550°C/24hr/AC.
IMI 829	Forging Stock ≤ 300mm ø	RT 540	930 570	820 480	9 9	15 25	As manufactured, surface cleaned & etched. 1050°C/≥ ½hr/AC+625°C/2hr/AC.
IMI 834	Forging Stock ≤ 300mm ø	RT 600	1030 585	910 450	6 9	15 20	As manufactured, surface cleaned & etched. Solution Treated & aged.
IMI 318 (Ti-6Al-4V)	Sheet	RT	960-1270	900	8	-	Annealed.700°C/20mins/AC. De-scaled.
	Plate <10mm	RT	895-1150	825	10	-	Annealed.700°C/20mins/AC. De-scaled & pickled.
	Plate 10-100mm	RT	895-1150	825	8	25	20% R of A for 25-100mm plate.
	Bar 150mm ø	RT	900-1160	830	8	25	Annealed.700°C/hr/25mm section/AC.
IMI 550	Wrought product	RT	1100	940	7	15	Solution treated 900°C/AC & aged.
Ti15-3	Wrought product	RT	785 1095-1335	773 985-1245	22 6-12	- -	Annealed. Aged.
Ti-17	Wrought product	RT	1105-1240	1030-1170	8-15	20-45	Solution treated & aged.

Key: All values, except where a range is given, are minimum values stated by the suppliers.
OQ: Oil Quenched; AC: Air Cooled.

47.2.7.2 Elevated temperature

The property data presented emphasises those alloys offering high temperature stability and their improvements over Ti-6Al-4V. Improvements in alloy development are shown in Figure 47.2.1, Figure 47.2.2, Figure 47.2.3 and Figure 47.2.4 for UTS, creep and fatigue curves.

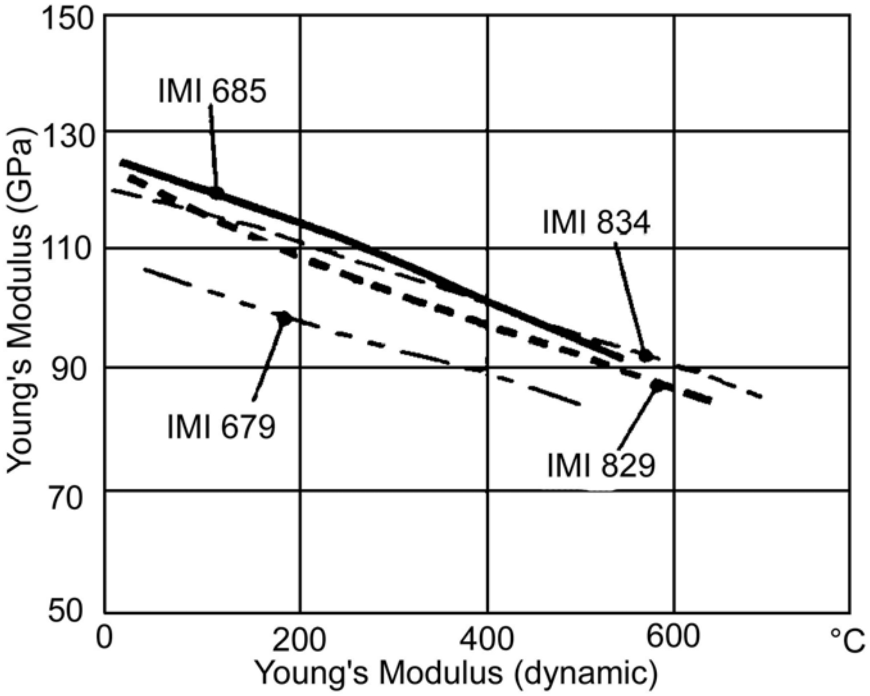


Figure 47.2-1 - Titanium alloys: Effect of temperature on stiffness

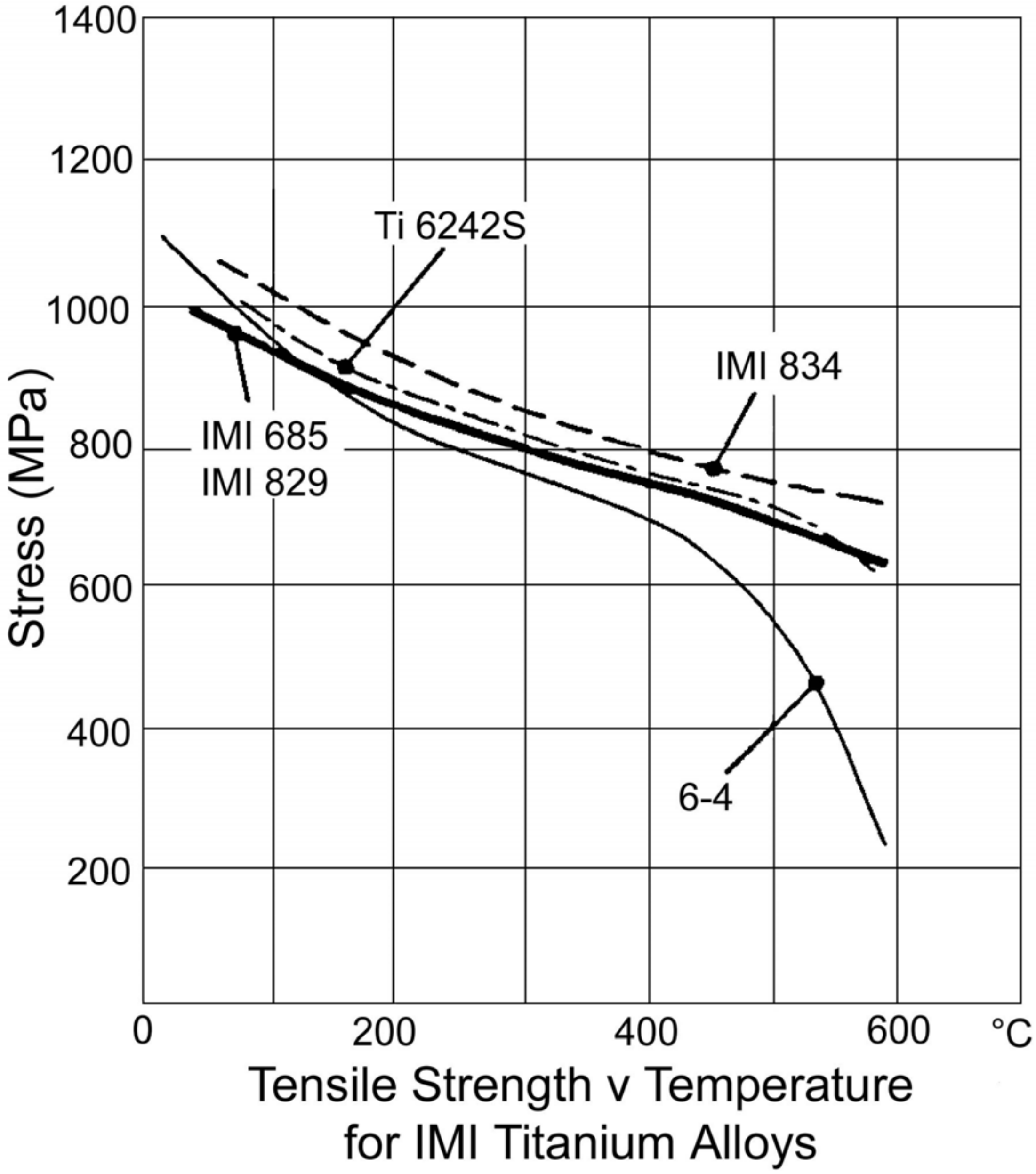


Figure 47.2-2 - Titanium alloys: Effect of temperature on strength

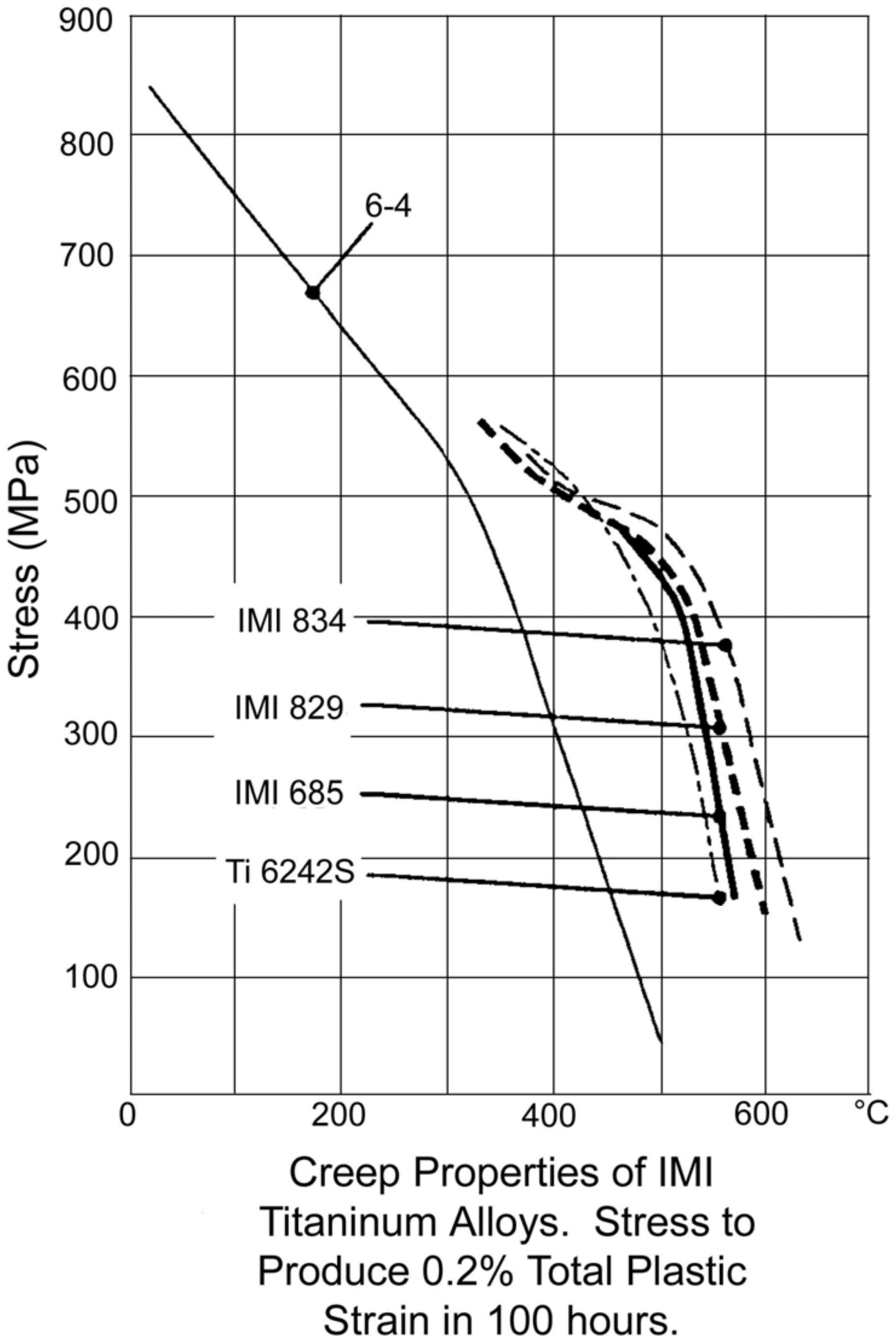


Figure 47.2-3 - Titanium alloys: Creep properties

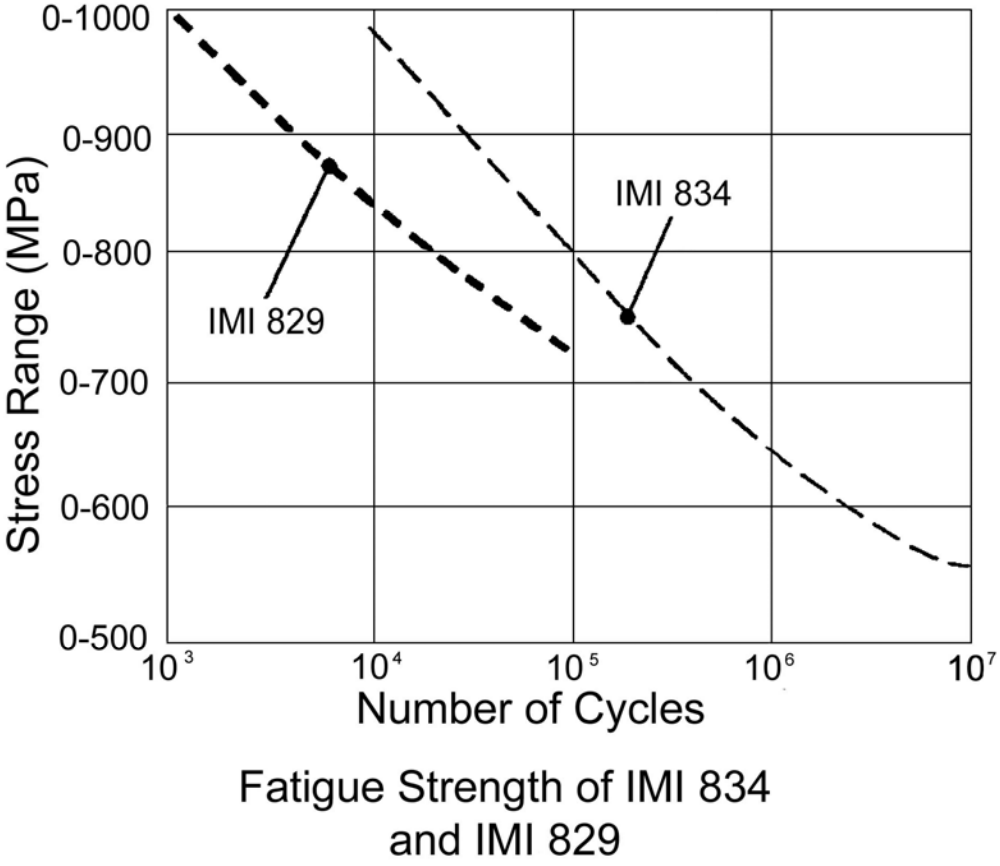
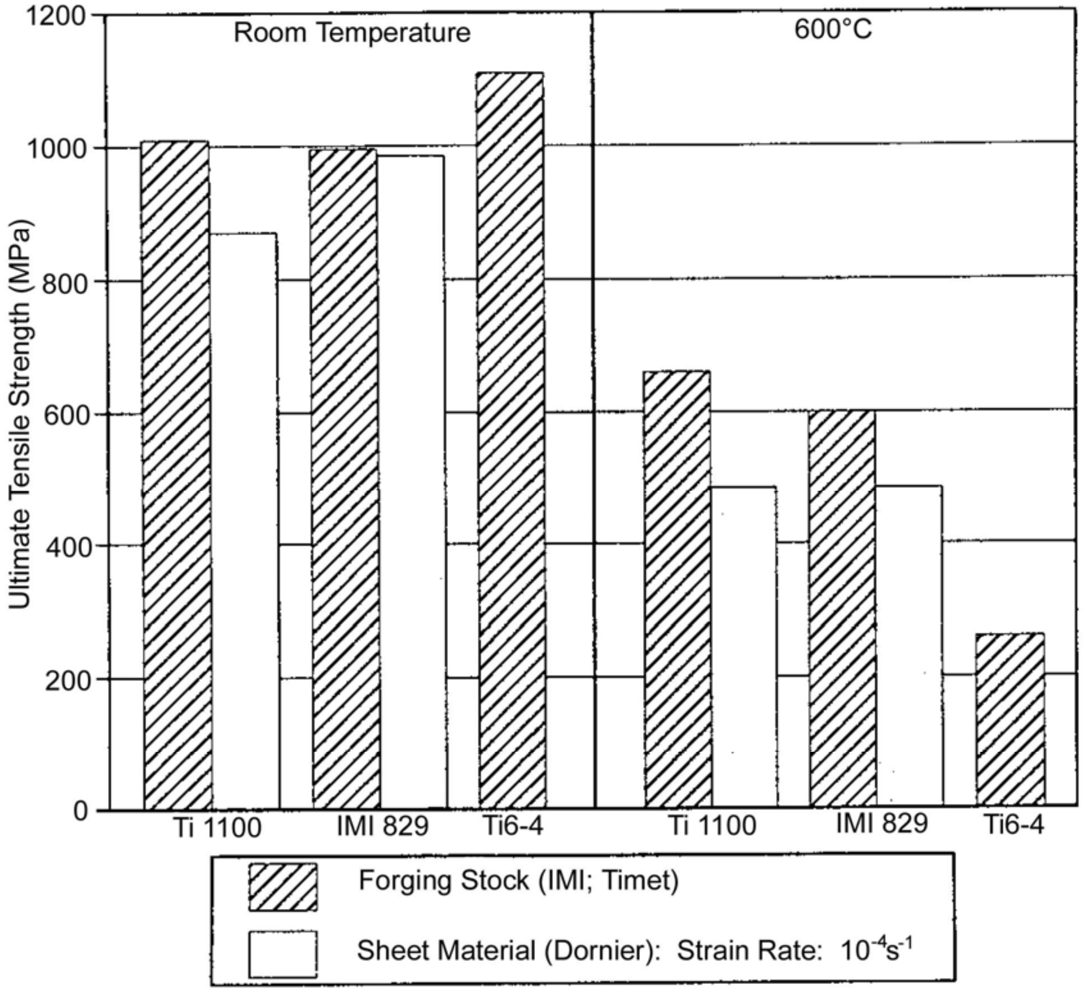


Figure 47.2-4 - Titanium alloys: Fatigue strength

In seeking to operate titanium alloys close to their maximum, Dornier have studied the possibility of SPF/DB components for spaceplane structural configurations, Ref. [47-5], [See: 47.4].

Figure 47.2.5 demonstrates the superiority of IMI 829 and Ti-1100 on strength retention at 600°C, Ref. [47-5]. This exercise established the viability of superplastic forming 0.8mm to 1.5mm sheet and achieving diffusion bonding simultaneously. For Ti-6Al-4V, the forming temperature should not exceed 935°C, whilst both high temperature alloys needed the bonding temperature to be in the range 950 to 980°C.



Ti-6Al-4V used as Reference

Figure 47.2-5 - Titanium alloys: UTS at elevated temperature for IMI 829 and Ti-1100

47.2.7.3 Fracture properties

[See: Table 47.2.5]

47.2.8 Physical properties

[See: Table 47.2.5]

Table 47.2-5 - Titanium alloys: Physical properties

Property	Alloy				
	Ti-6Al-4V (IMI 318)	IMI 685	IMI 629	IMI 634	6242S
Density (kg/m^3)	4420	4450	4540	4550	4540
β - Transus (°C)	-	1020	1015	1045	995
Thermal Conductivity (W m^{-1}°C^{-1})	6.7	4.2	-	-	-
CTE (10^{-6}°C^{-1}) :					
20 - 100°C	8.6	9.8	-	-	9.9
20 - 200°C	9.0	9.3	9.45	10.6	-
20 - 300°C	9.2	9.5	-	-	-
20 - 400°C	9.4	9.8	9.77	10.9	-
20 - 500°C	9.5	10.1	-	-	-
20 - 600°C	9.7	10.1	9.98	11.0	-
20 - 800°C	-	-	10.34	11.2	-
20 - 1000°C	-	-	10.39	11.3	-
Suitable Post-weld Treatments	-	550°C/4-8hrs/ AC	625°C/2hr/AC	625°C/ 1hr/AC	-
Fracture Toughness (MPa m^{½}) †	44-66 Equiaxed with 910MPa YS	68 For 910 MPa 0.2% PS	78 β heat treated condition	37 Aged: 700°C /2hrs	65-79 α-β heat treated & aged

Key: † - Typical RT Values; AC - Air Cooled

47.3 New alloys

47.3.1 Developments

New alloy developments have centred on:

- alloy modifications to assist fibre-matrix compatibility, and
- processing techniques to enable cost effective fabrication.

47.3.2 Processing techniques

47.3.2.1 General

Fabrication techniques which have potential cost reducing benefits are:

- Superplastic forming (SPF),
- Rapid solidification (RS) technology.

These techniques are also being used for titanium metal matrix composites.

47.3.2.2 Superplastic forming

[See: 47.4 and Chapter 72]

47.3.2.3 Rapid solidification

Rapid solidification (RS) has demonstrated the ability to produce thin foils with fine grain sizes for combination with reinforcement fibres. The consolidated composite had reduced reactions between the fibre and matrix which was attributed to a superplastic forming mechanism operating during the lower temperature consolidation.

Powder metallurgy titanium alloys are also believed to offer advantages over the foil form of matrix for MMCs. This however is the subject of on-going development.

47.4 Superplastic forming and diffusion bonding

47.4.1 Superplasticity

Superplasticity can be achieved with most metals. The alloy is heated to around 50% of melting and deformed at low strain rates up to many hundred percent strain. An essential characteristic of an SPF material is a fine, uniform grain size with limited texturing. Whilst the process is slow, complex, thin-walled, shapes with integral stiffening are feasible, which are not achievable by conventional forming processes.

47.4.2 Diffusion bonding

47.4.2.1 General

Two or more metal components are placed intimately in contact and temperature/pressure applied to achieve a homogeneous structure. The process results in a joint which is metallurgically undetectable, i.e. grain boundaries are not confined to the original joint faces. Bond strengths up to parent material properties are achievable.

47.4.2.2 Characteristics of titanium alloys

The ability of titanium to absorb its oxide layer at high temperature in an inert atmosphere is a phenomenon which makes this material readily bondable. These 'self-cleaning' conditions are obtained at the optimum SPF temperature for titanium alloys, so the SPF/DB process has become a practical proposition for titanium component manufacture.

47.4.3 SPF/DB fabrication

47.4.3.1 General

Combining superplastic forming and diffusion bonding into a combined processing route (SPF/DB) is an elegant one, offering a single-shot process to give complex configurations, including:

- Struts,
- Cylinders,

- Access panels, and
- Pressure vessels.

Combined knowledge and expertise is needed to understand the:

- Material, as it is strained,
- Jointing,
- Net-Shape fabrication.

[See: Chapter 72 – for SPF/DB titanium designs]

47.4.3.2 Cost factors

Cost saving in manufacture is the primary attraction of the SPF/DB process; especially for titanium alloys, with their importance in spaceplane development.

47.4.4 Materials

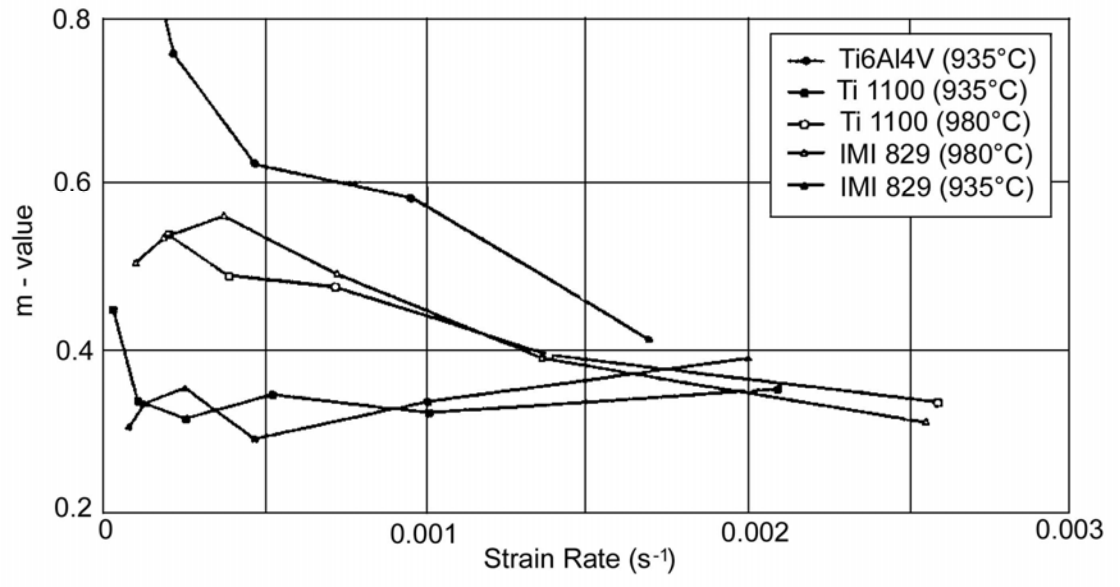
47.4.4.1 Ti-6Al-4V alloy

Ti-6Al-4V is by far the most common titanium alloy to which SPF/DB is applied. However, if the material has a suitable microstructure, most titanium alloys can be processed in this way.

47.4.4.2 IMI 829 and Ti-1100

Work by Dornier, Ref. [47-5], has demonstrated that the alloys IMI 829 and Ti-1100 can be formed and bonded, given close control of strain rate in relation to the forming temperature. Figure 47.4.1 provides the m-values (Strain Rate Sensitivity) for three alloys.

With IMI 829 and Ti-1100 materials, a temperature of 980°C is needed to ensure true superplasticity, whilst at 935°C plastic deformation and undesirable necking characteristics predominate. Ti-6Al-4V shows this m-value at 935°C. A minimum m-value of 0.5 is sought to demonstrate superplasticity.



IMI 834 has replaced IMI 829, [See: 72.4]

Figure 47.4-1 - SPF/DB fabrication: Titanium alloy *m*-values as a function of strain rate

47.5 Discontinuously reinforced Ti-alloys

47.5.1 Difficulties

Initial studies of discontinuously reinforced titanium alloys proved largely unsuccessful owing to the reactivity of the matrix with the reinforcement. For whisker and particulate reinforcement, little remained after the consolidation and hence no benefit in mechanical performance was achieved.

47.5.2 Particulate reinforcements

47.5.2.1 General

Certain particles can be used as reinforcements, including:

- boron carbide,
- titanium diboride,
- titanium carbide.

The use of titanium compounds enables compatibility with titanium alloys. Evidence of good matrix to particle adhesion is seen with 10 vol.% titanium carbide additions to Ti-6Al-4V, Ref. [47-10].

47.5.2.2 Particulate content

Work with all-particulate MMC materials suggests that reinforcement contents need to be kept modest (less than 20 vol.%) to avoid loss of ductility and toughness.

47.5.3 Processing

Particulate reinforced composites have been made by a powder route, with hot pressing for consolidation.

47.5.4 Properties

Low particulate contents are needed to avoid serious loss of ductility.

In the case of 10 vol.% Ti MMCp material, a small increase in modulus would be experienced with a 4% reduction in density. This is only a marginal improvement in performance considering the process difficulties.

The addition of TiC particles may improve the high temperature stability and creep resistance of Ti-6Al-4V. However, alloys such as IMI 834 and Beta 21S, with better inherent thermal performance, render particle additions to Ti-6Al-4V unnecessary.

47.5.5 Further development

Particulate Ti MMC materials can be worthwhile if based on the more advanced alloy compositions, including titanium aluminides, [See also: Chapter 49 – Intermetallic Materials].

At present, no significant commercial developments of this type can be described.

47.6 Continuous fibre reinforced Ti-alloy MMC

47.6.1 Composite development

47.6.1.1 General

Continuous fibre reinforcement of titanium alloys aims to achieve:

- Increased stiffness and strength
- Reduced material density
- Improved creep resistance, and
- Improved fatigue life.

Development of these materials has been driven by the need for efficient titanium composites in aircraft gas turbine engines and hypersonic spaceplanes, e.g. NASP. The commercial availability of some Ti-MMCs is given in Ref. [47-26].

47.6.1.2 Fibres

Initial development work on titanium composites concentrated on development of fibres having acceptable compatibility with the titanium matrix. The high reactivity of titanium causes severe fibre degradation during processing. This led to the introduction of selected fibre coating systems and reduced temperature processing techniques.

The high reactivity of titanium excludes the use of smaller diameter (5µm to 15µm) reinforcing fibres, such as carbon or silicon carbide. Efforts have therefore been concentrated on monofilaments.

In work going back twenty years, those studied have been the large diameter filaments (100µm to 200µm), including:

- Silicon Carbide (SiC)
- Boron Carbide coated Boron (B4C/B)
- Borsic (B/SiC)

47.6.1.3 Matrix alloys

Early work concentrated on the use of Ti-6Al-4V alloy as the matrix material, presumably because it was a well understood alloy and readily available. Ti-6Al-4V proved adequate for studying and refining process techniques but the composite has only modest thermal performance.

Later work moved to near-α and β alloys as a means of extending thermal capabilities towards 600 to 700°C.

The β-alloys can also be cold rolled to produce thin foils which are used to prepare composites by hot pressing. Development has progressed from these alloys to titanium aluminide matrices, [See: Chapter 49].

47.6.2 Monofilament reinforcements

47.6.2.1 Availability

With the rationalisation in commercial fibres, there are now only two monofilament options for titanium matrix composites (TMC):

- Textron silicon carbide: SCS-6 (140µm diameter).
- BP SIGMA: uncoated base fibre SM1040 (100µm diameter).

47.6.2.2 Filament Manufacture

Both are made by chemical vapour deposition (CVD) of silicon carbide on to a precursor wire. The wire is tungsten for SIGMA and carbon for SCS-6.

47.6.2.3 Filament coatings

The CVD process has been taken a step further to modify the outer filament surface to a chemical composition which is more compatible with titanium matrices. These coatings form the interface between fibre and matrix and ultimately define the level of mechanical properties attainable by the composite.

The coatings applied to commercial fibres are:

- SCS-6: The coating is 3µm thick and is carbon rich. The silicon content exhibits a maximum at the outer surface and at 1.5µm from the outer surface.
- SIGMA: Two variants, with coatings applied to the base fibre SM1040:
  - SM1140+: has a 4.5µm carbon coating. For use with aggressive alloys.
  - SM1240: has a duplex coating of 1µm overlayed with 1µm titanium diboride (TiB_2).

47.6.2.4 Characteristics

Both fibres exhibit reasonable tensile strengths, in excess of 3000MPa, but there is a degree of scatter. The manufacturers have improved the consistency of their respective processes to improve the claimed standard deviation from ± 500MPa to ± 200MPa. The large monofilament diameters influence the selection of composite process techniques.

47.6.3 Matrix selection

47.6.3.1 Thermal stability

To improve the thermal performance of titanium matrix composites (TMCs), Ti-6Al-4V matrices have been replaced by near-α, e.g. Timetal® 834 (IMI 834) and Timetal® 1100 (Ti-1100), and β systems.

[See also: 47.2 for conventional alloys]

In the USA, the progression seen in β-alloys has been:

Beta III → Ti-15-3 → Timetal® 21S (Beta 21S)

47.6.3.2 Availability

Matrix selection is also influenced by more practical considerations, such as the availability of thin foil for stacking and consolidation. The inability to obtain certain alloys in foil form, e.g. Ti6242S, has excluded their use in TMC materials made by this route. The selection of β-alloys has been driven by their ability to be readily cold worked into thin foils, whilst offering good intermediate temperature capabilities. The near-α alloys have higher temperature capabilities and are available in powder form; far less as foils.

The use of sputtering, Ref. [47-15], or powder routes for TMC preparation enables other alloy matrices to be considered.

47.6.3.3 Oxidation

Where high operating temperatures are envisaged for prolonged periods, oxidation resistance should be considered.

In this respect, Beta21S is better than Ti-15-3. However, for prolonged use >450°C, all TMC materials require an additional coating system to provide an oxygen barrier.

47.6.4 Composite process technologies

The handling characteristics of monofilaments are such that they are processed individually rather than as bundles or tows, as with traditional fibres.

Each monofilament is encapsulated with matrix and the overall composite consolidated. The matrix cannot be worked in the liquid state as it is too reactive.

Consolidation is therefore in the solid state, relying on diffusion bonding under pressure at temperatures below 900°C. The accepted processes are:

- Consolidation of filaments separated by metal foil layers using hot pressing or HIP techniques.

- Consolidation of powder-coated filament prepregs by hot pressing.
- Fusion of individually matrix-coated filaments which have been stacked or wound in the desired configuration, the matrix coating normally being applied by sputtering.

These processes lead to very wide variations in fibre volume fractions from 17% to 80%, with the range 35% to 45% being the most common. Key processing requirements are to obtain an even fibre distribution and avoid fibres touching each other.

47.7 Continuous fibre reinforced Ti-alloy MMC: properties

47.7.1 Composite optimisation

Owing to the high reactivity of titanium and its alloys, detailed optimisation of the composite system is always required to give high temperature capabilities in the range 450°C to 650°C and good thermo-mechanical fatigue (TMF) life.

Poor transverse strength in 90° plies and deleterious fibre-matrix interactions are the constraining factors.

47.7.2 Tensile strength and stiffness

47.7.2.1 General

The majority of published data provides simple unidirectional tensile stiffness and strength values for various fibre-matrix combinations, as shown in Table 47.7.1 and Table 47.7.2, Ref. [47-11].

Table 47.7-1 - Titanium matrix composites: Typical room temperature tensile properties

Matrix Alloy [See: Notes]	Fibre Type †	Fibre Volume %	Ultimate Tensile Strength		Modulus (GPa)	Notes
			Longitudinal (MPa)	Transverse (MPa)		
Ti-6Al-4V ⓪	None	Nil	890	890	120	Commercial Purity ( ) predicted values
CP-Ti	Borsic	28	860	276	193	
	Borsic	-	620	324	-	
Ti-6Al-4V	Boron	32	1000	340	204	
		-	(1630)	(286)	(201)	
Ti-6Al-4V	Borsic	28	970	>345	190	
Ti-6Al-4V ①	Borsic	35-40	895	365	205	
Ti-6Al-4V ②	Borsic	Not stated	813	324	207	
Ti-6Al-4V ③	Borsic	Not stated	827	289	200	
Ti-6Al-4V	B_4C/B	32	1450	>345	214	Range of properties are from materials made by different companies. (DWA and AVCO in U.S.A.)
Ti-6Al-4V	B_4C/B	Not stated	978-1054	303-310	-	
Ti-6Al-4V	B_4C/B	38	1550	>345	221	
Ti-6Al-4V ①	B_4C/B	Not stated	985-1033	324-351	199-207	
Ti-6Al-4V ①	B_4C/B	35-40	1055	310	205	
Ti-6Al-4V ②	B_4C/B	Not stated	875-1047	310	203-218	
Ti-6Al-4V ③	B_4C/B	Not stated	882-1068	317-344	215-229	
Ti-6Al-4V ①	SiC	35-40	820	380	225	
Ti-6Al-4V ②	SiC	Not stated	779	289	189	
Ti-6Al-4V ③	SiC	Not stated	771	379	196	
Ti-6Al-4V ①	SCS-6	Not stated	1040	338	240	
Ti-6Al-4V ①	SCS-6	35-40	1455	340	240	
Ti-6Al-4V ②	SCS-6	Not stated	909	303	233	
Ti-6Al-4V ③	SCS-6	Not stated	833	365	213	
Beta III	Borsic	Not stated	854	-	-	Ti-11.5Mo-6Zr-4.5Sn
Ti-10Mo	Borsic	Not stated	730	331	-	
Beta III	Borsic	Not stated	854	-	-	Ti-11.5Mo-6Zr-4.5Sn
Ti-10Mo	Borsic	Not stated	730	331	-	

Key: †: Borsic, boron and B4C fibres are no longer appropriate for use in titanium composites; ⓪: Mill annealed 732°C/2 hours/Air cooled; ①: After fabrication & low temperature 595°C/512 hours exposure; ②: After fabrication and 760°C/64 hours exposure; ③: After fabrication and 900°C/5 hours exposure

Table 47.7-2 - Titanium matrix composites: Typical strengths of UD SIGMA SiC reinforced alloys

Alloy	Filament (Vol.%)	UTS (MPa)	Modulus (GPa)
Ti-6Al-4V	35 - 38	1755	235
Ti-15-3-3-3	30 - 35	1450	230
Beta 21S	27 - 30	1470	185
Aluminium 6061	30 - 35	1200	180

There are wide variations in the data, but significant improvements in ambient temperature strength are feasible, although there are temperature limitations on property retention.

The transverse strengths of unidirectional materials are lower than the base matrix material.

47.7.2.2 Loading

Unidirectional TMC materials are attractive for applications with a single load direction, e.g. hoop stress. Multiple loads require more complex lay-ups with correspondingly reduced maximum strength capabilities.

47.7.3 Fatigue

Table 47.7.3 gives fatigue properties for various composites, Ref. [47-12].

Data are included for composites after a high-temperature treatment.

[See also: Thermo-mechanical fatigue (TMF)]

Table 47.7-3 - Titanium matrix composites: Fatigue properties

Matrix type [See: Notes]	Fibre type †	Fibre vol. %	Cycles to failure (x 10^4)	UTS (MPa)
Ti-6Al-4V ①	None	Nil	6	890
Ti-6Al-4V ②	None	Nil	4 to 6	-
Ti-6Al-4V	Borsic	35 to 40	6	895
Ti-6Al-4V	Borsic	Not stated	~1	-
Ti-6Al-4V	SiC	35-40	2 to 200*	820
Ti-6Al-4V	SCS-6	35-40	20	1455
Ti-6Al-4V ②	SCS-6	Not stated	~1	-
Ti-6Al-4V	B_4C/B	35-40	1000	1055
Ti-6Al-4V ②	B_4C/B	Not stated	3 to 10	-
Beta III ① (Ti-11.5Mo-6Zr-4.5Sn)	Borsic	Not stated	3 to 6	-
Ti CP	Borsic	Not stated	1 to 3	-
Ti-10Mo	Borsic	Not stated	1 to 2	-

Key: ①: Mill annealed 732°C/2 hours/AC; ②: After fabrication 955°C/8 hour exposure; †: Borsic, boron and B_4C fibres are no longer appropriate for use in Ti-composites; *: Poor consolidation of composite.

Test conditions: As fabricated 4 ply unidirectional specimens. $R = +0.1$, σ-max. = 515 MPa, Room Temperature. Axial Fatigue

47.7.4 Fracture toughness

The fracture toughness of TMC materials is difficult to assess because of the directionality. The level of matrix-to-fibre bonding also strongly influences the crack propagation characteristics.

47.7.5 Elevated temperatures

In preparing TMC materials every attempt is made to minimise deleterious chemical interactions between matrix and reinforcement, usually by using the lowest effective temperature for consolidation. Whilst this controls the problem at the processing stage, cumulative degradation can still occur in service at high temperatures.

47.7.6 Thermo-mechanical fatigue

47.7.6.1 General

Combined thermal cycling and stress cycling is called thermo-mechanical fatigue (TMF). An example of its effects is given in Ref. [47-20], [See also: Chapter 83].

47.7.6.2 Composite type

A symmetrical cross-ply laminate of SCS-6/Ti-15-3 was prepared, $[0/90]_{2S}$, consisting of 8-plies with a fibre volume fraction of 38% and an overall thickness of 1.69mm. The β-alloy Ti-15V-3Al-3Sn-3Cr was a favoured matrix material in the USA.

Simple tensile tests on the laminate indicated that first-ply failure (FPF) in the transverse 90° plies occurred at the applied stress of 450MPa at 427°C. Maximum failure strain for the composite were around 0.8%.

47.7.6.3 Test regimes

Two TMF test regimes were used:

- 'In-phase', where peak stress coincided with peak temperature.
- 180° 'Out of Phase'.

The thermal cycle operated between 149°C and 427°C over a period of 48 seconds. Applied maximum stress levels varied between 244MPa and 612MPa.

47.7.6.4 Effect of thermo-mechanical fatigue

Figure 47.7.1 shows a graphical presentation of the results from eight specimens. Although viewed as indicative only, it does demonstrate a number of features, including:

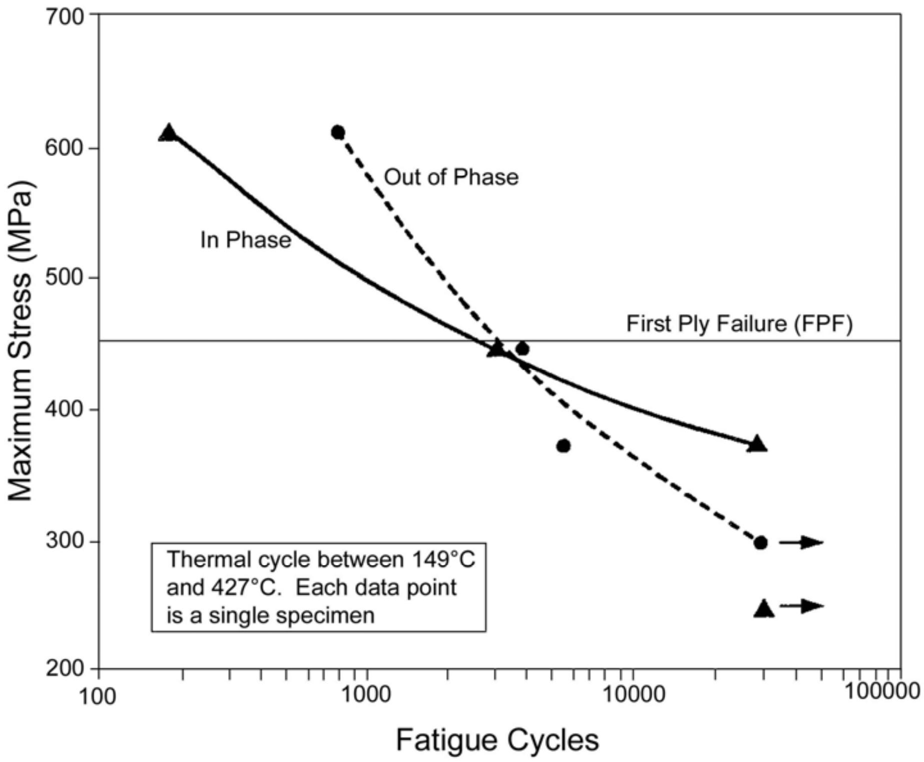
- At high stresses (i.e. above the FPF stress level), the fatigue life for in-phase TMF was less than for out-of-phase TMF conditions.
- Below the FPF stress, the lines cross and the fatigue life for in-phase TMF conditions shows a progressive improvement over the out-of-phase conditions.

This is not surprising as the residual stresses within a TMC are highest near ambient temperature reflecting the accumulated stress in cooling from the consolidation temperature. The FPF stress is significantly lower at RT compared to the 427°C value of 450MPa.

47.7.6.5 Damage mechanisms

The primary fatigue damage mechanism is transverse cracking originating at the fibre-matrix interface of 90° fibres. However, the final damage modes are dependent on the stress level and test conditions.

For tests above FPF level (427°C), the transverse cracks in 90° plies propagating towards 0° fibres were deflected in the longitudinal direction, owing to either high stresses or a weaker interface. This caused the transverse cracks in the 90° ply of the specimen to be deflected and coalesce on various levels in the specimen at failure. It also caused a localised necking or channelling effect of matrix material at points between failed 0° fibres generating local stress concentrations and limited ductile failure in the matrix materials.



Ti-6Al-4V used as Reference

Figure 47.7-1 - Titanium matrix composites: Fatigue life from in-phase and out-of-phase thermal-mechanical fatigue tests

47.8 Titanium alloys: Effect of hydrogen

47.8.1 Material degradation mechanisms

The effects of hydrogen on titanium alloys can be summarised as:

- Most commercial alloys are highly susceptible to degradation.
- Microstructure strongly influences mechanisms due to:
  - variations in hydrogen solubility.
  - hydrogen transport mechanisms.
- Alloys having mainly α phase degrade by repeated hydride formation and fracture at or near the gas-metal interface.
- Continuous β-phase (in α+β alloys) provides a path for hydrogen to penetrate material and form hydrides in neighbouring α phase or at α-β interfaces.
- Advanced Ti alloys for use at high temperatures consist primarily of intermetallic compounds. The effect of hydrogen on intermetallics is largely unquantified. Transport and hydride formation occurs via the α and β phases present.

[See also: Chapter 85]

Table 47.8.1 describes the mechanism of hydrogen embrittlement, and the effects at various temperatures and conditions, Ref. [47-24], [47-25].

Table 47.8-1 - Titanium alloys: Effect of hydrogen

Conditions	Characteristics	Comments
Hydrogen embrittlement (HE) mechanism	Absorption of hydrogen at ~90 to 150ppm causes hydride precipitation.	For Ti-10V-2Fe: Linked to β-phase stabilisation inhibiting martensite transformation.
Cryogenic Temperatures	Resistance to liquid hydrogen.	Insufficient heat to promote dissociation at 20K
Ambient to ~400°C	Erratic behaviour, not easily predicted. Factors include: • Oxide-free surface • Stress • Acicular microstructure • Increasing temperature • Increasing pressure Intact oxide films (without other active factors) reduce hydrogen penetration below ~450°C.	Turbine blades operating at 350°C found to chip in stressed regions (leading edge) owing to high hydrogen contents. Reduce hydrogen content by vacuum heat-treatment (700°C for 7 hours, typically).
>450°C	Sensitive to hydrogen	
Surface contamination	Fe & Fe-Ni surface contamination prohibits formation of Ti oxide film. These are sites for rapid hydrogen penetration & embrittlement of the alloy.	Ti structures fabricated with Fe-based tooling require: • Surface pickling to remove contamination. • Use of Ti brushes for scratch-brushing operations.

47.9 Titanium alloys: Effect of oxygen

47.9.1 Oxidation

47.9.1.1 General

Titanium is a reactive material and oxidises, although the reaction is minimised by the oxide film passivating the surface.

47.9.1.2 Elevated temperatures

At high temperatures the passivation is ultimately overcome and excessive oxidation occurs. This limits titanium alloys to around 500°C for continuous operation in air unless advanced alloys or protection systems are used.

[See also Chapter 85]

47.9.2 Ignition and burning

Under certain conditions of oxygen temperature and pressure, if scuffed or impacted then titanium alloys can ignite and sustain burning; as shown, for static and dynamic oxygen environments, in Table 47.9.1, Ref. [47-25].

Table 47.9-1 - Titanium alloys: Ignition and burn characteristics

Conditions	Characteristic
Static	Freshly exposed Ti surface in contact with oxygen causes ignition.
	Reaction is dependent on oxygen content and pressure, the lower the O_2 content, the higher the pressure needed.
	Pure O_2 static conditions pressure of ~2.5MPa required.
	Affected by purity of O_2 atmosphere. At O_2 concentrations <~47%, ignition does not occur.
	Ignition limits are not influenced by surface to volume ratio or by temperatures up to ~300°C.
Dynamic	Increased possibility of ignition
	Limited to oxygen concentration < 35%.
	Ignition will not occur in air.
	Ignition is not self sustaining in water or aqueous solution.
	Ignition may occur in vapour space above solution, if conditions are favourable.

47.10 Coatings and protection systems

47.10.1 Requirements

The use of currently commercially available alloys is limited to around 500°C due to their mechanical property degradation in oxygen and hydrogen environments, [See also: Chapter 85].

However, demands to optimise the weight of future space propulsion systems could result in titanium alloys being used in regions not experiencing excessive temperatures, primarily rotational parts. This can be achieved by either:

- Alloy development combined with novel processing techniques.
- With the aid of coatings.

47.10.2 Potential coatings

Table 47.10.1 summarises on-going studies of coating systems for titanium alloys, Ref. [47-24], [47-25].

[See also: 74.6]

Table 47.10-1 - Titanium alloys: Potential coating systems

Substrate	Coating composition	Application method	Comments
Ti-6Al-4V TiCP (99.5%)	NiCr SiC Si3N4 Al	Sputtering	Coating thickness 1 to 8 ±µm Natural oxide stripped before coating SiC cracked therefore not effective Thermal shock: SiC spalled NiCr & Al did not spall No metallurgical changes found with Si3N4 coatings
IMI829	Ti-8.5Si †	Sputtering	Coating thickness 50 to 80µm typically Coating polluted by Al No significant diffusion between coating/substrate at 700°C Structural change in coating to Si-rich phases Coating reduced oxygen penetration from 35 atomic% to 10 atomic% uniformly

Key: † : Actual composition Ti-8.6Si-0.48Al.

47.11 Ti-alloys and MMCs: Potential applications

47.11.1 Current use

Titanium alloys have traditionally filled applications operating in the temperature range 200°C to 600°C, i.e. above aluminium and below superalloys. This has placed titanium in and around power plants (engines) and for surfaces experiencing aerodynamic heating. The higher modulus of titanium sometimes promotes its use instead of aluminium.

Alloys such as Timetal® 834 and Timetal® 1100 assist in progressively increasing the temperature capability of titanium.

[See: Table 47.2.3 for aerospace alloys]

47.11.2 Developments

There are two significant developments in titanium technology which influence its use beyond its current role. These are:

- Superplastic Forming/Diffusion Bonding (SPF/DB): A production technique which allows complex but weight-efficient constructions to be made with the desired titanium alloy and, for certain components, at a lower manufacturing cost.

[See also: Chapter 72 - SPF/DB titanium designs]

- Titanium Matrix Composites (TMCs): The addition of continuous reinforcements, notably silicon carbide filaments, increases specific strength and thermal capabilities. This can prove attractive for applications experiencing loading in a single, predominant direction (UD composite).

[See: Table 47.7.1 for TMC development]

The evolution of titanium matrix composites is dependent on controlling the reactive nature of titanium by material composition and processing. The poor transverse properties severely limit the use of bidirectional composites.

47.11.3 Aerospace applications

47.11.3.1 General

A review of potential applications for titanium-based materials in given in Ref. [47-27]. This concluded that:

- Ideal applications are those subjected to highly-directional loadings at high temperatures.
- Successful fibre coating techniques are a prerequisite for optimising TMC characteristics. A magnetron sputtering technique proved successful.
- Use of orthorhombic titanium aluminides or oxidation resistance coatings enables the service temperatures to exceed 500°C. [See: 49.5 – Titanium Aluminides].

ONERA have several developments programmes for titanium-based materials.

47.11.3.2 Propulsion systems

Work on TMCs within Europe and the USA has considered improvements in the performance for turbine engine propulsion systems, particularly for highly-loaded components. This led subsequently to the possible application of TMCs in propulsion systems for reusable space vehicles.

47.11.3.3 Hypersonic vehicles

In the USA, TMCs are being evaluated for various structural and power plant elements under NASP and subsequently X-program vehicles.

Detailed information on the materials evaluated and their intended applications is restricted outside the US, Ref. [47-31].

Within Europe, FESTIP considered titanium-based materials for hot skin applications (mainly titanium aluminides and composites thereof), Ref. [47-29].

[See also: 49.5 – Titanium aluminides]

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Website: http://www.mmpds.org/

47.12.2 ECSS documents

[See: ECSS website].

ECSS-Q-70-71	Data for the selection of space materials and processes; previously ESA PSS-01-701.

48 Superalloys and their composites

48.1 Introduction

48.1.1 General

The superalloys are established aerospace materials for engines and turbine components; demonstrating many years of service, [See: 48.2; 48.15 for applications for superalloys].

[See also: ECSS-Q-70-71: Data for the selection of space materials]

48.1.2 Alloy development

Demands for improved engine performance have led to requirements for higher operating temperatures and longer service lives.

To increase their high thermal stability further, superalloy compositions and processing methods have developed jointly, such as:

- Directional Solidification (DS).
- Single Crystal (SC).
- Powder Metallurgy; including Oxide Dispersion Strengthening (ODS) alloys.

[See: 48.3 for the characteristics of these alloys]

Innovative component designs have developed, whereby alloy anisotropy (like composite anisotropy) is used to sustain directional loads.

48.1.3 Composites

Development of superalloy matrix composites is restricted by the availability of a reinforcement phase which can survive the high temperature processing required for molten superalloys.

[See: 48.4 and 48.5]

Work has concentrated on tungsten-based continuous reinforcement. These are large diameter filaments (>100µm, typically).

Compatibility with the matrix remains a problem, and often a diffusion barrier coating is needed on the 'fibre' to prevent excessive damage during prolonged high temperature use. Developments in Tungsten Fibre Reinforced Superalloys (TFRS) are described, along with mechanical property data, [See: 48.6]. The quantity of data is limited for any particular composite.

48.1.4 Service environment

Superalloy applications generally involve high temperatures, in combustion environments.

In aero-engines, oxidation and the possibility of scuffing resulting in ignition should be considered, [See: 48.8].

For space vehicles, both in engines and active cooling systems, hydrogen-induced material degradation should be considered; especially for reusable, long-life structures. The effects of hydrogen on superalloys are discussed; along with data on the possible property losses, [See: 48.7].

[See also: Chapter 85]

48.1.5 Coating systems

Operation in hot and hostile environments means that superalloy components often require a coating to prevent excessive oxidation, corrosion or other thermally induced damage, [See: 74.7].

Coating systems are commercially available, but are being developed further as operational temperatures increase.

The various types of coating system are described along with the factors to be considered for the design of the coated component, [See: 48.9, 48.10, 48.11, 48.12, 48.13 and 48.14].

48.2 Conventional alloys

48.2.1 General

This Topic provides an introduction to the superalloy class of materials, in terms of their role and requirements for aerospace applications. It does not provide extensive property data, but serves as a basis for the Topics which describe the more recent material developments.

Design data is available in MIL-HDBK-5; replaced by MMPDS, Ref. [48-49]

48.2.2 Alloy groups

48.2.2.1 General

Superalloys are generally grouped by their main alloy constituent:

- Nickel based.
- Iron based.
- Cobalt based.

Within each group there is a wide variety of alloys which differ both in composition and associated mechanical and physical properties.

48.2.2.2 Requirements

Each family of materials has steadily evolved since the 1940s to meet applications which demand increasingly good mechanical performance at higher temperatures coupled with good oxidation and corrosion resistance.

Figure 48.2.1 shows a development curve for superalloys with respect to processing improvements, Ref. [48-5].

48.2.2.3 Applications

The applications have tended to be related to turbine components, both for aircraft engines and land-based power generator units.

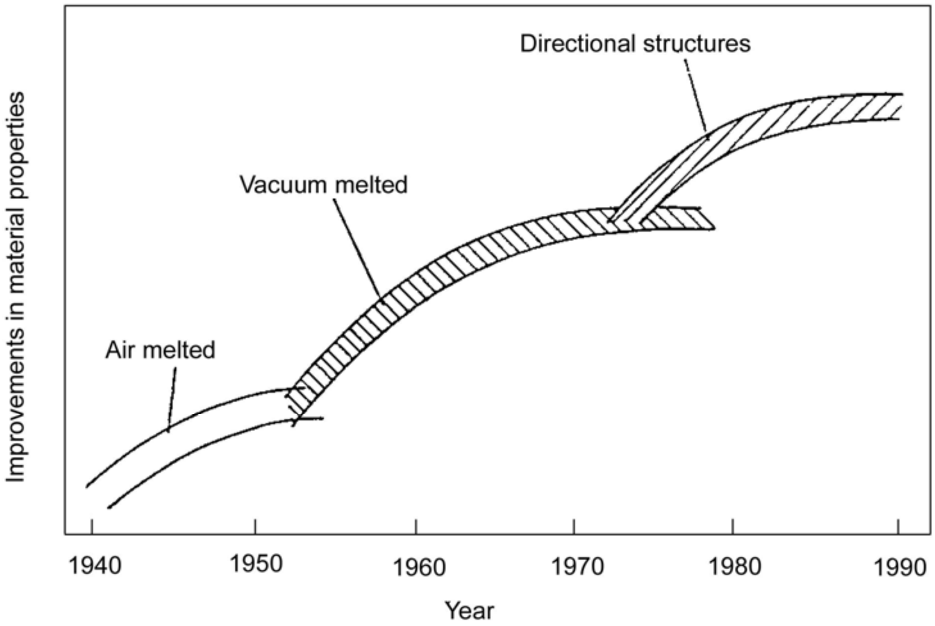


Figure 48.2-1 - Superalloys: Development Curve

48.2.3 Aircraft engine applications

48.2.3.1 Requirements

The superalloy material development has attempted to keep pace with demands from aero-engine manufacturers with exacting requirements for materials to help achieve improved engine performance in terms of, Ref. [48-2]:

- thrust-to-weight ratio,
- fuel consumption,
- increased service life (period between overhauls), and
- lower cost of ownership.

Table 48.2.1 lists the property requirements for aero-engine components met by ‘Conventional Superalloy’ designs, Ref. [48-2], [48-4], [48-6].

Modern aero-engines typically comprise of approximately 30% by weight superalloy, Ref. [48-3].

Table 48.2-1 - Superalloys: Property requirements for engine components

Application	Property requirements
Turbine discs	Operating temperatures 200 to 700°C typ.
	Cyclic stress up to 1100 MPa typ.
	Oxidising atmosphere
	Hot corrosion resistance (1)
	Centrifugal loading
	Rim temperature 677°C typ.
	Temperature gradients
	High yield stress
	Tensile strength to 700°C typ.
	Creep and creep fatigue resistance
	Low and high cycle fatigue resistance (LCF, HCF)
	Crack growth resistance
	Oxidisation resistance
Turbine blades	Hot corrosion resistance
	Centrifugal stresses 150 to 200 MPa, typ.
	Gas entry temperature 1377°C, typ
	Gas temperature at incipient melting point (2)
	Thermal gradients: Blade tip to root.
	Blade temperatures 1047°C, typ.
	Static and cyclic loading
	High temperature creep strength (at 0.8 Tm.) (3)
	Fatigue resistance
Gas turbine engines	Density
	Thermal conductivity
	Thermal emissivity
	Thermal expansion
	Melting point
	Stiffness
	Tensile strength
	Creep strength
	Fatigue strength
	Fracture resistance
	Impact resistance
	Toughness
Nozzle guide vanes and combustion hardware	High temperature properties similar to blades even though they are static components.
	Sheet form: High tensile and creep resistance.

Key: (1) By salts in marine environments & low grade fuel contaminants.
(2) Cooled blades with internal channels.
(3) Tm is the melting temperature in °C

48.2.3.2 Materials

Of the three generic classes, Nickel-based materials are most widely used because they possess certain beneficial metallurgical stability characteristics at high temperatures over Iron-based alloys, Ref. [48-3].

Cobalt superalloys have also been replaced by nickel-based alloys, partly because of an inability to provide further strengthening through conventional mechanisms, but primarily due to the world-wide shortage of Cobalt in the late 1970s. This led to a programme of work to reassess the levels of cobalt additions in other superalloy families, and reduced them without detriment to the alloy performance, Ref. [48-4].

Table 48.2.2 lists some of the alloys used for aero-engine components, Ref. [48-4], [48-5], [48-6], [48-7]. The list is not exhaustive.

48.2.3.3 Mechanical properties

Table 48.2.3 provides typical mechanical properties of some of the better known superalloys at various temperatures, Ref. [48-9].

Table 48.2-2 - Superalloys: For aero-engine component applications

Alloy designation [Manufacturer]	Application	Notes
Nickel based:		
Nimonic 901 [INCO]	disc	Denoted as Ni-Fe
Inconel 718 [INCO]	disc	Denoted as Ni-Fe
Rene 41 [TELEDYNE]	disc	-
Waspalloy [UN.TECH]	disc + blade	-
Astroloy [-]	disc	Powder Met. Variant
Rene 95 [TELEDYNE]	disc	Powder Met. Variant
IN 100 [-]	disc + blade	Powder Met. Variant also MERL 76 for HIP
Udimet 700 [SPEC. MTLS]	disc + blade	
Udimet 710, 720 [-]	disc	
PA101 [-]	disc	Powder Met. Alloy
AF115 [-]	disc	Powder Met. Alloy
AF2-1DA [-]	disc	Powder Met. Alloy
MAR-M200 [MARTIN MAR]		
MAR-M002		
MAR-M247		
Nimonic 80A [INCO]		
Nimonic 90		
Nimonic 105		
Nimonic 115		
Iron based:		
Discaloy [WEST. ELEC]	disc	
Tinadur	disc	
M308	disc	
A286	disc	
V57	disc	Principle Fe-based alloys used in USA
FV537	disc	
Cobalt based:		
FSX-414	Nozzle diaphragm casting	Weldability
MAR-M 322		
MAR-M 302		
IN 102		

Key: INCO: The International Nickel Co. Inc.; UN TECH: United Technologies Corp.;
TELEDYNE: Teledyne Allvac; SPEC. MTLS: Special Metals Corp.;
MARTIN MAR: Martin Marietta Corp.; WEST ELEC: Westinghouse Electrical Corp.

Table 48.2-3 - Superalloys: Typical mechanical properties

Alloy	**Form**	**Temp. (°C)**	**TS (MPa)**	**YS (MPa)**	**El (%)**	**R of A (%)**	***E* (GPa)**	**Notch TS (MPa)**	**Stress Rupture**		**DEWSIM (gcm^{-3})**	**Melting Range (°C)**	**Comments**
									100h	**1000h**			
Inconel 600	sheet	-253	1210	910	22	-	-	-	-	-	8.42	1354-1415	Hard, cold rolled, long dir.
		24	910	885	4	-	-	-	-	-			
	bar	-257	1280	1210	20	56	220	1530(a)					Cold drawn, long dir. (a) Kt = Not stated
		-253	1250	1100	30	58	-	-					
		-196	1160	1030	26	62	-	-					
		-78	985	910	20	56	-	-					
		24	940	890	15	56	170	1230(a)					
	bar	21	620	250	47	-	-	-					Not stated
		540	580	195	47	-	-	-					
		650	450	180	39	-	-	-					
		760	185	115	46	-	-	-					
		815	-	-	-	-	-	-	55	39			
		870	105	62	80	-	-	-	37	24			
Inconel 625	bar	21	855	490	50	-	-	-	-	-	8.44	1290-1350	(b) Solution Treated (ST):1150°C
		540	745	405	50	-	-	-	-	-			
		650	710	420	35	-	-	-	440(b)	370(b)			
		760	505	420	42	-	-	-	-	-			
		815	-	-	-	-	-	-	130(b)	93(b)			
		870	285	475	125	-	-	-	72(b)	48(b)			

Alloy	Form	Temp.	TS	YS	El	R of A	*E*	Notch TS	Stress Rupture		DEWSIM	Melting Range	Comments
		(°C)	(MPa)	(MPa)	(%)	(%)	(GPa)	(MPa)	100h	1000h	(g/cm^3)	(°C)	
Inconel 718	sheet	-253	1740	1340	16	-	-	1550(c)	-	-	-		Longitudinal dir. Aged:955°C/1hr/AC +720°C/8hr/FC to 620°C/10hr/AC (c) Kt = 10 transverse dir: Condition - as above: (c) Kt = 10
		-196	1730	1310	21	-	-	1560	-				
		-78	1490	1190	17	-	-	1470	-				
		24	1330	1090	18	-	-	1330	-				
	sheet	-253	1770	1370	16	-	-	1500(c)	-				
		-196	1700	1300	21	-	-	1500	-				
		-78	1480	1210	12	-	-	1450	-				
		24	1320	1100	18	-	-	1300	-				
	sheet	21	1280	1050	22	-	-	-	-				
		540	1140	945	26	-	-	-	-				
		650	1030	870	15	-	-	-	-				
		760	675	625	8	-	-	-	-				
	bar	-269	1810	1410	21	20	-	-	-	-			Longitudinal dir: Aged:980°C/45 min/AC +720°C/8hr/FC to 620°C/10hr/AC
		-196	1650	1340	21	20	-	-	-	-			
		24	1410	1170	15	18	-	-	-	-			
Inconel 718	bar	21	1430	1190	21	-	-	-	-	-			(d) 730°C/2hr.
		540	1280	1060	18	-	-	-	-	951(d)			
		595	-	-	-	-	-	-	860(d)	760(d)			
		650	1230	1020	19	-	-	-	690(d)	585(d)			
		760	950	740	25	-	-	-					
		870	340	330	88	-	-	-					

Alloy	**Form**	**Temp.** **(°C)**	**TS** **(MPa)**	**YS** **(MPa)**	**El** **(%)**	**R of A** **(%)**	***E*** **(GPa)**	**Notch TS** **(MPa)**	**Stress Rupture**		**DEWSIM** **(g/cm^3)**	**Melting Range** **(°C)**	**Comments**
									100h	**1000h**			
Inconel X-750	bar	-257	1720	1080	33	46	-	-	-	-	8.25	393-1425	Longitudinal dir. Annealed Aged: 700°C/20hr/AC
		-253	1700	1090	33	42	-	-	-	-			
		-196	1570	1050	32	45	-	-	-	-			
		24	1340	985	25	49	-	-	-	-			
	bar	21	1120	635	24	-	-	-	-	-			
		540	965	580	22	-	-	-	-	827(e)			(e) 1150°C + 840°C/24hr/? + 705°C/20hr/?
		650	825	565	9	-	-	-	-	-			
		760	485	455	9	-	-	-	-	-			
		870	235	165	47	-	-	-	83(e)	45(e)			
		925	-	-	-	-	-	-	58(e)	21(e)			
Rene 41	bar	21	1420	1060	14	-	-	-	-	-	8.25	1232-1371	Not stated
		540	1400	1010	14	-	-	-	-	-			
		650	1340	1000	14	-	-	-	-	-			
		760	1100	940	11	-	-	-	-	-			
		870	620	550	19	-	-	-	-	-			

Alloy	**Form**	**Temp.** (°C)	**TS** (MPa)	**YS** (MPa)	**El** (%)	**R of A** (%)	***E*** (GPa)	**Notch TS** (MPa)	**Stress Rupture**		**DEWSIM** (g/cm^3)	**Melting Range** (°C)	**Comments**
									100h	**1000h**			
Waspalloy	bar	21	1280	795	25	-	-	-	-	-	8.20	1339-1355	Not stated
		540	1170	725	23	-	-	-	-	-			
		650	1120	690	34	-	-	-	-	-			
		760	795	675	28	-	-	-	-	-			
		870	525	515	35	-	-	-	-	-			
MAR-M-246	DS	21	-	-	-	-	131	-	-	-	-	-	Longitudinal
		21	-	-	-	-	183	-	-	-			Transverse
		760	-	-	-	-	103	-	-	-			Longitudinal
		760	-	-	-	-	149	-	-	-			Transverse

48.2.3.4 Design

It is widely believed that aero-engine requirements have exceeded the capability of conventional superalloys and little can be gained by further alloy development alone. That said, there are innovative component designs in service which cope with 'over temperature' of gases impinging on superalloy blades and discs by incorporation of cooling channel systems. Blades are by their nature very complex components, as shown in Figure 48.2.2, and there is a possibility of further improvements with design, Ref. [48-6].

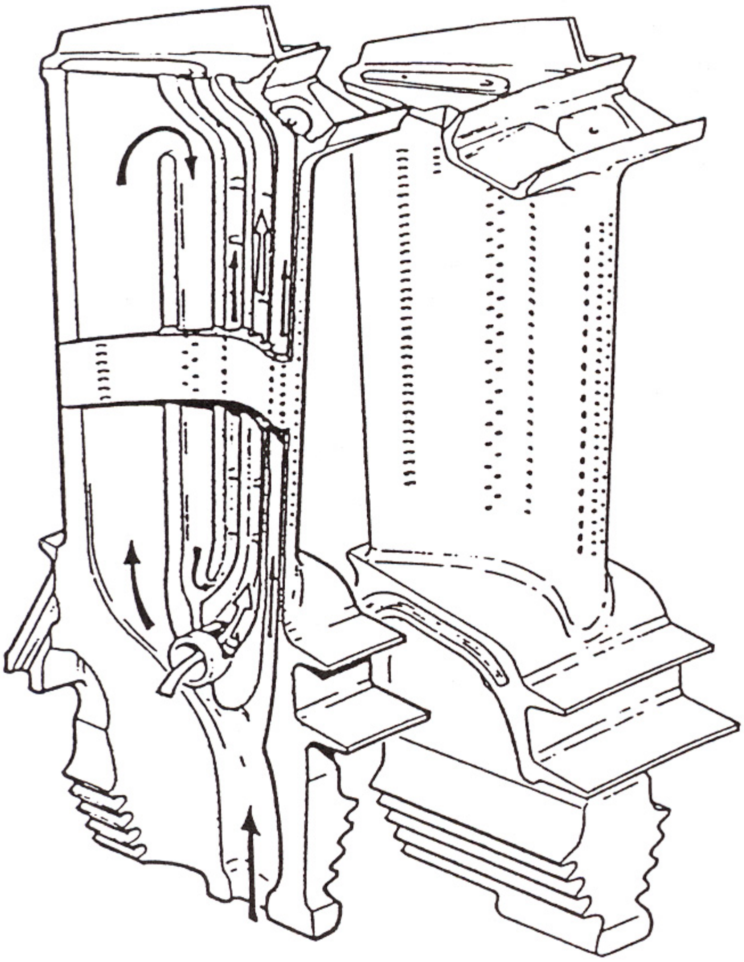


Figure 48.2-2 - Superalloys: Cooled turbine blade

48.2.4 Spacecraft engine applications

48.2.4.1 Operational conditions

The operating conditions for some turbines in advanced rocket engines are, in some respects, more severe than their air-breathing aero-engine counterparts.

Table 48.2.4 compares the operating conditions of rocket engine and aircraft engine turbines, Ref. [48-8].

Table 48.2-4 - Superalloys: Comparison of rocket engine and aircraft engine turbine operation

Service condition	Rocket engine ①	Aircraft engine
Fuel	Hydrogen/Methane	Petroleum distillate
Oxidiser	Oxygen	Air
Pressure (MPa)	38	2.8
Speed (rpm)	36000 to110000	15000
Tip speed (m/s)	564	564
Horsepower/blade	630	200 to 500
Inlet temperature (°C)	880 to 1 215	1435
Heat transfer coeff. (kW/m^2/°C)	306.6	2.84
Thermal transients (°C/sec)	17770	55
Starts	55 to 700	2400
Life (hours)	7.5 to 100	8000

Key: ① : Space Shuttle main engine (SSME). High pressure turbo-pump turbine

Most noticeable are the differences caused by the combustion of high pressure hydrogen fuel between:

- heat transfer coefficients, and
- thermal transients.

48.2.4.2 Requirements

For rocket engine turbines, Figure 48.2.3 compares the Space Shuttle and Aero turbine engine operating regimes, Ref. [48-8].

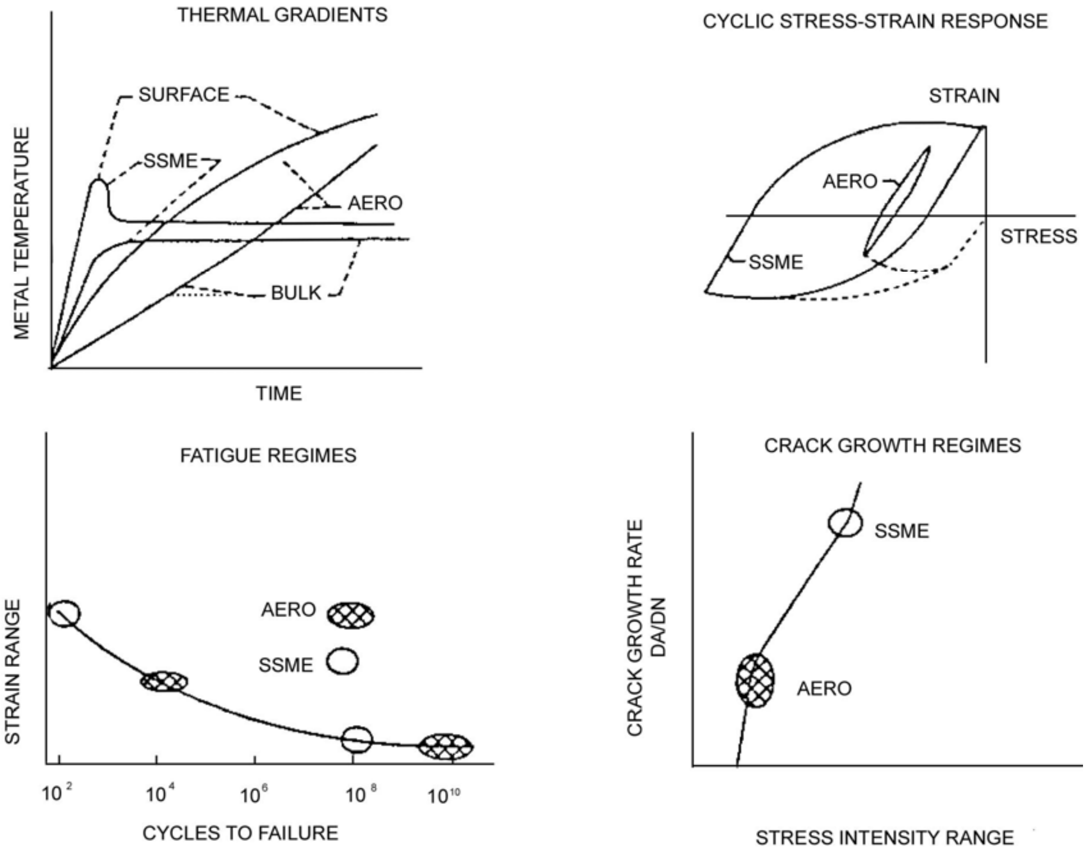


Figure 48.2-3 - Operating regimes for Space Shuttle and aero-engine turbines

The combination of fatigue both at low and high cycle and hydrogen environment have meant that the design aim of 7.5 hr (55 launches) was not been achieved with conventional superalloys.

48.2.4.3 Material development

Table 48.2.5 lists the material systems under evaluation for rocket engine application, Ref. [48-8].

Table 48.2-5 - Superalloys: Potential blade materials under evaluation for rocket engine turbine components

Type of material	Notes
Directionally solidified alloys (DS)	MAR-M246 + Hf eutectic alloys
Single crystal superalloys (SC)	[See: Table 48.2.6]
Rapid solidification (RS)	-
Fibre reinforced superalloys (TFRS)	[See: 48.6]
Monolithic ceramics	[See: Chapter 43]

Of these materials Single crystal superalloys (SC) and certain alloys within that group, as shown in Table 48.2.6, are considered to have potential for turbine propulsion systems in Space Shuttle, Ref. [48-8].

Table 48.2-6 - Single crystal superalloys: Potential use in rocket engine turbines

Alloy	Ranking †
AF56	Best
N5	
PWA 1480	
RR 2000	
N4	
CMSX-4C	
SC180	
SRR 99	
MAR-M246	
CMSX 2 0	
CMSX 2 CM	
	Worst
Key: †	Ranked on hydrogen strength ratio room temperature notch tension in high pressure hydrogen.

48.3 New alloys

48.3.1 Developments

48.3.1.1 Combined alloying and processing

The developments with superalloys have concentrated on enhancing properties by a combination of alloy modification and specialist processing techniques, such as:

- Directional solidification (DS)
- Single crystal (SC)
- Powder metallurgy (PM), e.g. directional recrystallisation of extruded powder, Hot isostatic pressing (HIP)
- Oxide dispersion strengthened (ODS)

48.3.1.2 Characteristics

The processing of the first three groups leads to materials with directional properties useful in turbine blades. The DS group are known as 'Insitu' or 'Natural' composites, where the strengthening phase is usually in chemical equilibrium with the matrix.

Oxide dispersion strengthened (ODS) alloys are not considered to be composites, as the dispersions are extremely fine (sub-micron) and interact with the host alloy at a microscopic level in the same way as the precipitates formed by alloying.

48.3.2 Directional solidification (DS)

48.3.2.1 Composition

In DS alloys, the composition is adjusted to produce a eutectic upon solidification.

Table 48.3.1 lists some of the eutectic systems under evaluation, Ref. [48-10], [48-11].

Table 48.3-1 - Reinforcing phases in directionally solidified (DS) eutectic superalloys

Composition	Type of reinforcement †
Co-TaC	Fibrous. 5 to 12 vol.%, typ.
Ni-TaC	Fibrous. 5 to 12 vol.%, typ.
Ni_3Al-Ni_3Nb	Lamella. 30 to 40 vol.%, typ.
γ / $\gamma'\delta$	-
Key:	†: Typical contents.

48.3.2.2 Application

The fibrous types of DS alloy are of interest for turbine blade applications, where the fibres can be aligned along the axis of the blade. Table 48.3.2 lists some DS alloys, Ref. [48-13].

Table 48.3-2 - Directionally solidified (DS) superalloys

Alloy	Composition (Balance - Nickel)
MAR-M 200+Hf	2.2Ti - 4.9Al - 9.5Co - 1Nb - 12W - 1.7Hf - 9.5Cr - 0.14C - 0.015B
Rene 80 H	4.7Ti - 3.1Al - 9.3Co - 4Mo - 3.8W - 0.72Hf - 13.9Cr - 0.15C - 0.015B
441	5.9Al - 11.7Co - 1.1Mo - 7.1Ta - 5.5W - 1.4Hf - 6.6Cr - 3.1Re - 0.06C - 0.02B
MAR-M 247	10Co - 8.4Cr - 0.6Mo - 10W - 3.3Ta - 5.5Al - 1Ti - 1.4Hf - 0.15C - 0.015B - 0.05Zr

48.3.3 Single crystal (SC)

These types of materials offer better creep and fatigue life than the DS family and are of interest for turbine blade applications. Their properties are highly anisotropic and are dependent on the crystallographic orientation.

Table 48.3.3 lists some of the Single Crystal (SC) alloys.

Table 48.3-3 - Single crystal (SC) superalloys

Alloy	Composition
NASAIR 100	BalNi-0Cr-1Mo-10.5W-3.3Ta-5.8Al-1Ti
"Alloy 3"	BalNi-5.1Co-8.7Cr-8Mo-10W-3.2Ta-5.4Al-1.1Ti-0.6Hf
CMSX-3	BalNi-4Co-7.5Cr-.5Mo-7.5W-6Ta-5.5Al-.0Ti-.1Hf
PWA 1480	BalNi-5Co-10Cr-4W-12Ta-5Al-1.5Ti
SRR-99	BalNi-5Co-8.5Cr-9.5W-2.8Ta-5.5Al-2.2Ti
AF 56	Other SC alloys investigated for use in N5 Space Shuttle Main Engine (SSME) Turbine
RR 2000	
N4	
CMSX-4C	
CMSX 2 0	
CMSX 2 CM	

48.3.4 Powder metallurgy (PM)

Production of superalloy materials by powder techniques became of interest when deficiencies in conventional processing methods were observed for highly alloyed variants. Compared with conventionally produced superalloys, PM superalloys are recognised as providing, Ref. [48-48]:

- improved strength,
- improved creep resistance,
- improved creep fatigue,
- better low-cycle fatigue properties.

These characteristics have been achieved by two main process-related developments, Ref. [48-48]:

- 'gatorising' (Pratt and Whitney) or isothermal forging: to reduce the fracture initiation and growth of those defects present. this process improves LCF properties compared with as-HIPped components. Where creep strength is the sole design criterion, as-HIPped components are used, but most engine applications use isothermal forging.
- finer powder (<106µm, often 44µm max.): to reduce the size of non-metallic defects.
- heat treatment: 'supersolvus' to increased grain size and damage tolerance. For Ni-based alloys, producing a gamma-prime phase (up to 64%, depending on the particular alloy composition).

PM superalloy development was accompanied by some technical problems, as summarised in Table 48.3.4, Ref. [48-4], [48-5], [48-8].

These have largely been overcome by, Ref. [48-48]:

- process control: when strictly controlled, this can successfully limit non-metallic defects during processing and after atomisation.
- contamination: significantly reduced by use of clean room environments, often with vacuum or inert gas screening and loading.
- fracture mechanics (defect size and crack growth rate): a major design criterion for PM application. Defining and limiting defects (inherent in PM products) is essential.

Table 48.3-4 - Powder metallurgy of superalloys

Process	Problem	Comments
Powder production	High oxygen levels	Process in vacuum & inert gas. Acceptable levels now 100 ppm.
Powder forging	-	Improved mechanical properties.
Extruded powder billet	-	Fine grain size & superplasticity.
Hot isostatic pressing (HIP) †	Limited deformation & recrystallisation	Alloy modified to fine tune C content and carbide stabilisers (Nb, Ta, Hf) for HIP alloys.
	Prior particle boundaries not eliminated	Improved if HIPped
	Exogenous defects	-
	Porosity in SC alloys act as initiators for fatigue cracks.	-

Key: † Potential cost reduction of 35 to 40% for turbine blades.

As a result, a family of powder metallurgy (PM) superalloys are commercially available. Some of these are listed in Table 48.3.5, Ref. [48-4], [48-48].

Table 48.3-5 - Powder metallurgy nickel-based superalloys: Composition

Alloy	Composition
AF115	BalNi-10.5Cr-15Co-2.8Mo-5.9W-1.8Nb-3.8Al-3.9Ti-0.05Zr-0.8Hf-0.02B-0.05C
AF2-1DA	BalNi-12Cr-10Co-3Mo-6W-1.5Ta-4.6Al-3Ti-0.35C
Astroloy	BalNi-15Cr-17Co-5Mo-4Al-3.5Ti-0.25B-0.03C (1)
IN100	BalNi-12.4Cr-18.4Co-3.2Mo-5Al-4.3Ti-.8V-0.06Zr-0.02B-0.07C
MERL76	BalNi-12.4Cr-18.5Co-3.2Mo-1.4Nb-5Al-4.3Ti-0.06Zr-0.4Hf-0.02B-0.025C (2)
N 18	BalNi-11.5Cr-15.7Co-6.5Mo-4.35Ti-4.35Al-0.02B-0.03Zr-0.02C-0.5Hf
PA101	BalNi-12.5Cr-9Co-2Mo-4W-4Ta-3.4Al-4.1Ti-.11Zr-1Hf-0.015B-0.016C
Rene 88T	BalNi-16Cr-13Co-4.0Mo-4.0W-3.7Ti-2.0Al-0.015B-0.03Zr-0.03C-0.7Nb
Rene 95	BalNi-13Cr-8Co-3.5Mo-3.6W-3.5Nb-3.5Al-2.5Ti-0.05Zr-0.01B-0.06C

Key: (1) Similar to UDIMET 700, APK 1, MTS1024.

(2’Powder metallurgy (PM) modification of IN100 atomised for direct Hot Isostatic Pressed (HIP) components.

PM processing techniques are also appropriate to the ODS class of superalloys, i.e. materials strengthened by oxide dispersions or by other similarly hard particles.

48.3.5 Oxide dispersion strengthened (ODS) alloys

Table 48.3.6 lists some compositions of commercial ODS superalloys. Yttria (Y_2O_3) is a stable oxide at high temperatures. Additions are made during powder production, Ref. [48-13], [48-46], [48-47].

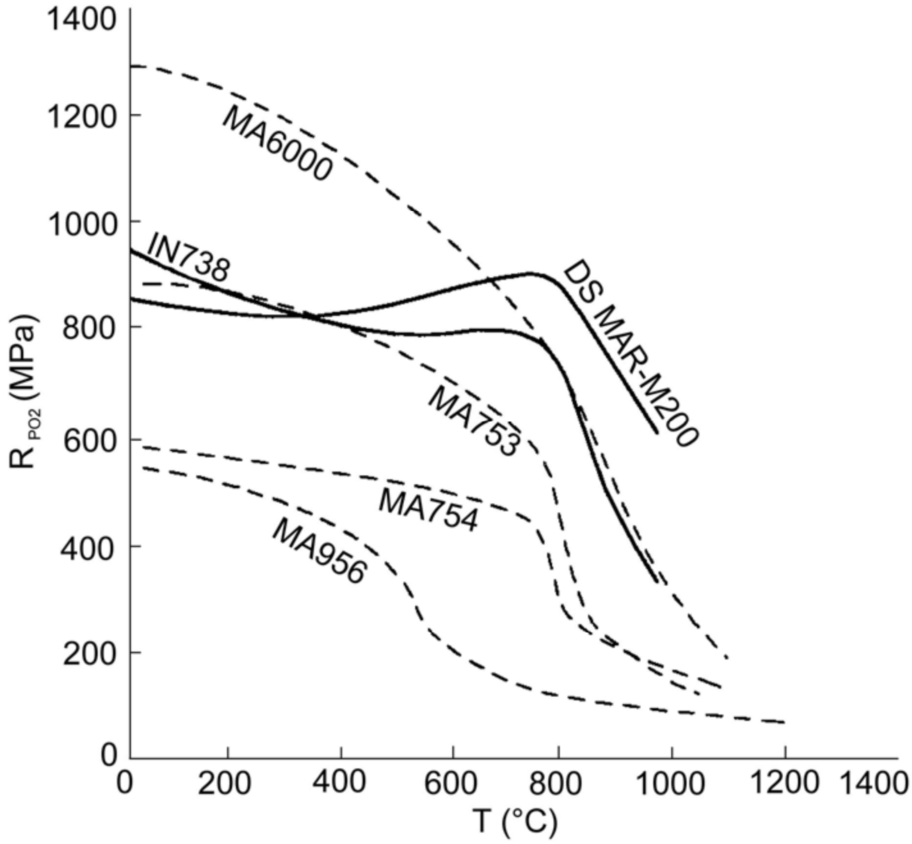
The resultant materials offer significant mechanical properties up to approximately 0.9 of their melting temperature, Ref. [48-13].

Table 48.3-6 - Oxide dispersion strengthened (ODS) superalloys: Composition

Alloy	Composition
MA 753	BalNi-20Cr-1.5Al-2.5Ti-0.05C-0.007B-0.07Zr-1.3Y_2O_3
MA 754	BalNi-1Fe-20Cr-0.3Al-0.5Ti-0.05C-0.6 Y_20_3
MA 758	BalNi-30Cr-0.3Al-0.5W-0.3Al-0.05C-0.37O (total) + Y_2O_3
MA 760	BalNi-19.5Cr-6Al-3.4W-1.2Fe-0.6C-0.3N-0.6O (total) + Y_2O_3
MA 956	BalFe-20Cr-4.5Al-0.5Ti-0.05C-0.5Y2O3
MA 6000	BalNi-15Cr-4.5Al-2.5Ti-0.05C-4W-2Mo-2Ta-0.01B-0.15Zr-1.1Y_2O_3
Alloy 51	BalNi-9.5Cr-8.5Al-0.05C-6.6W-3.4Mo-0.01B-0.15Zr-1.1Y_2O_3
Alloy 69	BalNi-9.5Cr-7Al-0.05C-8W-2Mo-1Ta-0.15B-1.1Y_2O_3
PM 1000	BalNi-20Cr-3.0Fe-0.5Ti-0.3Al-0.6Y_2O_3

Certain thermo-mechanical and recrystallisation procedures enable further property improvements in ODS alloys at high temperatures, Ref. [48-13], [48-14].

Figure 48.3.1 compares tensile properties of some ODS alloys and two cast alloys at elevated temperatures, Ref. [48-13].



0.2% Offset.

MAR-M™ Martin Marietta Corp.

Figure 48.3-1 - ODS superalloys: Comparison of yield strength with casting superalloys

A comparison between the tensile elongation for some ODS alloys and cast alloys is shown in Figure 48.3.2, Ref. [48-13].

Although the majority of effort has been placed on Y_2O_3 ODS materials, this strengthening mechanism is appropriate for other dispersoids having high temperature stability, e.g. nitrides, Ref. [48-5].

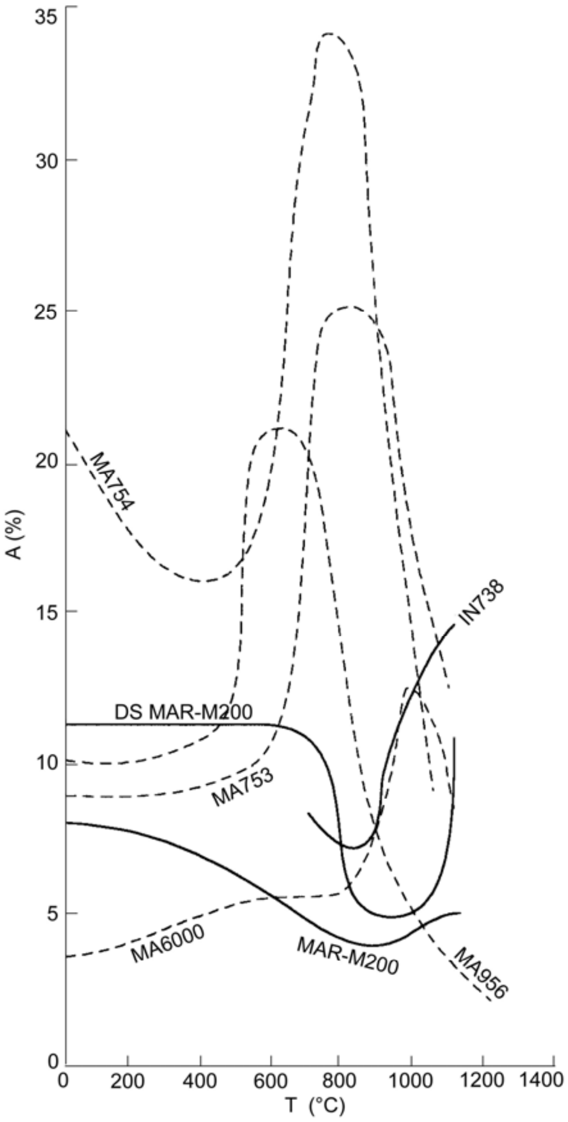


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Figure 48.3-2 - ODS superalloys: Comparison of tensile elongation with casting superalloys

48.4 Discontinuously reinforced composites

There are no discontinuously reinforced composites with deliberate additions of either:

- Particulates, or
- Whiskers.

The reinforcing media cannot survive processing with molten superalloys, given their melting ranges.

The nearest materials are the directionally solidified (DS) and oxide dispersion strengthened (ODS) variants, [See: 48.3].

[See: Table 48.5.1 for examples of discontinuous reinforcements examined for superalloys]

48.5 Continuously reinforced composites

48.5.1 Composite development

48.5.1.1 General

Continuous reinforcing fibres and filaments which survive processing in molten superalloys are extremely limited.

48.5.1.2 Reinforcements

Interest has focused on combining refractory metal reinforcement phases with superalloys to increase strength at high temperatures.

Table 48.5.1 lists the reinforcement phases considered for superalloys and notes on their success. Of those listed, Tungsten and thoriated tungsten (ThO_2)W wires have received most attention.

The typical range of diameters for continuous reinforcements is 100 to 500µm. They are monofilaments but are also described as wires in some publications, fibres or filaments in others.

Table 48.5-1 - Superalloy composites: Reinforcement phases

Type	Material	Comments
Particulate	HfO	Severe degradation during fabrication or subsequent thermal soak.
	ZrO	
Whisker	SiC	[See: 48.4]
	Si_3N_4	
	Sapphire	
	Alumina	
Continuous wires †	Mo	Attacked by Ni during fabrication.
	Nb	-
	(ThO_2)W	Less affected by matrix.
	W-Hf-C	Newer materials. Higher strengths.
	W-Hf-Re-C	

Key: † Typical diameter range: 100µm to 500µm.

48.5.1.3 Matrix alloys

Table 48.5.2 summarises a number of superalloys that have been considered as the matrix phase primarily with tungsten-based wires.

[See also: 48.6 for TFRS - Tungsten fibre reinforced superalloys]

Table 48.5-2 - Superalloys: Typical mechanical properties of matrix materials for composites

Property	Units	Temp (°C)	Alloy classification							
			Nickel-base			Cobalt-base			Iron-base	
			Hastelloy X (a)	Nimonic 80A (b)	Inconel 718 (b)	IN102 (b)	MAR-M 322 (c)	MAR-M 302 (c)	Discaloy (d)	FeCrAlY ③
Density	g/cm^3	-	8.22	8.19	8.19	8.55	8.91	9.21	7.95	-
Thermal Conductivity ①	Wm/K	-	9.7	11.2	11.2	-	-	-	-	-
Thermal Expansion ②	10^{-6}/K	-	13.8	12.7	13.0	-	-	-	-	14.0
0.2% Proof Stress	MPa	RT	358-380	621-740	1056	504	628	690	730	-
		760	262	504	628	386	379	386	428	-
		870	179	262	-	200	345	310	173	-
Tensile Strength	MPa	RT	787	1235	1276	959	828	932	1000	-
		760	435	758	676	441	628	704	483	-
		870	255	400	-	214	552	448	-	-
Young's Modulus	GPa	RT	195	-	200	-	227	227	195	-
		760	-	-	155	-	160	160	-	-
		870	-	-	-	-	150 nom.	150 nom.	-	-
Elongation	%	RT	43	24	22	47	3.2	2	40	-
		760	37	20	8	110	6.5	8	32	-
		870	50	34	-	110	12	11	33	-
Material Form			Sheet	Bar	Sheet	Bar	-	-	-	-
			Wrought	Wrought	Wrought	Wrought	Cast	Cast	Wrought	-

Key: (a) ™ Cabot Corp. (b) ™ The International Nickel Co. Inc.; (c) ™ Martin Marietta Corp.' (d) ™ Westinghouse Electric Corp.

① : At 20°C; ② : Between 20°C and 95°C; ③ : FeCrAlY alloys are only considered as superalloys with Oxide Dispersion Strengthening.

48.6 Tungsten fibre reinforced superalloy (TFRS) composites

48.6.1 Development

Studies of tungsten-based reinforcements in various superalloy matrices have considered:

- Refractory wires and their fabrication
- Optimisation of the matrix alloy composition
- Fabrication processes
- Fibre-matrix interaction
- Diffusion barrier technology
- Mechanical property determination

Owing to the large number of material combinations, data tends to be incomplete on any particular composite system.

48.6.2 Matrix alloys

48.6.2.1 General

Of the three prime superalloy classes, iron-based superalloys are more compatible with tungsten-based reinforcements, as shown in Table 48.6.1, of which FeCrAlY offers considerable promise, Ref. [48-15].

Table 48.6-1 - Tungsten fibre reinforced composites: Reinforcement and superalloy matrix

Reinforcement	Recrystallisation temperature of W reduced by: Ni, Al & Mn. Reaction of W with matrix.
Matrix	Formation of intermetallic and/or carbide compounds in proximity of fibre, reducing composite integrity.
Iron-based superalloys	Lower solubility of W in Fe, compared with Ni. Less active in promoting W recrystallisation. Fe-W intermetallics are more stable at high temperatures than W-Ni compounds.
FeCrAlY	High oxidation resistance High melting point Compatible with W

48.6.2.2 Diffusion Barrier Coatings

For other TFRS systems, effort has concentrated on developing diffusion barrier coatings to deter matrix-fibre interaction, Ref. [48-15]. The various types of coating, or combinations, being considered are:

- Hafnium compounds: HfN, HfO.
- Titanium compounds: TiC, TiN.
- Zirconium compounds: ZrC, ZrO_2.

This is a recognised method of reducing interdiffusion, but an optimised system should be used for each specific matrix.

48.6.3 Mechanical properties

48.6.3.1 General

Data on mechanical properties are largely drawn from research publications in which the number of material combinations are diverse. Data sets tend to be incomplete on any particular matrix and fibre combination.

48.6.3.2 Tensile

The properties shown in Table 48.6.2, Table 48.6.3 and Table 48.6.4 are an indication of what can be achieved from the various material systems, Ref. [48-15].

Table 48.6-2 - Tungsten fibre reinforced, nickel-based superalloys: Tensile properties of development composites

Filament	Matrix	Fibre vol (%)	Diffusion barrier coating	Fibre angle (°)	Test temp (°C)	0.2% YS (MPa)	UTS (MPa)	*E* (GPa)	Elong. (%)	R of A (%)
W	Ni	40-44	-	0	650	193	270	-	-	-
		"	-	0	930	70	127	-	-	-
		"	TiC	0	650	-	232	-	-	-
		"	TiC	0	930	-	117	-	-	-
		"	TiN	0	650	121	201	-	-	-
		"	TiN	0	930	60	99	-	-	-
W-2%Th0$_2$ ①	MAR M 200	50-55	-	0	870	-	1157	-	1.67	-
		"	-	0	980	-	839	-	8.6	-
		"	-	10	980	-	638	-	2.6	-
		"	-	45	980	-	440	-	>12.4	-
		"	-	90	980	-	449	-	9.0	-
		"	-	0	1090	-	595	-	24.5	-
		"	-	10	1090	-	430	-	24.8	-
		"	-	45	1090	-	147	-	29.7	-
		"	-	90	1090	-	119	-	29.4	
-	MAR M 200 only	-	-	-	870	-	840	-	-	-
-		-	-	-	980	-	523	-	-	-
-		-	-	-	1090	-	213	-	-	-
HSTW wire only	-	-	-	-	870	-	1371	-	-	-
	-	-	-	-	980	-	1212	-	-	-
	-	-	-	-	1090	-	1109	-	-	-

Key: ① Composites HIPped 1120°C, 138 MPa for 2 hrs.

Table 48.6-3 - Tungsten fibre reinforced, cobalt-based superalloys: Tensile properties of development composites

Filament	Matrix	Fibre vol (%)	Diffusion barrier coating	Fibre angle (°)	Test temp (°C)	0.2% YS (MPa)	UTS (MPa)	*E* (GPa)	Elong. (%)	R of A (%)
W-2%Th0$_2$	MAR M 332C	33	-	0	RT	-	345	-	0.2	-
	"	35	-	0	900	-	590	-	4.9	-
	MAR M 322D	43	-	0	980	537	545	-	4.7	-
	"	44	-	0	1093	488	520	-	3.2	-
	"	40	-	0	1150	392	420	-	4.0	-
	"	44	-	0	1315	96	103	-	-	-
	MAR M 322E	40	-	0	980	537	545	-	-	-
	"	38	-	0	1093	419	434	-	-	-
	"	40	-	0	1150	392	448	-	-	-
-	MAR M 332C only	-	-	-	RT	710	-	-	0.5	-
-		-	-	-	1093	214	214	-	3.6	-
-	MAR M 322E only	-	-	-	RT	303	448	-	9.0	-
-		-	-	-	900	276	386	-	18	-
-		-	-	-	980	110	117	-	-	-
W-2%Th0$_2$ only	-	-	-	-	RT	-	2170	-	-	6
	-	-	-	-	650	-	1791	-	-	30
	-	-	-	-	870	-	1780	-	-	28
	-	-	-	-	1093	-	1309	-	-	25

Table 48.6-4 - Tungsten fibre reinforced, iron-based superalloys: Tensile properties of development composites

Filament	Matrix	Fibre vol (%)	Diffusion barrier coating	Fibre angle (°)	Test temp (°C)	0.2% YS (MPa)	UTS (MPa)	*E* (GPa)	Elong. (%)	R of A (%)
W-1%Th0$_2$ ①	AISI 1095	-	-	0	RT	-	400	297	-	-
		-	-	0	RT	-	938	293	-	-
W-2%Th0$_2$ ②	304 SS	20	-	0	RT	-	650	-	-	-
		20	-	0	380	-	566	-	-	-
		20	-	0	600	-	470	-	-	-
		20	-	0	700	-	470	-	-	-
		20	-	0	980	-	300	-	-	-
		25	-	0	RT	-	540	-	-	-
		25	-	0	200	-	700	-	-	-
		25	-	0	360	-	625	-	-	-
		25	-	0	500	-	560	-	-	-
		35	-	0	RT	-	660	-	-	-
		35	-	0	200	-	840	-	-	-
		35	-	0	360	-	710	-	-	-
		35	-	0	500	-	760	-	-	-
		35	-	0	700	-	600	-	-	-
		35	-	0	980	-	470	-	-	-
W-2%Th0$_2$ ②	Kovar	25	-	0	RT	-	620	-	-	-
		25	-	0	600	-	500	-	-	-
W-1%Th0$_2$ ③	FeCrAlY	35	-	0	RT	-	620	179	-	-
		35	-	15	648	-	746	-	19	-
		35	-	45	648	-	551	-	29	-
		35	-	90	648	-	185	-	3.4	-
		35	-	15	760	-	552	-	13	-
		35	-	45	760	-	169	-	24	-

Filament	**Matrix**	**Fibre vol (%)**	**Diffusion barrier coating**	**Fibre angle (°)**	**Test temp (°C)**	**0.2% YS (MPa)**	**UTS (MPa)**	***E* (GPa)**	**Elong. (%)**	**R of A (%)**
W-1%Th0$_2$ ④	FeCrAlY	35	-	90	760	-	111	-	6.5	-
		35	-	90	RT	-	654	179	-	-
		35	-	0	648	-	737	-	3	-
		35	-	0	648	-	768	-	2.9	-
W-Hf-C ⑤	FeCrAlY	30	-	0	982	-	460	-	0.6	-
		30	-	0	1093	-	381	-	0.3	-
		50	-	0	982	615	684	152	3.2	-
		<38	-	0	982	665	724	151	2.4	-
		42	-	0	1093	428	>548	265	>1.6	-
		44	-	0	1093	540	607	-	3	-

Key:

① After heat treating

② Composites HIPped 1050 to 1200°C & 150 to 250 MPa

③ Composites hot pressed

④ As fabricated, after creep testing at: 1037°C for 1077 hrs. 1093°C for 99 hrs.

⑤ Composites hot pressed

48.6.3.3 Long-term elevated temperature use

With regard to the intended use of TFRS at elevated service temperatures, limited data are available on:

- fatigue,
- creep,
- impact, and
- oxidation resistance.

Generally the data have been produced for comparative purposes during studies on fibre-matrix interactions or processing technology. Therefore it is specific to the material and test conditions.

48.6.3.4 Thermal cycling

Table 48.6.5 provides an indication of thermal cycling resistance for a tungsten-reinforced FeCrAlY composite, Ref. [48-16]. The loss of RT tensile strength was attributed to matrix damage due to different fibre and matrix thermal expansion characteristics and improved fibre-matrix bonding permitting crack propagation across the bond into the fibres. No damage to the fibres was noted.

Table 48.6-5 - Tungsten fibre reinforced superalloy: Room temperature tensile strength of thermally cycled composite

Maximum cyclic temperature (°C)	RT tensile strength (MPa)	Replicates
Control	772	3
850	785	3
1000	655	2
1090	489	2
Key: Material - 4 ply 218 CS Tungsten fibre in Fe-22Cr-5.5Al matrix. Unidirectional. 37% fibre volume.		

48.6.4 Characteristics

Table 48.6-6 provides some general comments on TFRS systems, their advantages, and areas requiring further evaluation, Ref. [48-15].

Table 48.6-6 - Summary of tungsten fibre reinforced superalloy (TFRS) systems

Advantages	Disadvantages	Future development
Perceived operating temperature 1100°C +	RT Tensile properties less than matrix alone. W ductile-to-brittle transition temperature 150 to 370°C; flaw sensitivity in brittle state.	-
At elevated temperatures TFRS have superior properties: 1.7x at 1090°C $WTh0_2/Ni$ 3.2x at 980°C $WTh0_2/Co$	Development centred on air-breathing aero engine requirements.	Effect of rocket engine environment with H-based fuels required.
Improved stress rupture characteristics.	Some systems susceptible to thermal fatigue. FeCrAlY superior to other systems.	Full evaluation programme for most appropriate combination.
FeCrAlY good corrosion/oxidation resistance.	High density.	Need to establish long-term environmental stability.
Considerable experience in applying conventional superalloys to high temperature environments.	Offer ~100°C improvement over the conventional and new superalloys.	-

48.7 Effect of hydrogen

48.7.1 Degradation mechanisms

Hydrogen is known to be detrimental to the performance of a wide range of materials by changing:

- ductility (embrittlement)
- crack behaviour

48.7.2 Hydrogen embrittlement (HE)

The effects of hydrogen embrittlement (HE), depend upon, Ref. [48-17]:

- magnitude and extent of hydrogen interaction with the material,
- ease of hydrogen transport from the environment to the material.

Table 48.7.1 summarises several phenomena that have been determined, Ref. [48-17].

The effect of hydrogen on superalloys can be summarised as:

- Effects can be extensive.
- Influences deformation behaviour by interaction with dislocations.
- Reduces ductility by decreasing flow stress and enhancing planar slip.
- Affects lattice bond interactions at either grain boundaries or through grains.
- Leads to brittle hydride formation, causing lattice expansion, stable at and below RT
- Effects are active to temperature of approximately 600°C

Table 48.7-1 - Established mechanisms of hydrogen degradation in materials

Phenomenon	Characteristics
Hydrogen attack	Occurs at high temperature.
	Formation of a reaction product between hydrogen & alloying element, e.g. $H_2 + C \rightarrow$ methane, in steels.
	Both reactants diffuse to an internal interface to combine & form a cavity.
	Continued reaction produces high pressure gas pockets inside material.
Internal hydrogen pressure	Occurs at RT, or below, plus high temperatures.
	Diffusion of protonic hydrogen through material to interface.
	Depends on a supersaturation level.
	Reacts to form high pressure molecular H_2 gas pockets inside material.
	Molecular hydrogen is largely immobile.
Dislocation interaction	Wide temperature range.
	Does not require super saturation of protonic H.
	Strongly influences plastic behaviour.
Hydride formation	Protonic hydrogen levels above saturation.
	Reacts to form a brittle metal hydride.
	Hydrides precipitate at selected planes and local regions of high strain.

48.7.3 Hydrogen environment embrittlement (HEE)

In space propulsion units, where hydrogen (as a fuel or coolant) is in direct contact with the materials, additional factors have been identified. These are described as Hydrogen Environment Embrittlement (HEE) and occur without a 'hold-time'; i.e. without allowing hydrogen charging of the material, and are in addition to those effects denoted as HE.

Characteristic effects of HEE are shown in Table 48.7.2, Ref. [48-18].

For materials under prolonged high temperatures, factors associated with HEE and HE become important, and can act in synergy.

Table 48.7-2 - Characteristics of hydrogen environment embrittlement (HEE)

Condition	Characteristics	Comments
Environment	Occurs without H charging of material. Degradation of properties compared with air or inert environment, i.e. He.	-
Material	Effects thin surface layer which then cracks when deformed (strain-to-crack initiation). Relevant to all materials.	-
Mechanical properties	Lower tensile ductility. Tensile plastic deformation causes surface cracking. Sub-critical crack growth. Faster crack growth rates, both under cyclic and sustained loads. Reduced notched tensile strength.	Elastic properties and tensile yield strength largely unchanged
Temperature	Occurs between cryogenic up to ~1144K, typically. Most severe at approx. RT.	
Pressure and purity	Increases with increasing Hydrogen pressure. Sensitive to gas purity.	Pure hydrogen most severe.

48.7.4 Material sensitivity

48.7.4.1 General

Table 48.7.3 summarises the sensitivity of certain alloys with regard to their tensile property retention ratio in hydrogen and an inert atmosphere, i.e. helium, Ref. [48-18].

Table 48.7-3 - Sensitivity of superalloys to hydrogen

Alloy Spec.	Hydrogen Pressure (MPa)	Ratio H_2:He Notched UTS	Ratio H_2:He Unnotched R of A	Comments
Waspalloy	3.45	0.64(a)	-	Wrought
	48.3	0.77(b)	0.45	
	48.3	-	0.74	
IN 625	34.5	0.98(c)	0.48	Wrought
	48.3	0.78(b)	0.37	
IN 903	34.5	1.01(c)	0.98	Wrought
	48.3	0.98(c)	1.15	
A 286	34.5	-	0.93	Wrought
	34.5	1.00(c)	0.99	
Haynes 188	41.4	0.88(c)	-	Wrought
	3.45	0.98(c)	-	
	3.45	-	0.60	
Rene 41	48.3	-	0.17	Wrought
Hastalloy X	34.5	0.87(c)	1.00	
	51.3	0.88(c)	0.55	
MAR M 246	34.5	-	0.61	Conventionally Cast
	42.7	-	0.80	
	48.3	-	0.40	
MAR M 246	34.5	-	0.40	Directionally Solidified
	34.5	0.33(b)	0.30	
	48.3	0.24(b)	0.69	
MAR M 246	34.5	0.60(b)	-	Single Crystal
	34.0	0.18	-	
PWA 1480	34.5	0.84(b)	0.74	Cast
	34.5	0.49(c)	0.52	Cast
	34.0	0.49	-	Single Crystal
CM-SX2 Std	34.5	0.29(b)	0.17	Cast
	34.5	0.29(b)	0.17	
CM-SX2-CM	34.0	0.17	-	Single Crystal
CM-SX4-C	34.5	0.35(c)	0.81	Cast
	34.0	0.36	-	Single Crystal
RR2000	34.5	0.54(b)	-	Cast
	34.0	0.47	-	Single Crystal
IN 713 LC	48.3	-	0.38	Conventionally Cast
IN 718	48.3	0.83(b)	0.76	Cast
IN 718	34.5	0.54	0.31	Wrought RB †
	34.5	0.59	0.37	F †
	34.5	0.86	0.67	P †
	34.5	0.7	0.62	RB ‡
	34.5	0.57	0.54	F ‡
	34.5	0.86	0.78	P ‡
	34.5	0.71	0.34	RB *f*
	34.5	0.76	0.39	F *f*
	34.5	0.77	0.62	P *f*
AF 56	34.0	0.84	-	Single Crystal
N-5	34.0	0.84	-	Single Crystal
N4	34.0	0.46	-	Single Crystal
SC180	34.0	0.30	-	Single Crystal
SR99	34.0	0.25	-	Single Crystal
Rene N4	34.5	0.44(b)	0.49	Cast
	34.5	0.46(c)	0.48	

Key: (a) $Kt = 8.4$; (b) $Kt = 6.3$; (c) $Kt = 8.0$.;

† SA2: NASA Heat Treatment; [ST:940°C+A:718°C to 621°C];

‡ STA2: NASA Heat Treatment; [ST:940°C+A:816°C to 649°C];

R.B: Rolled bar; F: Forging; P: Plate;

f STA1: NASA Heat Treatment; [ST: 1052°C+A:760°C to 649°C]- used for Space Shuttle Main Engine.

48.7.4.2 Directionally solidified (DS) alloys

Table 48.7.4 compares the effect of hydrogen on directionally solidified MAR-M-246 (DS) with it's conventionally cast (CC) equivalent, for various test and surface conditions, Ref. [48-18].

Table 48.7-4 - Effect of hydrogen on MAR-M-246 superalloys

Temp (°C)	**Ratio H_2:He Notched UTS**	**Ratio H_2:He Unnotched UTS**	**Unnotched R of A**	**Comments ①**
Conventionally Cast				
RT	0.75	-	0.89	After 870°C/8 hr at 34.5 MPa H_2 or He. Tested in air.
Directional Solidification				
RT	0.97	-	0.71	After 870°C/8 hr at 34.5 MPa H_2 or He. Tested in air.
-73	0.83 [0.68]	-	- [0.47]	After 538°C/12hr at 34.5 MPa
24	0.28 [0.37]	-	0.28 [0.29]	H_2 Tested in H_2 (or He).
149	0.45 [0.71]	-	0 [0.17]	
RT	-	0.76	0.57	As ground 32 rms
RT	-	0.65	0.20	32 rms + 871°C/8h stress relief.
RT	-	0.86	0.62	Oxidised stress relief + glass bead hone. Tested in 34.5 MPa H_2.
Key: ① Values in brackets are for no H_2 pre-charging, but same test environment.				

48.7.4.3 Single crystal (SC) alloys

Table 48.7.5 shows that the performance of single crystal (SC) alloys in hydrogen is influenced by crystal orientation, Ref. [48-19].

Table 48.7-5 - Effect of crystal anisotropy on RT hydrogen performance of PWA 1480 single crystal alloy

Crystal orientation	**Ratio H_2:He Notched UTS**
<001>	0.57
<013>	0.65
<012>	0.73
<123>	0.74
<223>	0.76
<110>	0.79
<111>	0.88
Hydrogen pressure 34.5 MPa. $K_t = 8.0$	

48.7.4.4 DSE and ODS alloys

Limited data on DSE, ODS and FRS materials are summarised in Table 48.7.6, Ref. [48-18].

Table 48.7-6 - Effect of hydrogen on directionally solidified eutectic (DSE) and oxide dispersion strengthened (ODS) superalloys

Alloy Composition or Specification	Ratio H_2:He Notched UTS	Ratio H_2:He Unnotched R of A	Comments
Directionally Solidified Eutectic (DSE) Alloy			
Ni-45.5W	0.63	0.42	RT in 34.5 MPa H_2 or He.
Ni-19.7Nb-6Cr-2.5Al	0.60	0.08	Experience severe degradation.
Ni-21.75Nb-2.5Al	0.64	0.05	Extreme levels of secondary surface cracking plus fibre/matrix interfaces.
Oxide Dispersion Strengthened (ODS) Alloys			
MA957: T	0.34	0.13	RT in 34.5 MPa H_2 or He.
L	0.58	0	Combined effects of ODS & precipitation strengthening reduce HEE susceptibility; but no significant benefits over current materials.
MA6000: T	0.92	0.5	
L	0.86	4	
MA754: T	0.94	0.27	
L	0.96	0.19	

Key: T : Transverse. L: Longitudinal

48.7.4.5 Composites

A short study of a superalloy composite, Ref. [48-18], has shown that:

- Notched tensile values are largely unaffected at medium H_2 pressures and lower notch factors (less severe).
- Matrix shields fibres from H_2 degradation.
- Fibres act as 'barriers' to transverse, planar crack propagation in matrix.

48.7.5 Creep in hydrogen environments

48.7.5.1 General

To date, available data on creep performance in hydrogen are limited because the relatively short design lives of current rocket engines largely avoid creep phenomena. Creep characteristics are of importance for long-life, reusable vehicle concepts.

Preliminary studies indicate that:

- Life reductions in high pressure hydrogen are generally not severe.
- Creep ductility can be slightly affected, but are within the scatter bands for inert environment testing.
- Increased creep strain rate results in a reduction in the time to rupture.

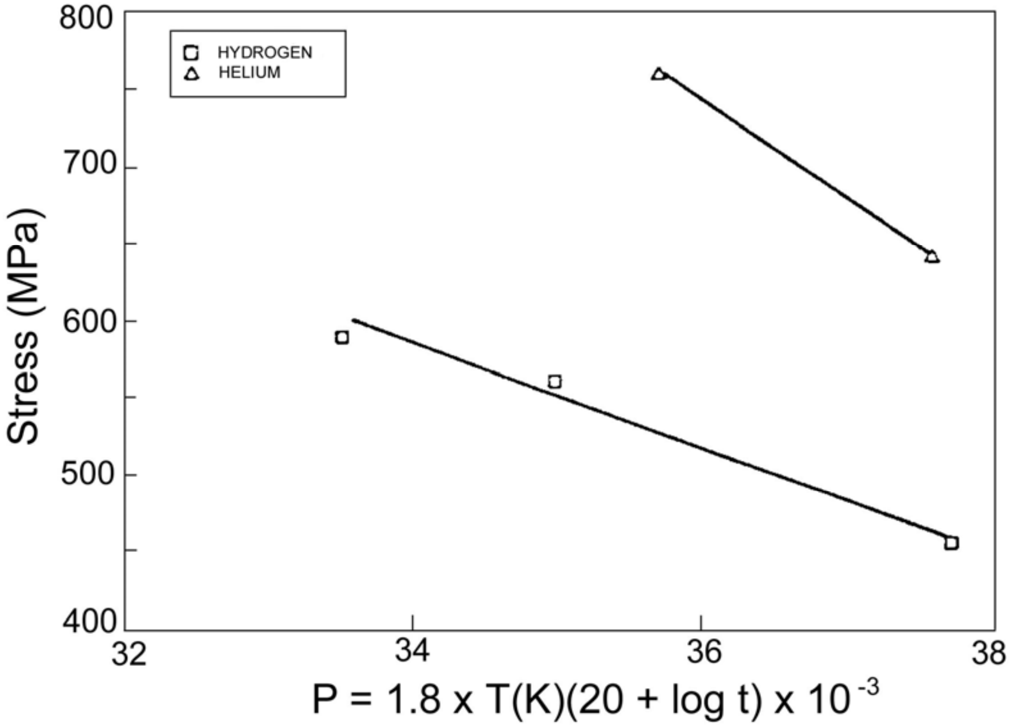
48.7.5.2 Creep-rupture

The effect of hydrogen on the creep-rupture (Larson-Miller type curve) behaviour of various alloys are summarised in, Ref. [48-18]:

- Figure 48.7.1 and Figure 48.7.2 shows the effect of heat treatment on Inconel 718. STA are standard heat treatments for Space Shuttle engine parts.
- Figure 48.7.3 for Inconel 625.
- Figure 48.7.4 for Waspalloy.

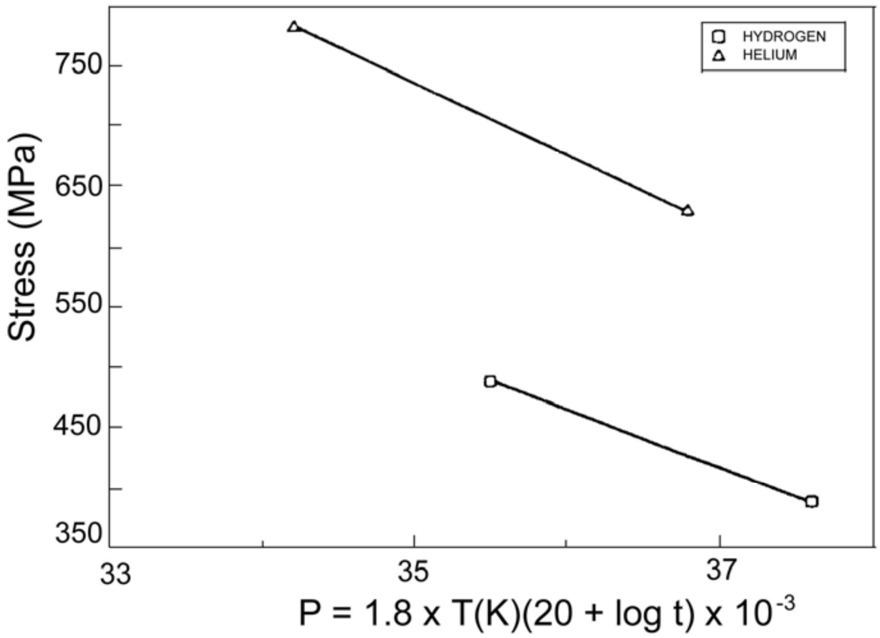
The effects of processing on MAR-M-246 alloy on creep-rupture are summarised in, Ref. [48-18]:

- Figure 48.7.5 for conventionally cast.
- Figure 48.7.6 for directionally solidified.
- Figure 48.7.7 for single crystal.



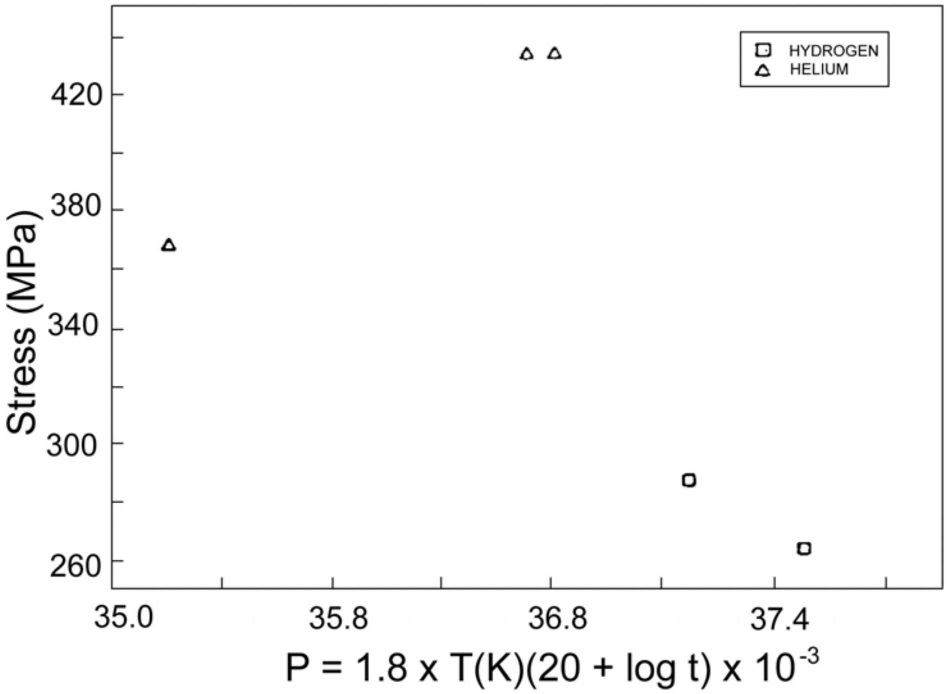
Hydrogen pressure: 34.5 MPa.

Figure 48.7-1 - Effect of hydrogen on creep rupture of Inconel 718 STA2



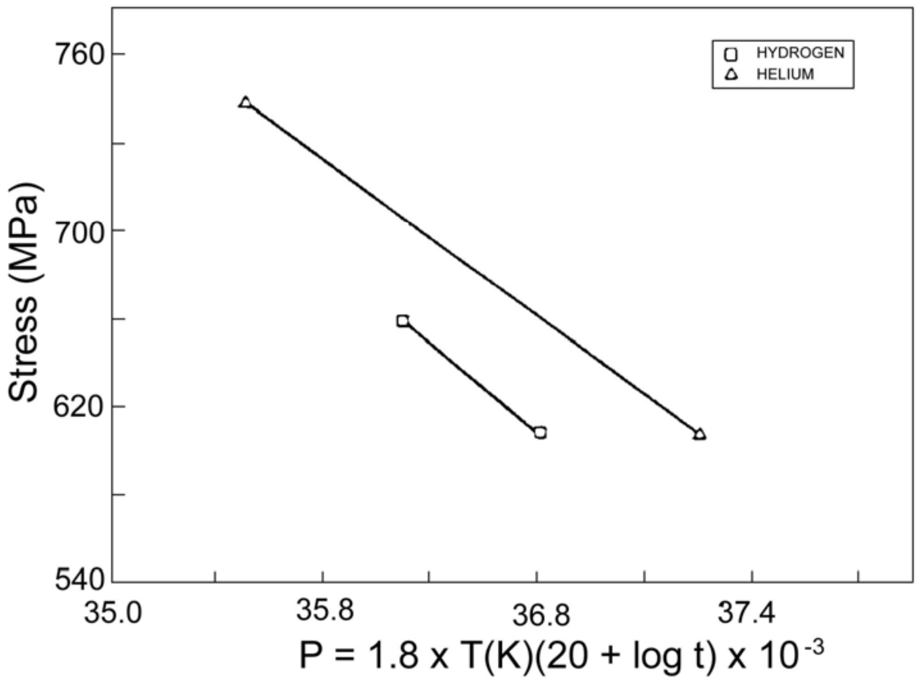
Hydrogen pressure: 34.5 MPa.

Figure 48.7-2 - Effect of hydrogen on creep rupture of Inconel 718 STA1



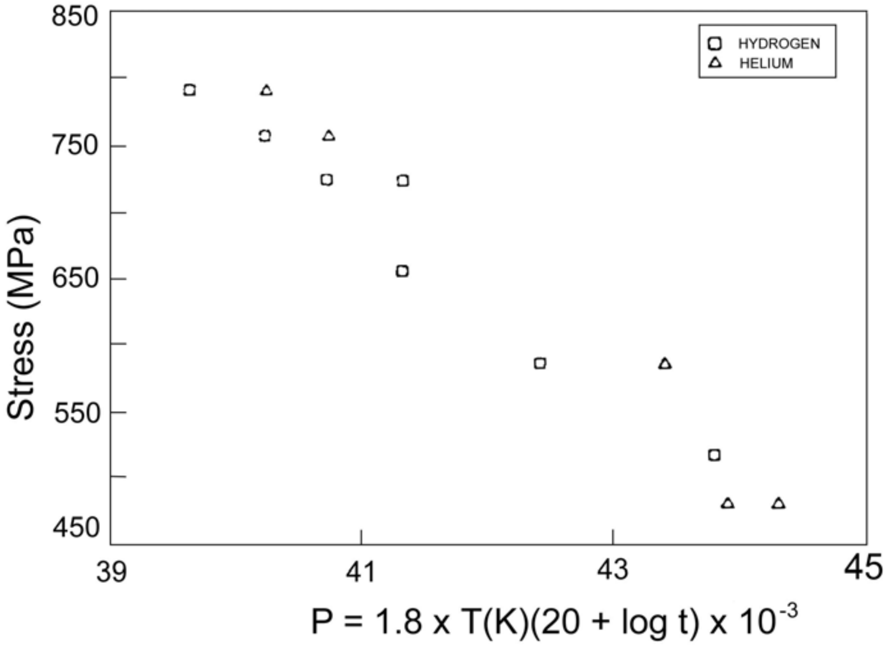
Hydrogen pressure: 34.5 MPa.

Figure 48.7-3 - Effect of hydrogen on creep rupture of Inconel 625



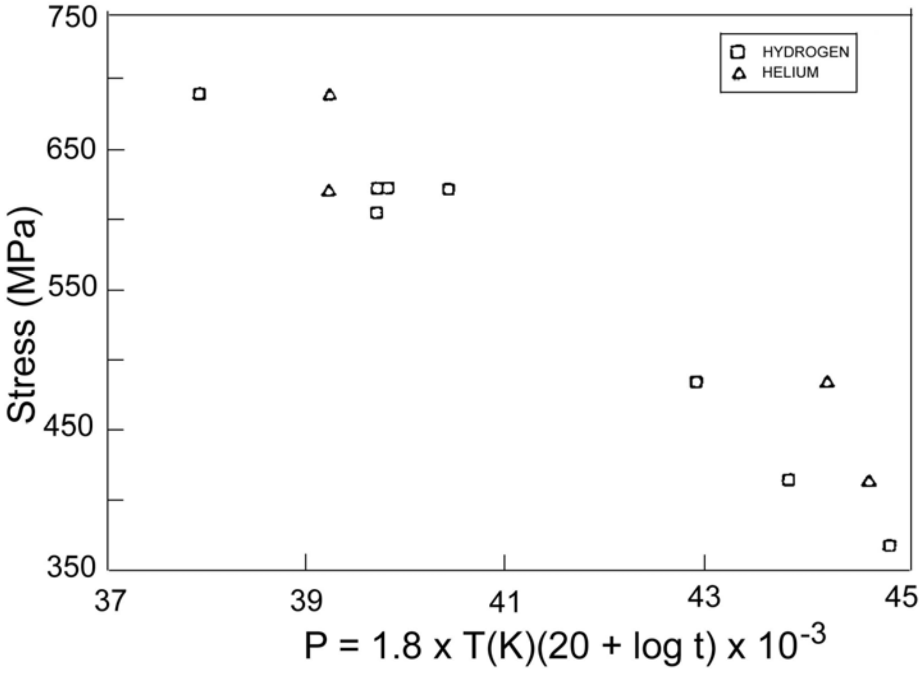
Hydrogen pressure: 34.5 MPa.

Figure 48.7-4 - Effect of hydrogen on creep rupture of Waspalloy



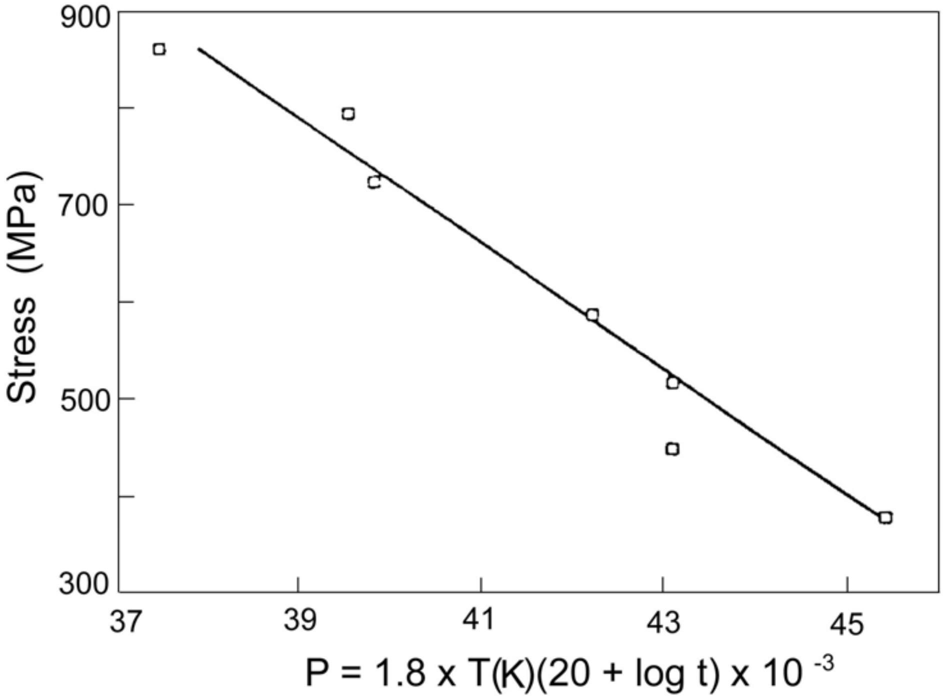
Hydrogen pressure: 34.5 MPa.

Figure 48.7-5 - Effect of hydrogen on creep rupture of MAR-M-246 conventionally cast



Hydrogen pressure: 34.5 MPa.

Figure 48.7-6 - Effect of hydrogen on creep rupture of MAR-M-246 directionally solidified



Hydrogen pressure: 34.5 MPa.

Figure 48.7-7 - Effect of hydrogen on creep rupture of MAR-M-246 single crystal

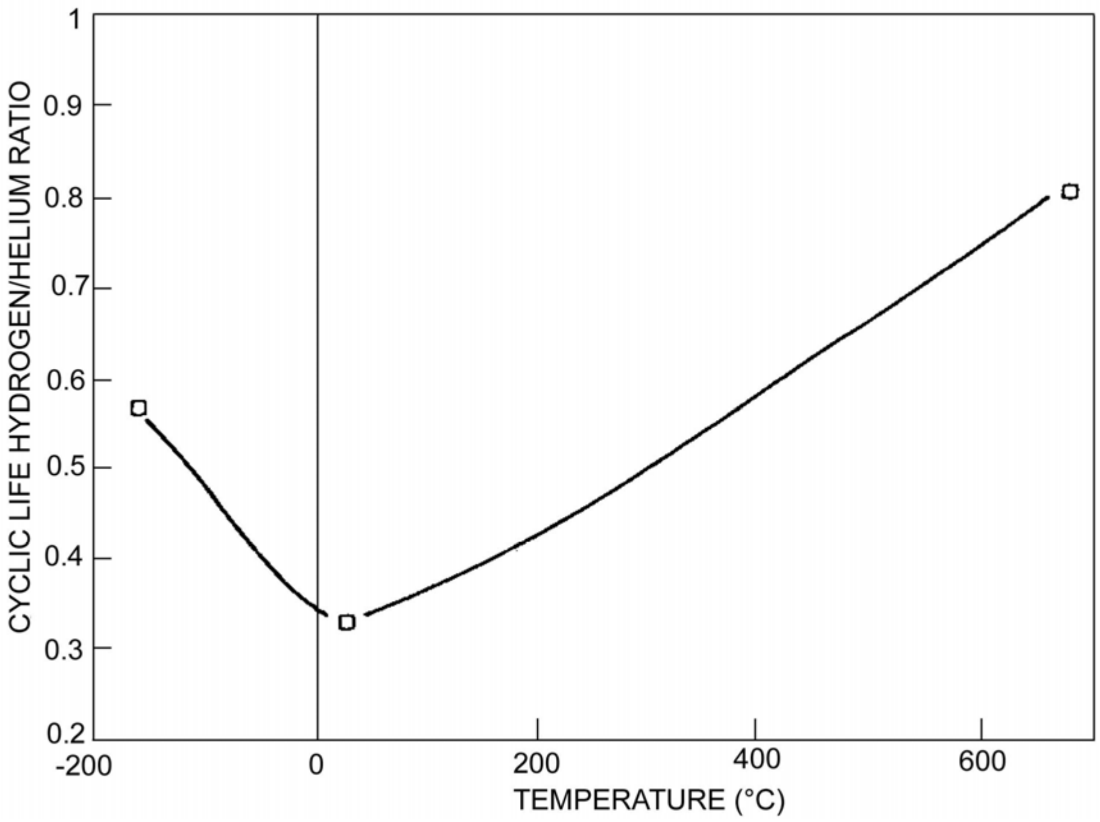
48.7.6 Fatigue in hydrogen environments

48.7.6.1 Low cycle fatigue (LCF)

In general, alloys exhibiting low sensitivity to high pressure hydrogen in tensile testing show similar levels of reduction to LCF in HEE.

Figure 48.7.8 shows the maximum life reduction occurs at ~RT for IN718, Ref. [48-18].

Table 48.7.7 summarises LCF studies on other alloys, Ref. [48-18].



Hydrogen pressure: 34.5 MPa. 2% strain rate.

Figure 48.7-8 - Low cycle fatigue (LCF) life of Inconel 718 against temperature

Table 48.7-7 - Low cycle fatigue (LCF) life degradation of superalloys in hydrogen environments

Alloy	Condition	Test temperature, (°C)	Strain range, (%)	LCF life loss, (%)
Inconel 718	STA2	25 677 -162	2 2 2	67 20 -75
Inconel 718	STA 1	677	1	5
Inconel 625	-	25	2	88
Hastelloy X	-	25	2	-100
Waspalloy	-	677	1.8	50
IN 100	-	677	1	69
Haynes 188	-	677	1.5	33
A286	-	25 677	2 2	0 0
DSMAR M 200	-	677	1	-400
DSMAR M 246	-	760 871	2 2	8 -87
CCMAR 246	-	750 871(a)	0.5 0.5	14 62

Key: (a); load control; H_2 Pressure 34.5 (MPa).
STA 1 & 2: NASA Heat treatments used for Space Shuttle Main Engine parts.

48.7.6.2 High cycle fatigue (HCF)

To date, studies on HCF have been inconclusive. Indications are that:

- Crack propagation is affected if hydrogen penetrates to the crack tip.
- High mean stress fatigue is most strongly affected.

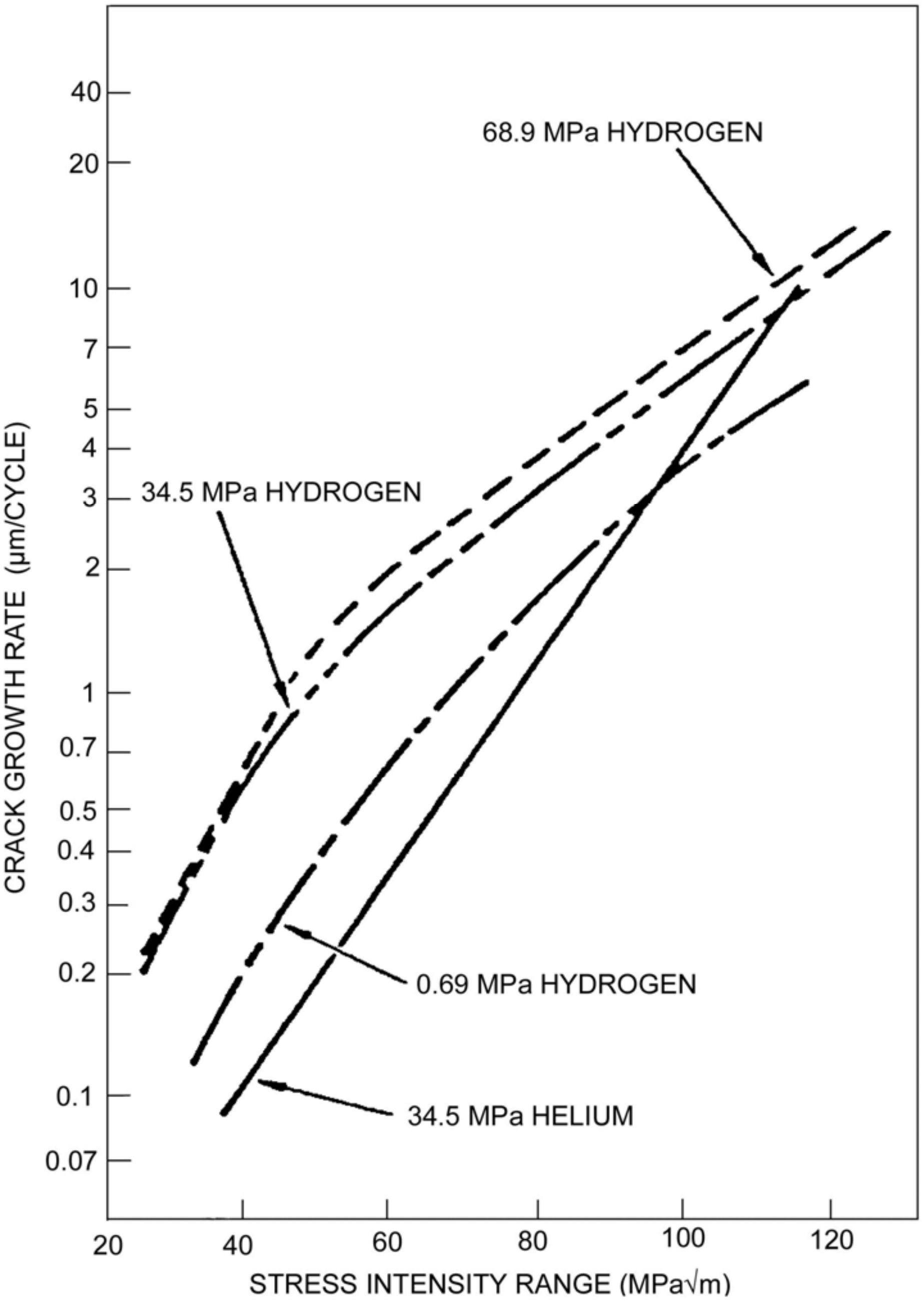
48.7.7 Fracture characteristics

Hydrogen environment influences the fracture characteristics, including:

- Threshold stress intensity.
- Crack propagation rate.

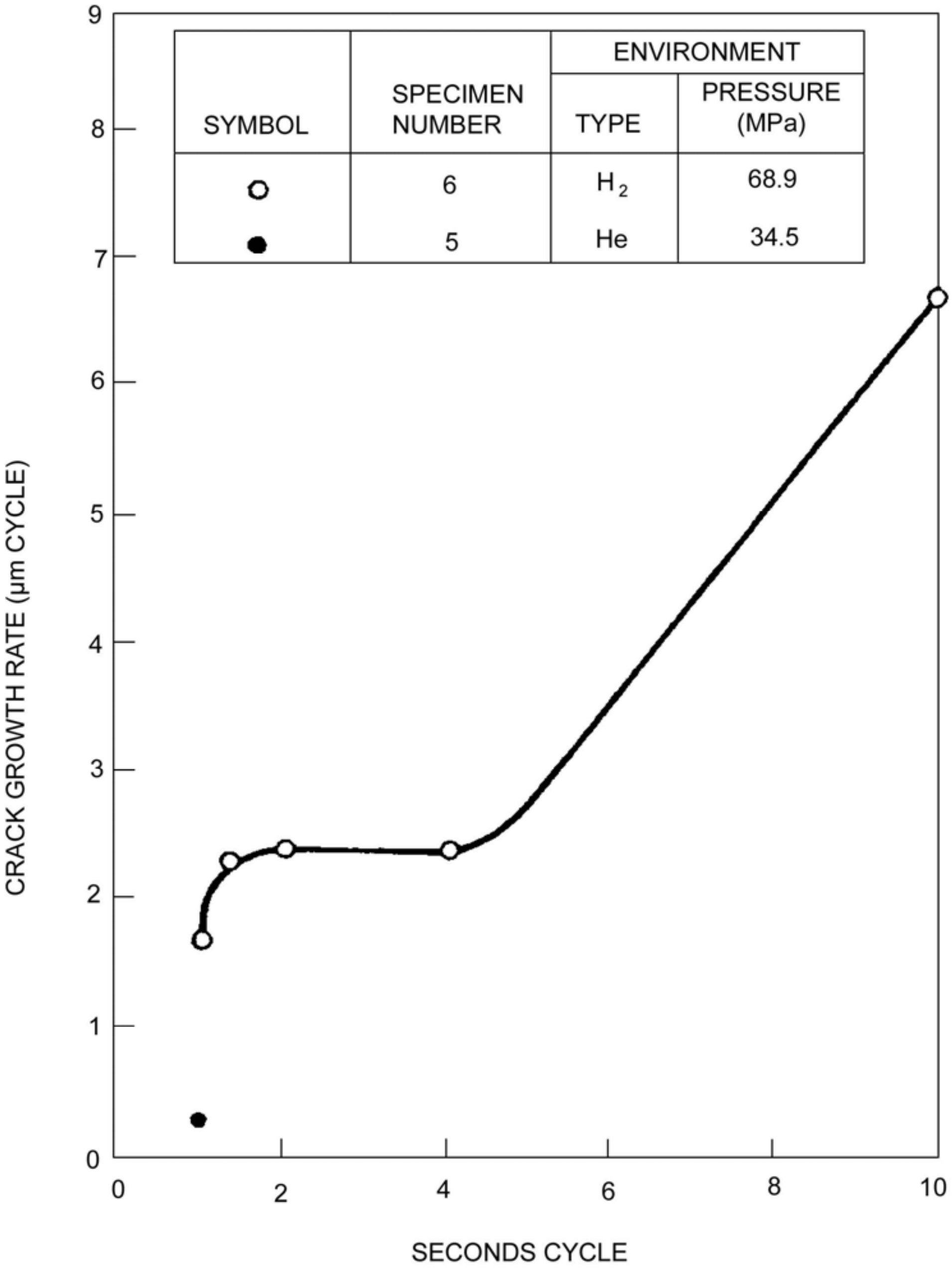
Figure 48.7.9 shows the effect of stress intensity on crack growth rates of IN718 in various hydrogen environments, Ref. [48-18].

In Figure 48.7.10 the crack growth rates of IN718 are related to cycle rates in various hydrogen environments, Ref. [48-18].



Conditions	Pressure (MPa)	Temperature
Helium	34.5	RT
Hydrogen	0.69 34.5 68.9	

Figure 48.7-9 - Superalloys: Crack growth rate of IN718 under various stress intensities and hydrogen environments



Conditions	
Stress Intensity	54.7 (MPa)
Hydrogen	68.9 (MPa)
Temperature	RT

Figure 48.7-10 - Superalloys: Crack growth rate of IN718 as a function of cyclic rates and hydrogen environments

48.8 Effect of oxygen

48.8.1 Material selection factors

Factors associated with material selection include:

- oxidation resistance,
- effect of oxygen diffusion into the material,
- ignition and burn resistance.

[See also: Chapter 85]

48.8.2 Oxidation

The prime concerns of oxidation are that it:

- reduces the component load-bearing cross sectional area, and
- introduces sources of stress concentrations, detrimental to fatigue resistance.

The mechanisms involved are:

- surface scaling
- internal oxidation
- oxide spalling
- oxide vaporisation

Oxidation resistance is largely dictated by:

- material composition, and
- the ability to form an adherent, stable, oxide layer throughout its range of operating temperatures and environments, e.g. oxidative, reducing.

48.8.3 Oxidation resistance

48.8.3.1 Conventional alloys

The oxidation resistance is provided by the Cr and Al present, plus Ta for Ni and Co-based alloys, at temperatures up to ~900°C, by the formation of a dense Cr_2O_3 layer.

At temperatures above 1000°C, the oxide morphology changes to the more volatile CrO_3 with an accompanying loss of protection, and also causing preferential oxidation at carbide lines.

For high temperatures, the formation of Al_2O_3 gives added resistance, but this has poor adherence unless Y, Hf or Zr is present in the base alloy composition, Ref. [48-9].

48.8.3.2 High temperature alloys

For those alloys particularly developed to enhance mechanical performance (creep resistance) at very high temperatures, i.e. to ~1200°C, the levels of Cr and Al present in compositions are generally too low to provide sufficient oxidation resistance alone. Under these conditions the use of a protective coating is advisable.

[See: 48.9; Chapter 74]

48.8.4 Ignition and burn

48.8.4.1 General

Under certain conditions of oxygen temperature and pressure, most materials if impacted or scuffed can ignite and sustain burning. This characteristic is most important in applications involving rotational machinery in warm gaseous O_2 environments, often at very high O_2 pressures, e.g. oxygen turbo-pumps.

48.8.4.2 Ignition hazards

Ignition hazards can be classified as, Ref. [48-20]:

- Mechanical rubbing (e.g. turbine tips, bearings), caused by:
  - Thermal expansion and creep
  - Engine start-up and shut-down transients
  - Tribology of different materials
- Debris impact of foreign materials

48.8.4.3 Material sensitivity

Nickel and copper offer the best impact and burn resistance, as shown in Table 48.8.1, which ranks materials on their calculated 'Burn Factor'. This ranking has been confirmed by experiment under high pressure oxygen, Ref. [48-20].

Table 48.8-1 - Ignition and burn characteristics of materials in oxygen environments

Material	Ranking ①
Zirconium Copper	Best
Nickel 200	↓
Silicon Carbide	
Monel 400	
K Monel 500	
Inconel 600	
316 Stainless Steel	
Invar 36	
Hastelloy X	Worst

Key: ① Calculated Burn Factor, B_F:
where:

$$B_F = \frac{H^0 f}{\alpha} = \frac{\text{heat of oxidation}}{\text{thermal diffusivity}}$$

48.9 Coatings and protection systems

48.9.1 Requirements

Often high mechanical performance cannot be achieved at high temperatures, because superalloys do not have sufficient levels of Al or Cr in their chemical compositions to form and maintain a stable oxide scale, [See: 48.8].

For applications such as first-stage blades and vanes in gas turbine engines, a coating is normally applied to improve their oxidation and corrosion resistance, Ref. [48-24].

The objective of such coatings is to provide a barrier between the environment and the component, in terms of:

- long-term stability with respect to the oxidation and corrosion environment, but also against inter-diffusion with the substrate alloy.
- resistance to thermal cycling and thermal shock.
- load-bearing capability.

[See also: Chapter 74]

48.9.2 Types of coatings

Numerous types of coatings have been developed to combat aggressive environments. The work continues as demands for improved engine efficiency through higher operating temperatures, and higher thrust are made. In general coatings can be described as either:

- Metallic: alloys capable of forming and maintaining stable oxide scales (usually Al_2O_3) under service conditions
- Ceramics: oxides or mixtures of stable oxides.

The methods of applying coatings also describe specific coating types and are grouped as either:

- Diffusion, where alloy surface compositions are enriched in Al, Cr or Si or where native oxides are 'manipulated' through thermodynamic principles to form more stable types; [See: 48.10].
- Overlay, where either a metallic or ceramic layer is deposited onto the component surfaces, [See: 48.11].

In regions where components experience high heat fluxes or intense gas wash, the application of a ceramic layer (having low thermal conductivity and high melting point) can prevent overheating and erosion. These are called ‘Thermal barrier coatings’ (TBCs), and are essentially thicker ceramic overlay coatings, [See: 48.12].

48.9.3 Coating systems

Various coating systems have been developed to combat oxidation and corrosion or high heat fluxes. Many are commercial products and have demonstrated their performance in aircraft engines.

48.9.4 Coated components

A coated component becomes a complex material system:

Coating + Interface + Substrate

It requires knowledge of mechanical performance and chemical effects (such as diffusion kinetics) when exposed to thermal cycling for extended periods.

If a component is to be coated, the design has to fully consider the effect the coating has on the substrate material properties; in both the long and short term, [See: 48.13].

48.9.5 Hydrogen fuel

For space engines using hydrogen fuel, it is generally perceived that coatings which prevent hydrogen transport into the material are of benefit in reducing (or avoiding) the effects of hydrogen embrittlement. Such coatings are either:

- Barrier, to prevent hydrogen transport, or
- Catalytic, to discourage dissociation and encourage association.

However, owing to the kinetics of hydrogen diffusion, both types of coatings need to be continuous at all times. With one imperfection, hydrogen can enter the material substrate and then is prevented from diffusing out by regions of intact coating. Consequently more damage can result by the use of a coating, especially as coating integrity is difficult to inspect, Ref. [48-17].

48.10 Diffusion coatings

48.10.1 Types of coatings

Some different types of diffusion coatings can be obtained by:

- Chromising
- Aluminising
- Platinum Aluminide
- Selective Oxidation
- Silicide
- Modified Native Oxides

Their selection depends on:

- substrate alloys, and
- service conditions

Table 48.10.1 summarises the various types of diffusion coatings along with their uses and limitations, Ref. [48-25], [48-26], [48-27]. All have been developed to enhance the oxidation and corrosion resistance of superalloys (notably Ni-based) for gas turbine applications.

Commercially available types are given in Table 48.10.2, Ref. [48-25].

Table 48.10-1 - Diffusion coatings for superalloys: Various types and use

Coating	Application	Benefits	Limitations	Comments
Chromising				
Diffusion of Cr into substrate forming chromium oxide on exposure.	Low alloy steels in industrial & marine gas turbines.	Resistance to low temperature sulphidation corrosion. Temperature range 973 to 1023K.	Chromia scales worse than alumina scales at >1123K in high velocity gas-streams.	Owing to volatility of chromium oxide.
Aluminising : Low and high activity pack				
Diffusion of Al into substrate forming NiAl coat (Ni-based substrate) or CoAl coat (Co-based substrate). Forming Al_2O_3 on exposure.	Ni-based & Co-based super-alloys in aero-engines (industrial/ marine gas turbines).	Inexpensive. Easy to apply and strip during overhaul. Proprietary coating media 'Packs' available. Ability to form & replenish Al203 scale.	Used where metal temperatures/environment not severe. Brittle. In exacting conditions, coating may crack due to rapid thermal cycling & allow substrate corrosion. Poor thermal fatigue.	Extensively used satisfying ~90% of applications. High Ductile→Brittle transition temperature. Coating thickness 50μm typ.
Platinum aluminide				
Diffusion as above of Pt into coating & substrate. Exact coat composition depends on proprietary process.	As above.	Proprietary coating media 'Packs' available. Extensive aero-engine service. Good high temperature hot corrosion (Type I) resistance.	Susceptible to low temperature hot corrosion. (Type II)	Platinum deposited prior to aluminising.
Selective oxidation				
Controlled oxidation of substrate to form more stable oxides.	Superalloys with sufficient levels of Cr & Al.	Controlled oxidation of substrate. No second phase added to surface.	Modest oxidation-corrosion resistance. Poor Adhesion. Seldom solely Al_2O_3 formed (due to substrate).	Not appropriate for high temperature applications (oxide stability).
Silicide				

Coating	Application	Benefits	Limitations	Comments
Diffusion of Si into substrate forming Al-Si, Ni-Cr-Si, Ni-Cr-Al-Si compounds forming SiO_2 on exposure. Amorphous SiO_2 layer (<10µ m).	Industrial & Marine Gas Turbine blades. Ni- & Co-based superalloys. Ni-based superalloy.	Resistant to vanadium-containing fuels. Decay to Al_2O_3 stable oxide.	Brittle. Low melting point. Low thermal shock resistance. Rapid diffusion between coat & substrate. Experimental study (in static air).	Not appropriate for high temperature applications. Need further study for in-service environment.
Modified native oxides				
See: Selective oxidation	-	-	-	-

Table 48.10-2 - Diffusion coatings: Commercially available types

Coating type	Designation	Supplier
Aluminide	Codep B	-
	RPS320	Rolls Royce plc
	PWA273	Pratt & Witney Aircraft Co
Platinum-Aluminide	LDC-2	Deutch Edelstahlwerke Akteingesellschaft
	RT22	Chromalloy †
	LDC-2E	Howmet Thermatech Div. †
	JML1	Johnson Matthey
Key: †	USA source.	

48.11 Overlay coatings

48.11.1 Development

48.11.1.1 General

Metallic coating systems were developed to improve oxidation and corrosion resistance of superalloys at high temperatures to generally overcome the brittleness of diffusion type coatings. Their development is strongly linked to methods enabling effective deposition of 'alloys'.

48.11.1.2 Metallic coatings

The metallic coatings are based on the MCrAlY formulation, where:

- M = Nickel and/or Cobalt and/or Fe†.
- Chromium: >20 wt% typ. for corrosion resistance.
- Aluminium: >6 wt% typ. high temp oxidation resistance.
- Yttrium: <1 wt% typ. to promote oxide adherence.

† Iron-based coatings are not appropriate for gas turbine use.

48.11.1.3 Coating formulation

The precise coating formulation can be adjusted with respect to:

- Substrate alloy composition.
- Operating thermal regimes.
- Operating corrosive species.

As a consequence, a wide variety of formulations have been developed and are commercially available, as shown in Table 48.11.1, Ref. [48-28].

Table 48.11-1 - Commercially available MCrAlY overlay coatings

Coating Composition (wt.%)	Designation	Company	Application Method
Co-18Cr-8Al-0.5Y	LCO29	Union Carbide	PS(argon)
Co-18Cr-11Al-O.3Y	ATD5	Airco Temescal	EB-PVD
Co-19Cr-10Al-0.5Y	LOC5	Union Carbide	PS(argon)
Co-23Cr-12Al-0.3Y	ATD2	Airco Temescal	EB-PVD
Co-23Cr-13Al-0.6Y	LCO7	Union Carbide	PS(argon)
Co-30Cr-5Al-0.5Y	ATD14	Airco Temescal	EB-PVD
Co-32Ni-21Cr-7.5Al-0.5Y	LCO22	Union Carbide	PS(argon)
Co-32Ni-21Cr-8Al-o.5Y	Amdry 995	Alloy Metal	LPPS
Co-23Ni-30Cr-3Al-0.5Y	LCO37	Union Carbide	PS(argon)
Co-10Ni-25Cr-7Al-0.6Y-5Ta	Amdry 996	Alloy Metals	LPPS
Ni-17Cr-6Al-0.5Y	Amdry 961	Alloy Metals	LPPS
Ni-22Cr-10Al-1.0Y	Amdry 962	Alloy Metals	LPPS
Ni-25Cr-12Al-0.3Y	ATD16	Airco Temescal	EB-PVD
Ni-25Cr-5Al-0.4Y	Amdry 963	Alloy Metals	LPPS
Ni-38Cr-11Al-0.3Y	ATD1	Airco Temescal	EB-PVD
Ni-22Co-18Cr-12Al-0.3Y	ATD7	Airco Temescal	EB-PVD
Ni-20Co-42Cr-5Al-0.3Y	ATD9	Airco Temescal	EB-PVD
Ni-22Co-21Cr-7.5Al-0.5Y	LN21	Union Carbide	PS(argon)
Ni-23Co-20Cr-8.5Al-0.6Y-4Ta	Amdry 997	Alloy Metals	LPPS
Ni-0.5Co-20Cr-11Al-0.5Y-0.5Mo	LN34	Union Carbide	PS(argon)
Fe-24Cr-8Al-0.4Y	Amdry 970	Alloy Metals	LPPS
Fe-24Cr-11Al-0.6Y	ATD8	Airco Temescal	EB-PVD

Key:	
	PS(argon) - Plasma Spray, under argon.
	EB-PVD - Electron Beam Physical Vapour Deposition.
	LPPS - Low Pressure Plasma Spray.

Later work has concentrated on additions of Tantalum and Hafnium to further enhance coating performance on superalloys; as shown in Table 48.11.2 along with coating recipe and substrate alloy.

Table 48.11-2 - Overlay coatings: Later studies with MCrAlY type coatings and superalloys substrates

Coating Composition (wt.%)	Substrate	Application Method	Comments
Ni-l7Cr-12Al-O.4Y	B1900 + Hf	PVD LPPS	Ref. [48-29]
Ni-23Co-18Cr-13Al-0.6Y	U700	-	-
CoCrAlY + 4.5 or 3Ta	IN 100 MAR M 002	LPPS PS	Ref. [48-30]
NiCoCrAlYTa	CMSX2	LPPS	Ref. [48-31]
NiCoCrAlTa	MA 6000	LPPS	Ref. [48-31]
Ni-23Co-20Cr-8.5Al-4Ta-0.6Y	CMSX2	LPPS	Ref. [48-32]
Co-10Ni-25Cr-7Al-5Ta-0.6Y	IN 100	LPPS	Ref. [48-32]
NiCrAlYTa	Hastelloy X	ED	Bond coat for TBC, Ref. [48-33]
NiCoCrAlYTa	CMSX2 Cotac 784	LPPS PS(Vac)	Ref. [48-34] Ref. [48-35]
NiCrAlY	IN713LC	PS(p.p)	Ref. [48-36]
NiCoCrAlYTa	X40	PS(p.p)	Ref. [48-36]
NiCoCrAlY (PWA276)	PWA 1480	LPPS	Pratt & Whitney Aircraft Co. designations
PWA286	Alloy 185	-	Ref. [48-37]
NiCrAlHf	Rene 80	Laser(RS)	Increased Hf content in solid solution. Ref. [48-38]

Key: PVD: Physical Vapour Deposition
LPPS: Low Pressure Plasma Spray
PS: Plasma Spray
ED: Electrophoretic Deposition
PS (vac): Plasma Spray, under vacuum
PS (p.p.): Plasma Spray, partial pressure
Laser (RS): Laser (Rapid Solidification)
TBC: Thermal Barrier Coating

48.12 Thermal barrier coatings (TBC)

48.12.1 Function

The objective of thermal barrier coatings (TBCs) is to provide protection to selected regions of components experiencing high heat fluxes or intense gas wash, such as:

- combustion chambers
- nozzle guide vanes
- rotor blades.

All-over-coatings are prone to cracking and spalling.

48.12.2 Coating construction

TBCs normally comprise of three layers, as shown in Figure 48.12.1.

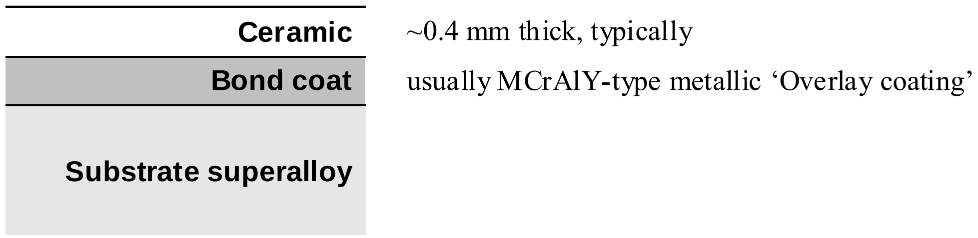


Figure 48.12-1 - Thermal barrier coating: Typical construction materials

Table 48.12.1 summarises the types of material systems, including their attributes and problems, Ref. [48-25], [48-39].

The development is on-going, so Table 48.12.2 presents a summary of later work which is aimed at optimising their performance.

Table 48.12-1 - Thermal barrier coatings: Material systems

Ceramic layer	Bondcoat layer
Zirconia, commonly with Magnesia and Yttria additions to partially stabilise, ①	To accommodate thermal strains between substrate and ceramic layer, ④
Zirconia has a high melting point and low thermal conductivity.	Act as mechanical key for ceramic layer, ②
Porous, hence permeable to oxygen and corrosive species, ⑤	Act as impermeable layer between porous ceramic and substrate.
As-deposited coatings have uneven stress state. Annealing heat treatment, ③	Oxidation corrosion of bond coat due to permeable ceramic layer.

Key:
① Fully-stabilised Zirconia has poor thermal shock performance.
② A very rough ceramic/bond coat interface may cause a higher stress state in the ceramic leading to premature failure by cracking adjacent to the interface.
③ Annealing may cause a slight increase in Thermal Conductivity, depending on ceramic composition.
④ Differences in CTE between the bond coat and ceramic tend to cause cracking adjacent to their interface.
⑤ Cracking allows accommodation of thermal fatigue stresses.

Table 48.12-2 - Thermal barrier coating technology: Later studies

Ceramic layer composition [Application method]	**Bond coat composition [Application method]**	**Substrate alloy**	**Comments**
$ZrO_2+8Y_2O_3$ [PS]	NiCrAlYTa [EP + Aluminising]	Hastalloy X	Bond coat is cellular. Improved thermal shock. Cells act as crack stoppers. Carbide layer at Bond Coat/ Substrate interface due to C-content of Hastelloy. Bond coat: 200µm. Ceramic: 300µm, Ref. [48-33].
ZrO_2+CaO, MgO,Y_2O_3 additions [PS]	NiCrAl [PS]	IN 100	Bond coat: 0.1mm. Ceramic: 0.4mm. ZrO2+7Y2O3 gave best thermal cycling resistance, Ref. [48-39].
$ZrO_2-6Y_2O_3$ [-]	NiCrAl [-]	Superalloy	Finite Element Modelling of coating mechanical performance. Stress State Model, Ref. [48-40].
$ZrO_2-6Y_2O_3$ [PS]	NiCrAlYb	MAR M 200+Hf	Effect of Yb additions on diffusion mechanisms on bond coat. Morphology of oxide(s) on bond coat. Thermal cycling resistance, Ref. [48-41].
	CoCrAlYb CoCrAlY	MAR M 509	
	FeCrAlYb FeCrAlY [PS]	Fe-22Cr-5.8Al-0.5Co	
Key: PS - Plasma spraying; EP - Electrophoretic deposition			

48.13 Coating influence on design

48.13.1 Factors

48.13.1.1 General

In recommending the use of a coating, there are a significant number of factors to be evaluated with respect to the particular material system, i.e. coating(s) and substrate alloy, for a given service environment.

Many coating-substrate alloy systems have been the subject of intense metallurgical examination. Although fundamental to the understanding of how various systems interact, detailed information is not given here.

48.13.1.2 Technical

Table 48.13.1 summarises the factors associated for coating systems offering oxidation and corrosion resistance, Ref. [48-34].

Table 48.13.2 compares technical aspects of diffusion and overlay coatings.

Table 48.13-1 - Coating design: Factors associated with coating systems for oxidation and corrosion resistance

Coating property	Requirements	Location		
		Coating surface	Coating bulk	C:S Interface
Oxidation/ Corrosion resistance	Operating environment is known:			
	- temperature(s)	X	X	X
	- corrosive species	X		
	- erosive species	X	X	
	- design life	X	X	X
	Low rates of scale formation	X		
	Uniform surface attack	X		
	Stable surface oxide (thermodynamically)	X		
	Ductile surface scales	X		
	Adherent surface scales	X		
	High concentration of scale forming elements in coating (self-repairing)	X	X	
Interface stability	Low rate of diffusion across interface at service temperatures			X
	Limited compositional changes across interface			X
	Avoidance of brittle phase formation in service			X
Good adhesion	Matched coating to substrate properties to reduce stresses at interface			X
	Optimised surface condition prior to coating			X
	Minimise stress during coating process			X
Mechanical strength	Coatings should withstand service loading: - creep - fatigue - impact - thermally induced		X	X
	Well matched coefficient of thermal expansion		X	X
	Coating does not adversely affect component performance	X	X	X
	Coating heat treatments does not affect component heat-treatments	X	X	X
Key:	C - Coating; S - Substrate.			

Table 48.13-2 - Coating design: Comparison of technical factors for diffusion and overlay coatings

Diffusion coatings	Overlay coatings (MCrAlY Types)
Environmental resistance	
Chromising: Forming Cr oxide surface. Corrosion resistance to sulphates at temperatures <1123K (high velocity gas streams).	Contain ~7wt% Al to form Al_2O_3. Increase Cr content to combat hot corrosion (sulphate contamination).
Aluminising: Formation of NiAl or CoAl in Ni-base & Co-base superalloy respectively. Forming Al_2O_3 surface scales. Temperatures <1100°C; not too corrosive. Prone to thermal fatigue cracking.	Too high Cr or Si content (used to combat Type II hot corrosion) may affect diffusional stability of C:S interface at high temperatures. Cr oxide provides oxidation resistance up to ~900°C. Al oxide provides oxidation resistance up to ~1200°C. Al oxide-scales are not adherent when thermally cycled. ∴ add Y.
Modified aluminides: >1100°C. Improved thermal fatigue.	Presence of Cr to combat acid or basic fluxing mechanisms (Type I & Type II hot corrosion).
Chemical compatibility (Interface stability / Adhesion)	
Interdiffusion across interface Al→ Substrate; Ni→ Coating, depending on alloy composition.	Interdiffusion effects between coating/ substrate lowers oxidation resistance of coating, notably Ti.
	Diffusionally stable systems are: NiCrAlY on Ni-base or Fe-base substrates, CoCrAY on Fe-base.
	Unstable systems are: CoCrAlY on Ni-base, FeCrAlY on Ni-base or Fe-base.
Mechanical strength	
Aluminide CTE < substrate at high temps Ductile → Brittle transition temperature > 600°C typical.	Carbide interface forming for MCrAlY on Co-base (less for CoCrAlY) (preferential oxidation path &/or spalling of coating).
Complex structure, difficult to determine intrinsic properties.	CTE difference should not exceed 2 x 10^{-4} /K.
	Ductile→Brittle transition temp increases with increasing Al content (100 to 600°C).
	Some compositions exhibit superplasticity.

48.13.1.3 Economic

In addition to technical factors, the economic factors to be considered include:

- availability and cost of coating materials.
- availability and cost of coating equipment, including temperature-time (energy) demands per batch size.
- subsequent heat treatments:
  - densification of coating,
  - recovery of substrate alloy mechanical properties.

48.13.2 Effect of coatings on mechanical properties

The combination of a coating and a substrate alloy becomes a complex material with each part optimised for a particular function:

- Coating: environmental resistance,
- Interface: maintain coating adherence and minimise inter-diffusion effects,
- Substrate: high temperature mechanical performance.

Consequently each part possesses different:

- chemical compositions,
- metallurgical structures,
- bulk properties, such as:
  - stiffness
  - strength
  - creep resistance
  - fatigue resistance
  - thermal properties, e.g. CTE, thermal conductivity.

The mismatch in properties causes coating-substrate interactions which can influence the overall properties of the component. Operation at high temperatures causes compositional changes (diffusion) which in turn causes the initial properties to change throughout the service life. Coatings and substrate alloys should be evaluated together, not as independent quantities.

The overall mechanical performance of the coated material system is affected by:

- environmental conditions experienced (during testing or in service) and,
- coating application method.

48.13.3 Chemical interaction

48.13.3.1 Oxidation

Oxidation reduces the Al content of coatings due to the formation of Al_2O_3 surface scales. This can increase the ductility of the coating with increasing time in-service.

48.13.3.2 Diffusion

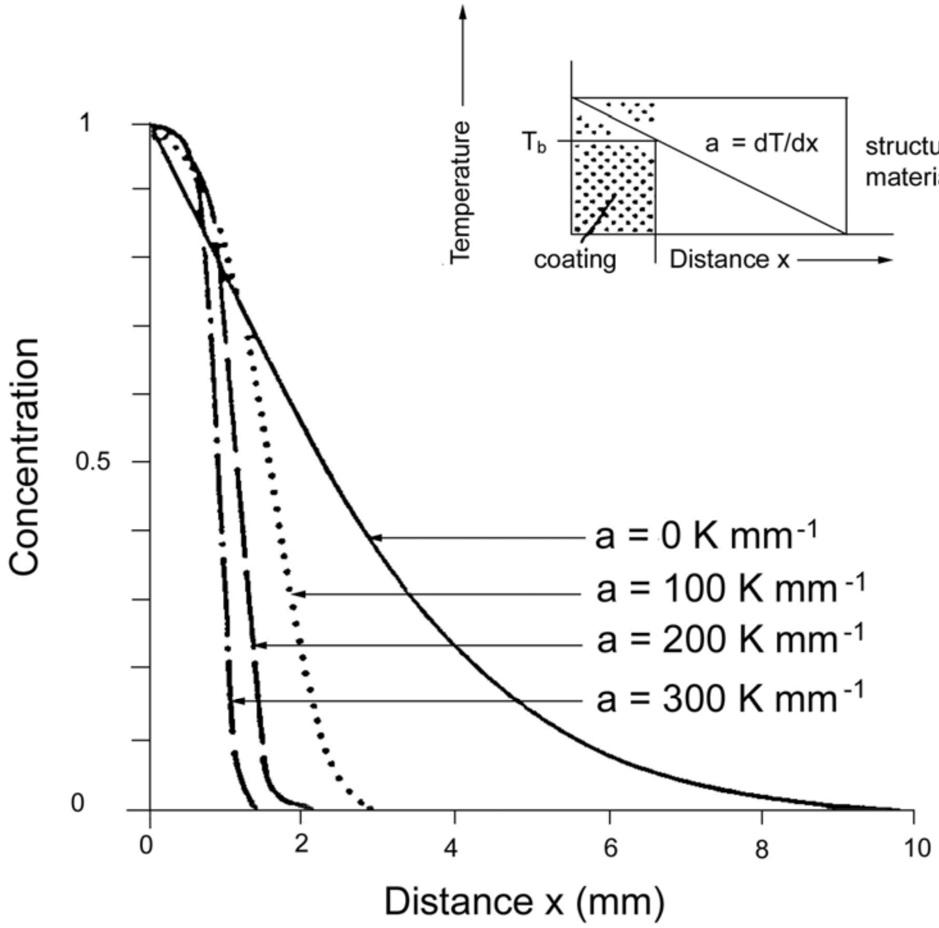
Higher chromium and aluminium contents (in hot corrosion resistant coatings) than the substrate alloy results in increasing Al and Cr in the inter-diffusion zone, causing the formation of brittle phases. Diffusion can also lead to Kirkendall voids, giving porosity near the coating-to-substrate interface. These pores can act as crack initiation sites and give rise to debonding of the coating.

In uncooled components, the inter-diffusion zone can be small compared with the overall material thickness. Increasing temperature increases the inter-diffusion zone.

In a cooled component, the thin walls of substrate alloy can become the entire inter-diffusion zone, i.e. the whole material composition is changed, hence mechanical properties are altered.

Temperature gradients reduce diffusion penetration depths. This effect is summarised in Figure 48.13.1, Ref. [48-44].

At grain boundaries diffusion of coating elements can be significantly enhanced; penetration is greater than expected from bulk diffusion calculations.



Diffusion of Al in a Ni-based alloy.
Surface temperature: 1400K
$D_0 = 1.0$ cm^2/s
Diffusion time: 30 000 hours
$E = 250$ kJ/mol

Figure 48.13-1 - Coating design: Effect of temperature gradients on diffusion

48.13.4 Residual strains

48.13.4.1 Property mismatch

Mismatch of physical or mechanical properties between coating and substrate causes residual or additional strains which promote premature cracking and spalling of the coating; causing a loss of protection.

Coating cracks also act as initiation and propagation sites for substrate cracks during fatigue or creep loading. The relevant properties are, Ref. [48-44]:

- Modulus (*E*)
- Coefficient of thermal expansion (CTE)
- Thermal conductivity
- Yield stress
- Fracture strain and toughness
- Creep and relaxation behaviour.

The initial stress state can be approximated by *E* and CTE differences in coating and substrate during processing, based on the processing temperature. A hypothetical temperature can be determined for a stress-free state.

It is assumed that:

Diffusion or **Annealing** Heat Treatment Temperature	<	**Deposition** Temperature	<	**Service** Temperature

Residual strains and stresses can be calculated by:

$$E_{rc}\Delta\alpha\Delta T \qquad [48.13\text{-}1]$$

$$\sigma_{rc}\ \frac{E_c\Delta X\Delta T}{1-\nu} \qquad [48.13\text{-}2]$$

48.13.4.2 Thermal expansion

Residual strain is at a maximum near the coating-substrate interface. If differences in CTE are too large, coatings can crack during cooling after deposition. These effects can be reduced by minimising CTE differences to ~2 x 10^{-6}/K.

Where CTE (coat) < CTE(substrate), such as TBC ceramics, the coating has residual compressive stresses and strains.

Partially stabilising ZrO_2 (using MgO, CaO, Y_2O_3) reduces:

- volumetric phase transformations, and
- minimises residual stresses.

The processing temperature is chosen to be as low as possible.

Internal stresses can reach from 200MPa to 450MPa owing to CTE mismatch, causing de-bonding of coatings which in turn are local hot-spots.

48.13.4.3 Processing

Non-isothermal (spray) processes increase residual stresses by:

- Contraction of droplets on surfaces
- Phase transformations

To counteract these effects, adjust the coating cooling processes or preheat the substrate.

The modulus can be anisotropic due to process parameters. For brittle coatings, ductility is dependent on coating thickness.

Compressive stresses can be generated as a result of lateral growth of the coating.

48.13.4.4 Ductile → Brittle transition temperature

The strains need considering with respect to the ductile → brittle transition temperatures (DBTT) of coatings. If a coating experiences too higher strain whilst it is brittle, cracks result whereas strains can be accommodated without fracture when coatings are above their DBTT.

48.13.5 Tensile behaviour

48.13.5.1 General

Coated components can be treated like composite materials; using the ‘Rule of Mixtures’, an approximation of modulus and strength of the material system (coat and substrate) can be made. Because coating thicknesses are usually small compared with that of the substrate, e.g. 0.1 to 0.3mm coating compared with 1 to 5mm blade; the coatings do not have much influence, other than reducing the overall cross-sectional area of the substrate alloy, Ref. [48-44].

Load is transferred from the substrate alloy to the coating by shear stresses at the interface:

- Shear stress exceeds bond strength: The coating detaches.
- Bond strength exceeds shear stress: The coating follows the extension of the substrate alloy until:
  - High *E*, brittle coating: Cracking occurs before the UTS of the substrate.
  - Low *E*, ductile coating: deforms up to UTS of the substrate.

48.13.5.2 Residual stress

Residual stresses or strains affect this behaviour and are added (if tensile) or subtracted (if compressive). Tension results in premature crack formation, the converse is true for compression.

Table 48.13.3 provides typical tensile properties of coated CMSX-2 (SC) and Cotac 784 (DS) alloys, Ref. [48-34].

Table 48.13-3 - Coating design: Tensile properties of coated material systems

Materials system		**Thermal history (2)**	**Test temp. (°C)**	**Mechanical properties**			**Comments**
Coating [Thickness, μm]	**Substrate (1)**			**UTS (MPa)**	**YS (MPa)**	**Elong (%)**	
None [-]	CMSX-2 (SC)	ST:1315°C/30 Mins/ACA:1050°C/ 16h/AC+ 850°C/24h/AC	RT 850 1050	1157 1019 483	1021 860 415	13 - -	-
Aluminide (High Activity) [75μm]	CMSX-2 (SC)	ST + A. Coat: 700°C/7h/?+ diffusion HT (as for alloy)	RT 850 1050	1049 1044 492	1043 953 417	0.8 25 30	-
Ni-23Co-20Cr-8.5Al-4Ta-0.6Y (3) [100μm]	CMSX-2 (SC)	ST + A Coat: PS(vacuum)+ diffusion HT (1st alloy ageing treatment)	RT 850 1050	1071 1068 474	1061 967 396	13 26 29	RT: Coat fractured at 0.5% ε and failed at c:s interface. At high temps., no cracks seen prior to rupture of test piece.
[None]	Cotac 784 (DS)	ST:1250°C/90 min→ 1180°C/AC A:1050°C/16hr/AC+ 850°C/24h/AC	900 1100	844 366	707 342	8.7 7.7	-
Ni-23Co-20Cr-8.5Al-4Ta-0.6Y [100μm]	Cotac 784 (DS)	ST + A Coat: PS(vacuum)+ diffusion HT (lst alloy ageing treatment)	RT 900 1100	1228 823 344	786 690 324	9.8 9 10	RT: Coat fractured at 0.5% ε and failed at c:s interface. At high temps., no crack seen prior to rupture of test piece.

Key: (1) SC: Single crystal; DS Directionally solidified. [001] direction.
(2) ST: Solution treatment; A: Ageing; AC: Air cool; PS(vacuum): Plasma spray under vacuum.
(3) Coating composition + application method produces superplasticity >800°C.

48.13.6 Fatigue resistance

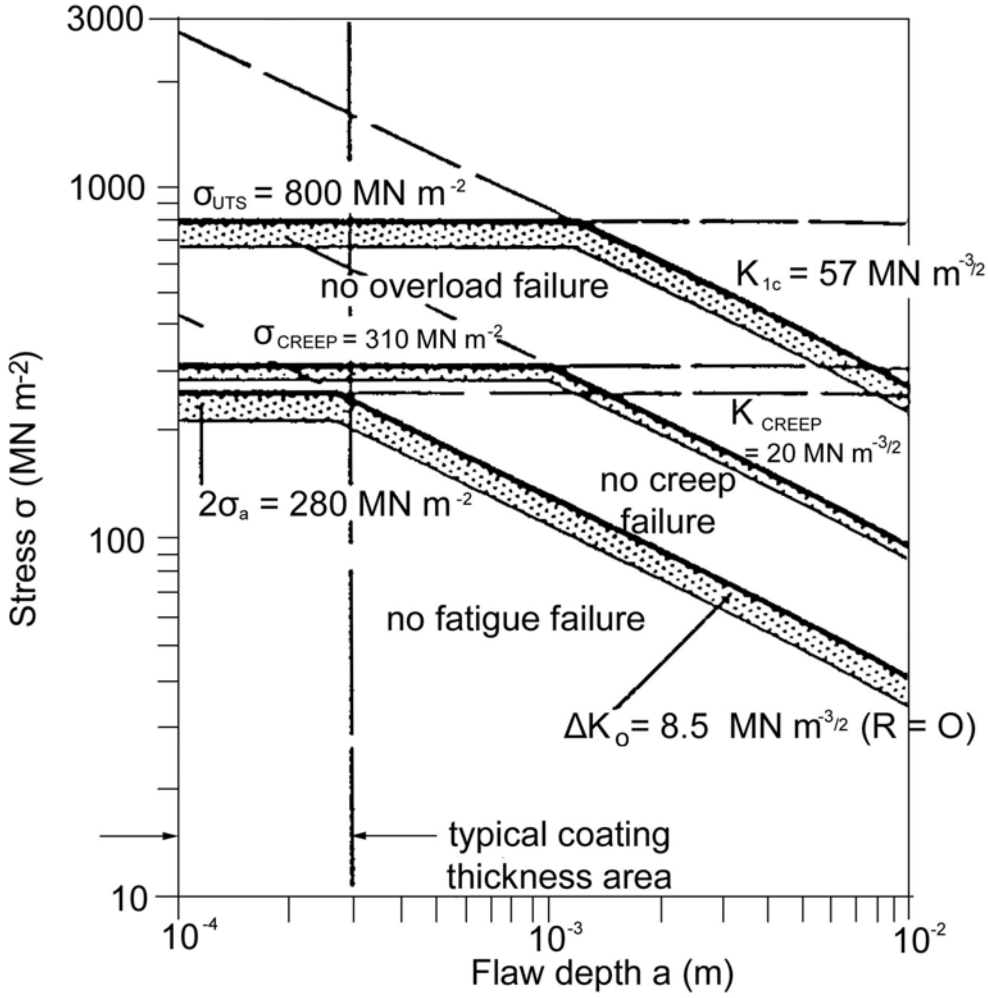
48.13.6.1 General

For cracked coatings, fracture mechanics determine whether the crack depth is significant to stimulate brittle fracture or sub-critical crack growth due to fatigue or creep conditions, as shown by:

$$K_1 > K_{1c} \quad \text{instability}$$

$$K_1 > \Delta K_{1.th} \quad \text{fatigue}$$

Given certain conditions, the reaction of a substrate alloy to crack depth (coating thickness) can be determined from failure diagrams; an example is shown in Figure 48.13.2, Ref. [48-44].



Boundary conditions: 850°C for ~200hr and RT.

Figure 48.13-2 - Coating design: Example of failure diagram for IN-738LC

Table 48.13.4 shows typical fatigue properties of coated Rene 80 and CMSX-2 (SC) alloys, Ref. [48-35], [48-45].

Table 48.13-4 - Coating design: Fatigue properties of coated material systems

Material system		**Thermal history**	**Test temp. (°C)**	**Fatigue life, *Nf* (x10^3 cycles)**	**Comments**
Coating	**Substrate**				
Codep B (Low activity aluminide)	Rene 80	ST + A: not stated Coat: 1068°C/6h/?	900	286 ± 103	Fatigue Test: 90 Hz; R = 0.1 Coating HT changes micro-structure of substrate alloy; crack initiates in coating, change in c.s.a.
-	Rene 80	ST + A: not stated 1068°C/6h/? (simulated coat H.T.)	900	764 ± 261	-
Aluminide (high activity) [75µm]	CMSX-2 (SC)	ST:1315°C/30 mins/AC A:1050°C/16hr/AC + 850°/24 hr/AC Coat: 700°C/7 hr/?	870	Significantly lowers HCF resistance. At 107 cycles stress reduced by 100 MPa. Similar effect as for aluminide/CMSX-2 combination.	Fatigue Test: 70 Hz; Load ratio R = 0.95
Ni-23Co-20Cr-8.5Al-4Ta-0.6Y [100µm]	CMSX-2 (SC)	ST + A as above Coat: PS (vacuum) + diffusion (1st alloy ageing temp)	870	Cracks initiate at coating-to-substrate interface. Cracks also observed on surface of coating. Change in mechanism from uncoated, where cracks initiate from internal micropores of alloy.	-

Key: HT: Heat treatment; c.s.a: Cross sectional area; ST: Solution treatment; A: Aged; SC: Single crystal; PS(Vacuum): Plasma spray in vacuum.

48.13.6.2 High cycle fatigue

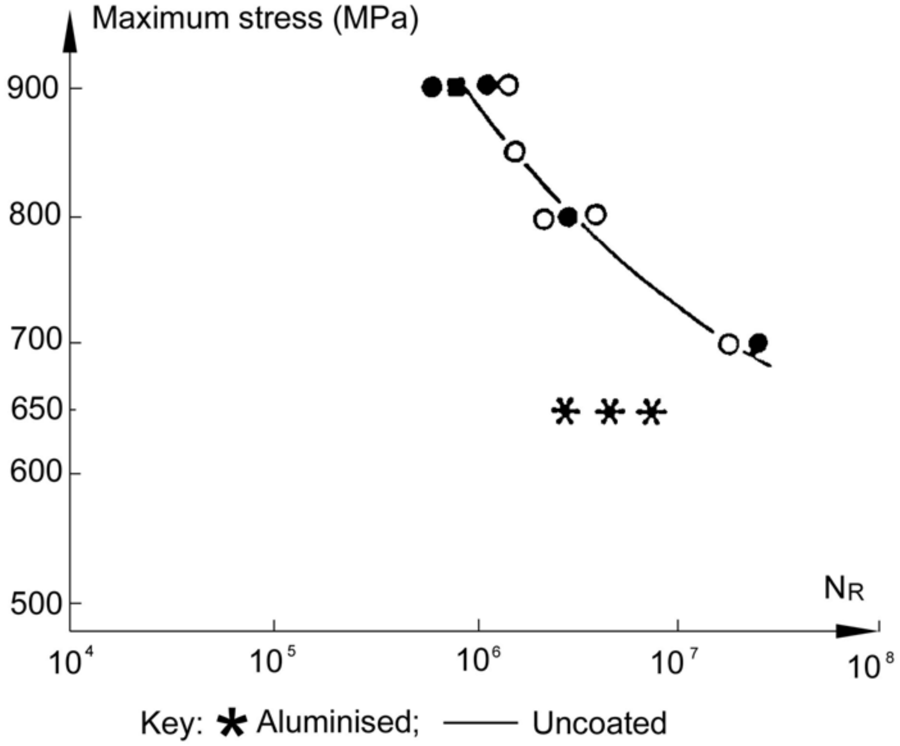
HCF behaviour is strongly influenced by crack initiation conditions. Factors include, Ref. [48-44]:

- Fatigue limit of coating,
- Modulus,
- Particle size within coating,
- Coating residual stress/strains,
- Surface roughness.

Fatigue initiation sites include:

- Cracks,
- Internal pores in substrate (notably cast alloys),
- Interface defects (porosity, brittle precipitates).

Figure 48.13.3 shows the effect of HCF on Coated CMSX-2 alloy, Ref. [48-34].



Temperature: 870°C.

Figure 48.13-3 - Coating design: High cycle fatigue characteristics of coated CMSX-2

48.13.6.3 Low cycle fatigue

LCF behaviour is largely unaffected by coatings, and tends to be similar to the thermal fatigue response.

48.13.6.4 Thermal fatigue

Thermal fatigue performance is largely dependent upon:

- Coating thickness
- Ductile → Brittle transition temperature
- CTE mismatch

Coatings with optimum thickness and CTE mismatch above the DBTT do not significantly influence thermal fatigue characteristics.

48.13.7 Creep and relaxation

Creep behaviour of a coated system is compared with that of the substrate alloy and separate coating material in Figure 48.13.4 and Figure 48.13.5, Ref. [48-44].

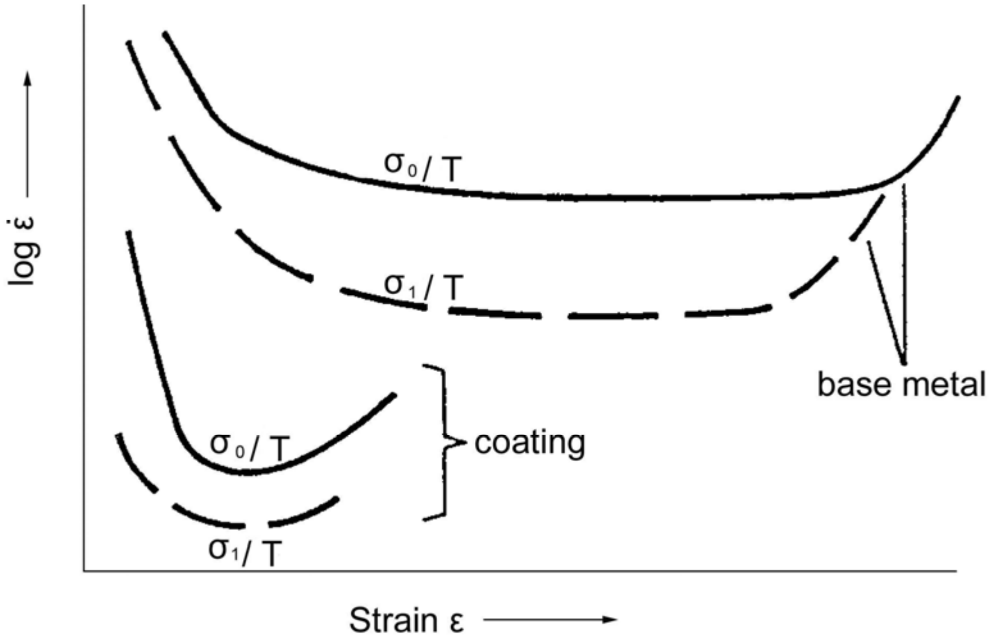


Figure 48.13-4 - Coating design: Schematic creep curves for substrate metal and coating

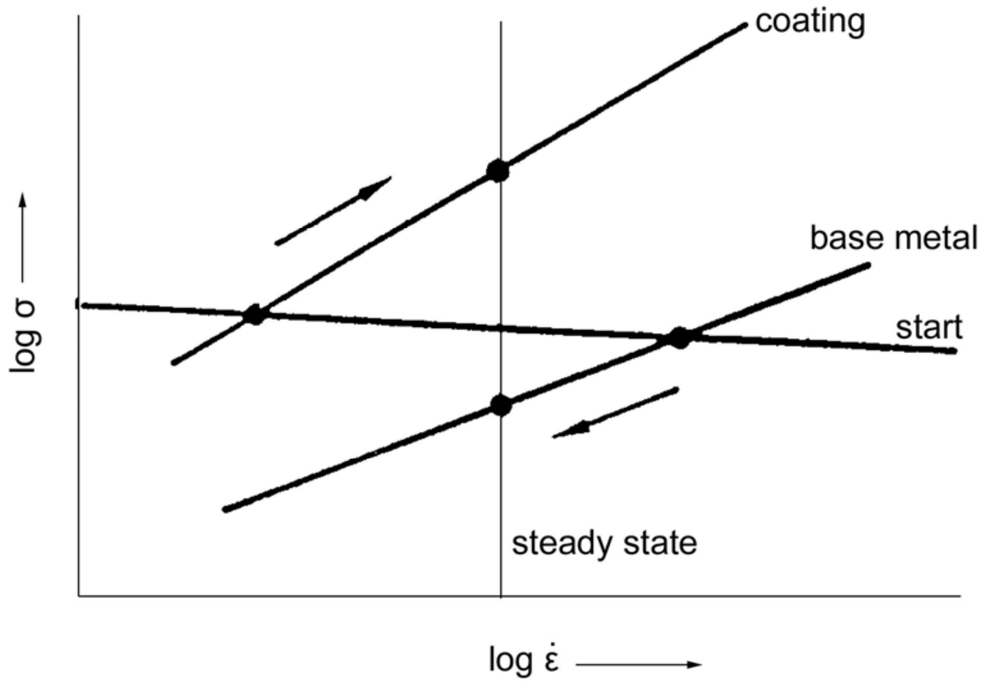


Figure 48.13-5 - Coating design: Schematic creep curves for coated system

Coatings with high DBTT are more creep resistant with lower creep ductility. However, when steady-state creep conditions are achieved (after initial load at temperature) the more creep-resistant part is forced to creep faster than normal, provoking a higher damage rate.

Coatings with fine-grained structures are often less creep-resistant than the substrate alloy. Hence the alloy creep behaviour predominates. Failure is dictated by the creep ductility of each part of the material system.

In practice, creep behaviour is sensitive to:

- coating process,
- heat treatment due to coating process,
- residual stresses,
- crack initiation (surface of coat-substrate interface),
- diffusion of coat into substrate especially at grain boundaries,
- reducing effective cross-sectional area of substrate.
- different creep behaviours of substrate and coat, especially at low strains.

Creep rupture characteristics for CMSX-2 alloys with various coatings are shown in Figure 48.13.6, Ref. [48-34].

The effect of coatings on Cotac 784 alloy is shown in Figure 48.13.7, Ref. [48-34].

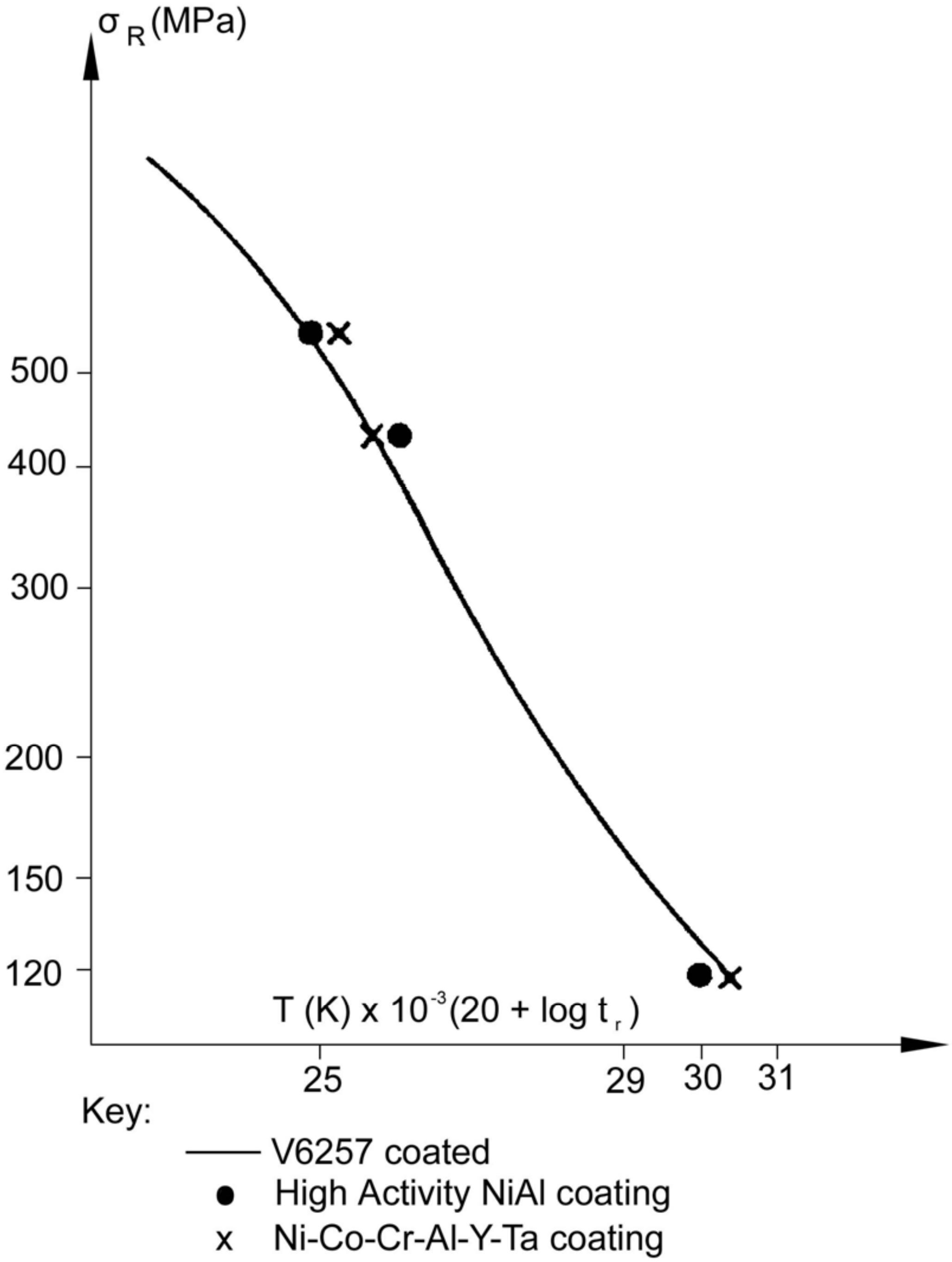


Figure 48.13-6 - Coating design: Effect of coatings on stress rupture properties of CSMX-2 alloy

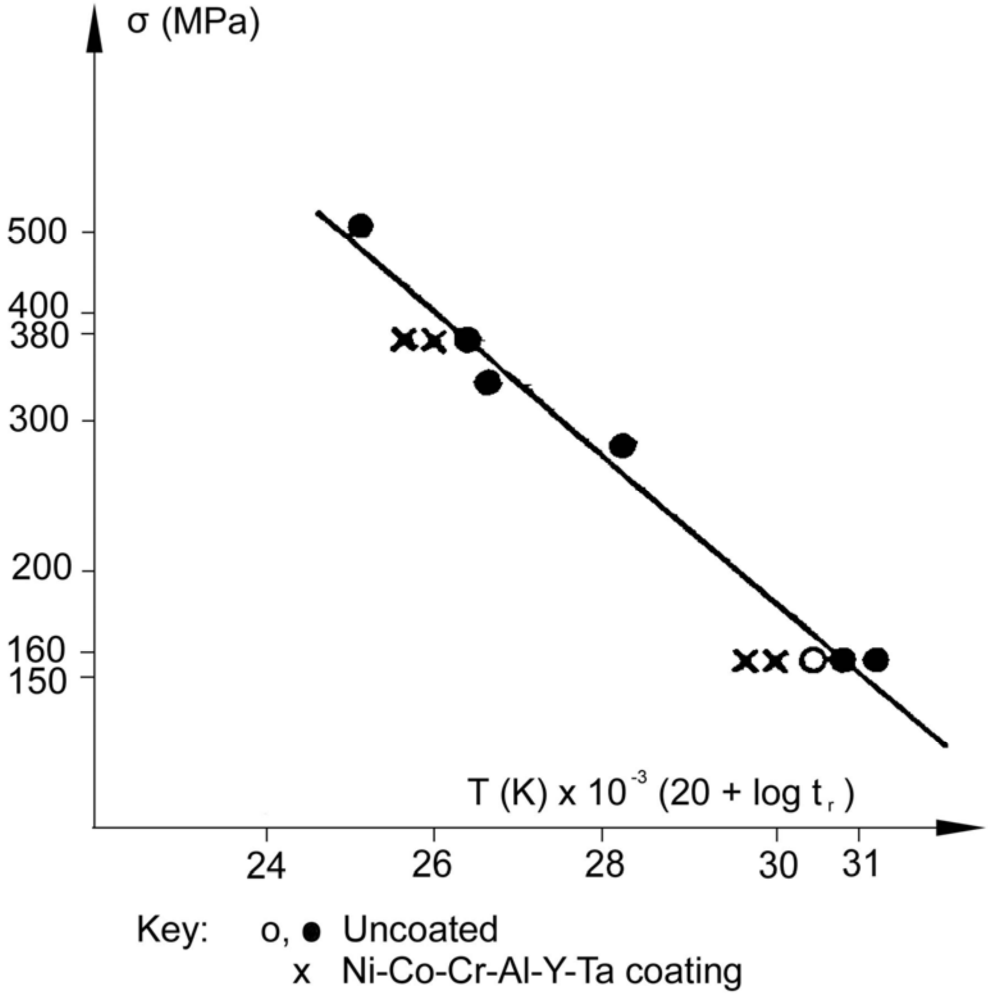


Figure 48.13-7 - Coating design: Effect of plasma sprayed coating on stress rupture properties of Cotac 784 alloy

Table 48.13.5 shows typical creep properties of Rene 80, CMSX-2 (SC) and Cotac 784 (DS) alloys, Ref. [48-35], [48-45].

Table 48.13-5 - Coating design: Creep properties of coated material systems

Material system		Thermal history	Test temp. (°C)	Creep rupture life	Min creep rate, (h^{-1})
Coating	Substrate				
Codep (low activity aluminide)	Rene 80 ①	ST+A: not stated Coat: 1068°C/6hr	900	38.6 ± 6.5	99 ± 14
None	Rene 80	ST+A: not stated + 1068°C/6hr (simulated coating HT)	900	43.2 ± 4.5	119 ± 43
Ni-23Co-20Cr-8.5Al-4Ta + 0.6Y [100μm]	CMSX-2 (SC)	ST:1315°C/30 mins/ AC A:1050°C/16hr/AC + 850°C/24hr/AC + Coat:PS (vacuum) + Diffusion (Ist alloy ageing temperature)	850 1050	Negligible effect on rupture stress. Creep deformation is dictated by the alloy metallurgical structure. Coating procedures matched to alloy heat treatment. Limited interdiffusion between coat & substrate.	
Ni-23Co-20Cr-8.5Al-4Ta + 0.6Y [100μm]	Cotac 784 (DS)	ST: 1250°C/90 mins→ 1180°C/AC A: 1050°C/16hrs/AC + 850°C/24 hr/AC Coat: PS (Vacuum) + Diffusion (as for alloy)	900 1100	Coating lowers creep strength. Life reduced by 20 to 30% at 900°C & 50% at 1100°C. Large deformations. Interdiffusion disrupted the metallurgical structure responsible for inferring creep resistance to the alloy.	

Key: ① Coating: heat treatment changes microstructure of alloy: change in c.s.a; cracks initiate in coating.

HT: Heat treatment; SC: Single crystal; A: Aged; ST: Solution treatment; c.s.a: Cross sectional area; PS(Vacuum): Plasma spray in vacuum

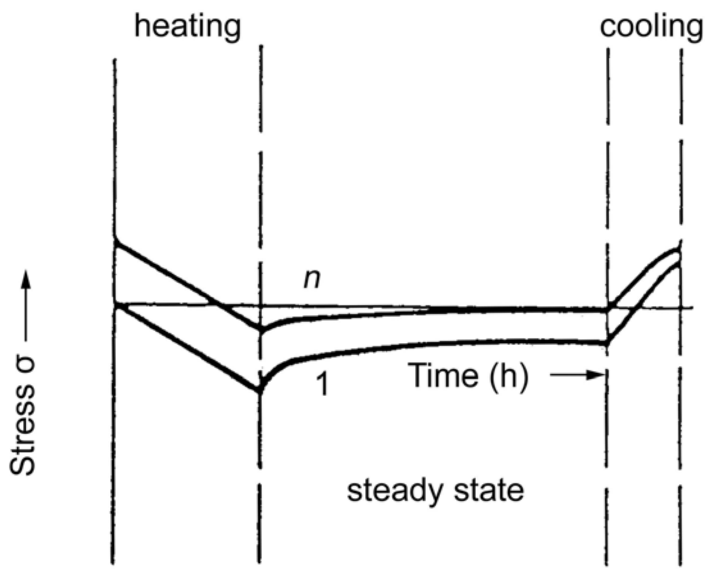
48.13.8 Creep fatigue

For a temperature gradient, cyclic temperature changes and loading all act together and each cycle requires analysis; as the fatigue cycle dictates the load on the next creep period, and vice versa.

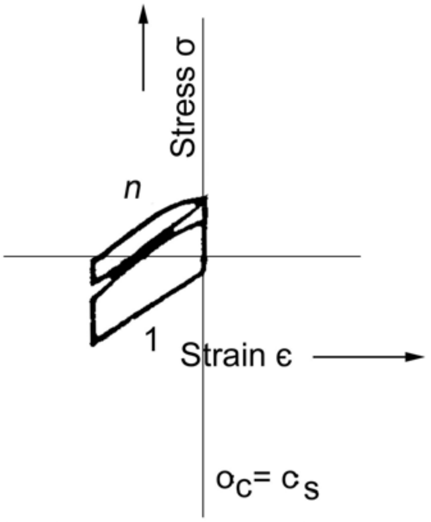
Figure 48.13.8 shows a typical stress-time response for a cooled gas turbine blade, Ref. [48-44].

Factors influencing creep fatigue include:

- Coating application method,
- Thermal history, i.e. heat treatments,
- Test method,
- Environment, and
- Temperature(s).



A. Stress-time Response of the Surface of a Cooled Turbine Blade



B. Stress-strain for Sequential Heat Cycles, 1: first cycle, *n*: nth cycle

Figure 48.13-8 - Coating design: Typical creep fatigue effects for cooled gas turbine blades

48.14 Coatings: Future developments

48.14.1 Materials

The work is likely to concentrate on optimising:

- coating systems for single crystal (SC), directionally solidified (DS) and other high performance alloys,
- bond coat formulations for TBC systems (both for ceramic and substrate),
- ceramic layer compositions with respect to bond coat.

The modification of substrate alloys is not viewed as an available option. Changes in alloy compositions result in changed properties and processing parameters.

48.14.2 Service temperature

All the factors require optimisation for every increase in operating temperature; which imposes more severe thermal cycling, and thermo-mechanical strain regimes for increasing service times.

48.14.3 Hydrogen environments

Hydrogen fuel environments impose higher thermal transients and heat flux effects than those of carbon-based fuels. The intention to use hydrogen in active cooling systems of 'Thermal Management Systems' in Single-Stage-to-Orbit (SSTO) vehicles leads to the development of coatings to combat the known detrimental effects of hydrogen on materials, [See: 48.7]. Two philosophies exist to combat this problem:

- Design components on the basis of known and proven material performance data in hydrogen environments.
- Develop protective coatings.

With regard to coating development, Ref. [48-17]:

- Barrier coatings are deemed unreliable as their benefit is negated by the smallest defect which enables hydrogen to enter the material and then traps it beneath the regions of intact coating.
- Catalytic coatings could prove more effective provided that their compositions are optimised to be lightweight, effective, easy to apply and can be guaranteed to give complete coverage.

48.15 Superalloys: Potential applications

48.15.1 Conventional alloys

48.15.1.1 Resumé

The main features of conventional superalloys can be summarised as:

- Superalloys are used for high-temperature applications usually in the range 700°C to 1200°C.
- For space use, their high density is a significant drawback.
- The huge pool of knowledge relating to gas-turbine engine and their use in other high-temperature, aggressive industrial environments, means that superalloys can be used in the foreseeable future for:
    - Engines: PM alloys are used by European and US manufacturers, e.g. 1.4kg cooling plates; 640kg compressor disk, Ref. [48-48].
    - Propulsion units.
    - Thermal protection systems for spacecraft.

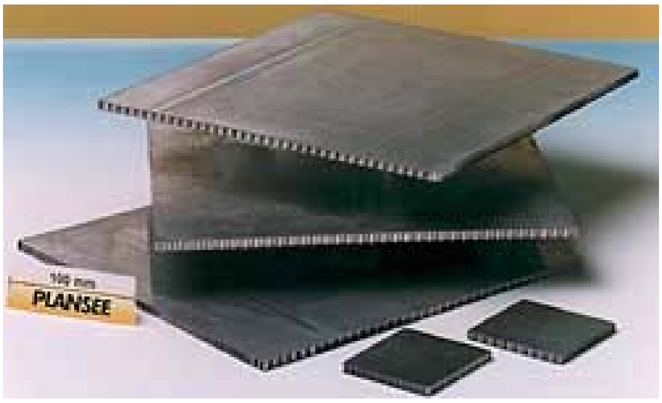
- Proven materials, e.g: superalloys, have considerable attractions over newer systems, such as ceramic matrix composites.
- Other materials, when proven, are likely to erode their use rather than superalloy consumption increasing, e.g. titanium aluminides in engine components. [See: Chapter 49].

48.15.1.2 Applications

Other than within engines and power plants, reusable spaceplane concepts have provided the impetus for further superalloy developments. Honeycomb panels for the external hot structures of the Venture Star spaceplane have been produced from foils of PM 1000 (Ni-based ODS) with PM 2000 (Fe-based ODS) superalloy, Ref. [48-46]. The characteristics of these materials which make them suitable for this applications include, Ref. [48-46]:

- Ni-based PM 1000:
  - excellent creep strength at high temperatures,
  - hot gas corrosion resistant up to 1100°C,
  - superior low cycle fatigue properties up to 1300°C,
  - optimised emissivity properties for space applications up to 1300°C.
- Fe-based PM 2000:
  - extraordinary creep resistance up to 1300°C,
  - high hot strength,
  - excellent oxidation resistance,
  - high stability against high-speed gas flows at temperatures up to 1100°C.

The honeycomb panels, shown in Figure 48.15.1, are assembled by brazing, Ref. [48-46].



Brazed PM 1000 (Ni-based) / PM 2000 (Fe-based) honeycomb panels

Figure 48.15-1 - Superalloys: Space applications – Hot structure

The advantages provided by these metallic external panels on spaceplanes include, Ref. [48-46]:

- cost-efficient maintenance,
- easy ‘operability’,
- self-healing oxide layer with high emmissivity.

48.16 References

48.16.1 General

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48.16.2 ECSS documents

[See: ECSS website]

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49 Intermetallic materials

49.1 Introduction

49.1.1 Types of intermetallic compounds

An intermetallic compound is a chemical compound having a fixed (stoichiometric) composition. In alloys, intermetallic compounds form from the alloy constituents in the solid solution. They are often used as strengthening mechanisms.

Interest has focused on certain of the aluminium-containing compounds [See: 49.2], including:

- Nickel , [See: 49.3].
- Titanium, [See: 49.5].
- Iron-based, [See: 49.7].

All these are widely publicised as Aluminides. Aluminide is a general term. Each of the compounds has certain characteristics which can be viewed as either advantages or disadvantages depending on the intended application.

49.2 Aluminide development

49.2.1 Features

Table 49.02.1 summarises features of various aluminides, Ref. [49-3]. Their high aluminium content means that, in general, aluminides offer good high-temperature oxidation resistance.

Table 49.2-1 - Intermetallic compounds: Comparison of aluminide groups

Type	Chemical compound	Melting point (°C)	Density (kg/m^3)
Titanium Aluminide [See: 49.5]	Ti_3Al TiAl	1600 1460	4200 3900
Nickel Aluminide [See: 49.3]	Ni_3Al NiAl	1390 1640	7500 5900
Iron Aluminide [See: 49.7]	Fe_3Al FeAl	1540 1330	6700 5600

Effort has been put into developing the aluminide intermetallic compounds as they offer certain inherent strength and stiffness benefits as a result of their:

- crystallography, combined with
- lower densities than the superalloy family, but
- similar melting points.

There are two significant deficiencies which halted initial studies into these materials:

- Brittleness at ambient temperatures.
- Lack of adequate creep resistance at high temperatures.

Renewed interest resulted from improvements in ductility and creep resistance (achieved by 'doping' or 'micro-alloying'), and advances in analytical and materials processing techniques.

49.2.2 Applications

49.2.2.1 Aeroengines

The aim of developing the aluminide materials is to, Ref. [49-1], [49-20], [49-22]:

- replace certain aero-engine parts to enable operation at higher gas or component temperatures to improve their efficiency and save fuel.
- decrease engine weight and operating stresses, primarily for rotating or moving parts, to improve service life of discs, shafts and associated bearing mechanisms.

Demonstrator parts for certain engine components (blades and compressor rotors) have been fabricated and evaluated, Ref. [49-1], [49-2], [49-20]; mainly titanium aluminides, [See: 49.5].

49.2.2.2 Space

The European FESTIP programme investigated intermetallic materials for several space applications. Within the family of intermetallics, titanium-aluminides were considered more advanced than the Ni- and Fe-based materials or refractory metal silicides ($MoSi_2$, $NbSi_2$), Ref. [49-23].

Potential applications included:

- structural hot skins and in thermal protection systems (TPS) for spaceplanes, Ref. [49-21], [49-23].
- matrix phases for intermetallic matrix composites (IMC), Ref. [49-19], [49-23].
- protective coatings for conventional Ti-alloys, Ti-based composites (TMC) and Ti-aluminides, Ref. [49-19].

Titanium-aluminide intermetallic matrix composites (IMC) are also described in literature as titanium matrix composites (TMC), Ref. [49-19].

[See: 49.5 – Titanium aluminides]

49.2.3 Property data

Data presented for materials under development are limited and largely taken from laboratory research publications. For the commercially more advanced intermetallics, data are mainly single source or proprietary.

- Some aluminide systems, notably titanium-based, [See: 49.5] are undergoing a full methodical mechanical and environmental evaluation for:
  - aeroengine components, Ref. [49-19], [49-20].
  - space applications, Ref. [49-21].
- Materials processing techniques are optimised for certain applications and advanced for others, [See: 49.8].
- Joining techniques are under development, [See: 49.8].
- Inspection is under development: methods are likely to be similar to those applied to more conventional metals used in aerospace; including those specifically developed for powder metallurgy (PM) superalloys.

49.2.4 Availability

Initially, licensing arrangements were offered by Oak Ridge National Laboratory (ORNL), who conducted most of the pioneering work on intermetallics.

Of the most promising of these materials, titanium-based compositions are now commercially available in Europe and finding applications, Ref. [49-21].

[See: 49.5 – Titanium aluminides; 49.11 – Potential applications]

49.3 Nickel aluminides

49.3.1 Characteristics

49.3.1.1 General

The nickel-aluminides are based on either the NiAl or Ni_3Al compounds. Table 49.3.1 compares the characteristics of the basic nickel aluminide systems under development, Ref. [49-4].

Table 49.3-1 - Nickel aluminides: Characteristics of NiAl and Ni3Al intermetallic compounds

Compound	Advantages	Disadvantages	Notes
NiAl	Density. High melting point. Excellent cyclic oxidation resistance to 1300°C. Good creep resistance.	Brittle.	Ductile→Brittle transition temperature: 300 to 600°C, typ. Aided by adding rare earth elements. Comparable to superalloys.
Ni_3Al	Ductility. Usable strength to ~800°C. Processable.	High density. Melting point. Oxygen embrittled.	Ductility by B doping. In oxidising atmospheres at intermediate temperatures. Improved by Cr additions.

49.3.1.2 Effect of micro-alloying or doping

The lack, so far, of a significant improvement in the ductility of NiAl without seriously compromising the melting point, service temperature and oxidation resistance, has proved a stumbling block to its further development.

Boron doping of Ni_3Al induces some ductility. Interest has focused on this material, primarily at Oak Ridge National Laboratory (ORNL), USA.

Additions of other elements, at the ppm level, have been shown to improve certain inherent characteristics of the base compound. Table 49.3.2 details the compositional ranges of two types of Ni_3Al systems and the effects of doping with certain elements, Ref. [49-5]. Consequently a family of doped or micro-alloyed Ni_3Al-based materials is under development. Table 49.3.3 lists the composition of the various materials, Ref. [49-5], [49-6], [49-7], [49-8].

Table 49.3-2 - Nickel aluminides: Compositions (based on Ni_3Al) under development

Typical composition range (atomic%)	Effect of 'doping' or 'micro-alloying' elements	
Ni-base; Al 18±2; Cr 8±2; Zr (or Hf)1.0±0.8; B 0.15±0.1	Cr	Reduces dynamic embrittlement in oxidising atmospheres at high temperatures.
	Zr or Hf	Improves high temperature strength by solid solution hardening.
	B	Improves grain boundary strength & ductility at ambient temperatures.
Ni-base; Al 18.5±1.5; Fe 13.5±2.5; Cr 5.5±2.5; Zr (or Hf) 0.25±0.15; B 0.1±0.04	Fe	Improves hot working ability.
	C & Ce	Small additions to control grain size & improve hot ductility.

Table 49.3-3 - Nickel aluminides: Composition, material designation and sources

Composition	Material designation [Company]
BalNi-11.3Al-0.6Zr-0.02B(wt%)	IC50 [ORNL]
BalNi-8.5Al-7.8Cr-0.8Zr-0.02B(wt%)	IC218 [ORNL]
BalNi-8.5Al-7.8Cr-1.7Zr-0.02B(wt%)	IC221 [ORNL]
BalNi-16.6Al-8Cr-1.0Zr-0.1B(wt%)	IC264 [ORNL]
BalNi-23Al-1.0Hf-0.2B(at%)	IC72 [ORNL]
BalNi-21.5Al-0.5Hf-0.18B(at%)	IC145 [ORNL]
77Ni-22.5Al-0.5Hf + 0.1B(at%)	IC137 [ORNL]
66Ni-24Al-10Co + 0.25B(at%)	Research Alloy [GE]
66Ni-24Al-10Co + 0.75B(at%)	Research Alloy [GE]
76.4Ni-23.1Al-0.5Hf + 0.10B(at%)	Research Alloy [GE]
Key: Bal - Balance; at% - Atomic percent; wt% - Weight percent	

49.4 Nickel aluminides: Properties

49.4.1 General

The data for the Ni_3Al systems given here are indications of the range of properties which can be offered by these materials.

49.4.2 Mechanical properties

49.4.2.1 Tensile strength (Yield and UTS)

Ni_3Al shows an increase in Yield Strength with increasing temperature up to approximately 500°C to 600°C and then decreases, Ref. [49-5], [49-9]. The exact temperature varies with the composition of the material.

As with all engineering metals, the strengths attainable are dependent on both composition and condition.

Table 49.4.1 presents typical properties for the ORNL IC50 alloy at elevated temperatures for various thermo-mechanical or cold work conditioning; including, for comparative purposes, basic data on the IC218 and IC221 materials, Ref. [49-6]. These have yet not been subjected to such a detailed investigation as IC50.

Table 49.4-1 - Nickel aluminides: Mechanical properties at elevated temperatures with various conditioning

Temp (°C)	YS (MPa)	UTS (MPa)	Elong (%)	R of A (%)	Condition
IC50 [ORNL]					
25	337	587	13.1	16.8	Direct cast bar. As-cast condition.
400	393	487	4.3	9.5	
600	447	452	6.2	12.2	
800	-	455	2.7	0.8	
1000	-	181	4.0	0.0	
25	468	1307	41.8	48.4	Direct cast bar annealed after casting 60% swaging + anneal + 60% -swaging + annealed at 1100°C.
400	527	1049	26.8	20.4	
600	610	688	5.6	7.8	
800	494	549	2.7	4.4	
1000	136	159	63.5	46.6	
25	1260-1430	1514-1592	3.0-10.0	4.4-18.7	Direct cast bar. 60% swaged + 1100°C anneal + 60% swaged + 1100°C anneal + 20% cold reduction.
400	1150	1253	2.4	5.6	
600	920-940	923-998	1.4	0.5-2.7	
800	555	603	1.4	0.5	
1000	165	188	7.0	14.3	
RT	432	1205	32.13	23.25	Annealed 1100°C/1 hour.
200	452	1081	21.52	16.90	
400	467	858	12.38	10.71	
600	606	735	3.64	6.18	
800	583	612	3.25	3.81	
1000	223	265	11.62	8.73	
RT	1355	1498	5.75	7.35	10% Cold work.
200	-	-	-	-	
400	118	1276	2.46	5.03	
600	786	803	5.17	1.37	
800	696	729	2.41	1.13	
1000	234	325	6.50	7.78	
RT	1454	1560	3.33	7.31	20% Cold work.
200	1306	1373	3.31	2.83	
400	-	876	1.07	1.33	
600	-	631	1.70	0.85	
800	629	700	1.65	3.60	
1000	168	169	0.72	1.25	
RT	1685	1179	0.25	2.81	40% Cold work.
200	1597	1678	1.69	4.13	
400	-	1441	4.05	0.39	
600	1143	1310	5.77	4.50	
800	689	775	8.78	6.83	
1000	141	190	33.58	38.73	
IC218/221					
RT	586	1310	20	18	Not stated.
427	724	1241	17	15	
649	793	965	15	15	
760	758	931	15	17	
871	586	690	15	17	
982	310	379	10	17	

49.4.2.2 Modulus

Table 49.4.2 shows the effect of temperature on the modulus of the ORNL IC materials, Ref. [49-6]. The retention of stiffness at elevated temperatures, such as at 600°C, is viewed as one of their advantages.

Table 49.4-2 - Nickel aluminides: Modulus at elevated temperature

Alloy	**Temperature (°C)**	**Modulus (GPa)**
IC50	25	171
	400	150
	600	148
	800	118
	1000	93
	1075	-
	1097	53
IC218	25	226
	400	167
	600	-
	800	171
	1000	-
	1075	80
	1097	-
IC221	25	216
	400	-
	600	-
	800	-
	1000	-
	1075	-
	1097	-

49.4.2.3 Ductility

For Ni_3Al boron-doped materials, the ductility decreases substantially with increasing temperature. A pronounced minimum is observed between 600°C to 850°C for tests conducted in air. This effect has been attributed to embrittlement by gaseous oxygen. It is improved with chromium additions which promote formation of a chromium oxide film which acts as a barrier to oxygen.

Ductility is affected by the processing route used. This too is linked with the presence of oxygen, usually retained in powders.

49.4.2.4 Fatigue

Data are limited on fatigue performance of the nickel aluminides. Table 49.4.3 gives some preliminary data for the IC218 and IC221 materials, Ref. [49-6].

Table 49.4-3 - Nickel aluminides: Preliminary fatigue test data for IC218 and IC221

Alloy	**Condition**	**Fatigue data**	
		Δσ (MPa)	***Nf* (cycles)**
IC218	Hot extruded, cast billet. Cold swage at RT. + 1050°C/1 hour anneal + 800°C/1 day	605	$>10^{-7}$
		641	1.6 x 10^{-6}
		690	3.9 x 10^{-5}
		793	6.7 x 10^{-4}
		862	1.1 x 10^{-4}
IC221		690	9.8 x 10^{-6}
		741	2.0 x 10^{-6}
		793	4.5 x 10^{-5}
		862	1.23 x 10^{-5}
		910	1.5 x 10^{-4}
Test conditions:	Temperature 600°C vacuum. Triangular wave function, frequency 20 Hz. R = σ min/σ max = 1		

49.4.2.5 Creep

First indications are that nickel aluminides in the cast condition offer a higher creep resistance (700°C to 900°C) than wrought Waspalloy, but only a moderate improvement in the wrought condition. This observation requires substantiation during a full testing programme.

49.4.3 Oxidation resistance

The ability of Nickel aluminide materials to produce an alumina (Al_2O_3) film at 100°C to 1100°C provides resistance to oxidation. However, non-chromium-containing alloys are sensitive to embrittlement by gaseous oxygen causing a significant loss in ductility. The Cr-containing alloys produce a mixed Al_2O_3-Cr_2O_3 protective coating to help resist embrittlement.

49.4.4 Aqueous corrosion

Nickel aluminides, notable Ni_3Al offer good resistance to the majority of corrosive media.

49.4.5 Coefficient of thermal expansion (CTE)

Table 49.4.4 gives some typical values of CTE measured for a Ni_3Al based material, Ref. [49-4], [49-6]. The measurements were made as part of a research programme and are therefore for guidance only.

Table 49.4-4 - Nickel aluminides: Coefficient of thermal expansion

Alloy	Temperature range (°C)	CTE (10^{-6} / °C)
76%Ni-24%Al	27-327	12.5
	427-727	14.8
	727-1027	16.8
75%Ni-25%Al	27-327	12.5
	427-727	14.8
	727-1027	16.8
NiAl	Not stated	14.5

49.5 Titanium aluminides

49.5.1 General

The titanium aluminide materials are based on compounds of:

- TiAl: γ-titanium aluminides (ordered face-centred tetragonal $L1_0$ structure)
- Ti_3Al: α- or α_2-titanium aluminides (ordered hexagonal $D0_{19}$ structure).

Initial work concentrated on single-phase intermetallics, which are described in literature by their base compound, e.g. Ti_3Al, or by their metallurgical structure, e.g. α2-Ti_3Al.

Further work has considered two-phase intermetallics in which the limitations of one compound can in theory be offset by the other. These tend to be described as γ-titanium aluminides and are technically advanced and commercially available.

[See also: 49.9 for orthorhombic titanium aluminides]

49.5.2 Characteristics

Table 49.5.1 compares the characteristics of the titanium aluminide systems, Ref. [49-4], [49-24].

Table 49.5-1 - Titanium aluminides: Comparison of characteristics

Compound	Advantages	Disadvantages	Notes
Single-phase γ-TiAl	Density	Brittle	-
Single-phase α-Ti_3Al	Density	-	Additions of Nb to achieve ductility but increase density.
		Oxidation tolerance.	For applications >700°C, coating advised.
Two-phase γ-TiAl	Density	-	Contains both TiAl and Ti_3Al compounds giving a controlled amount of each phase, i.e. γ and α_2 in the resulting microstructure.

For space applications, other important characteristics include, Ref. [49-24], [49-25]:

- high elastic modulus,
- low density,
- high resistance to hydrogen absorption,
- good oxidation resistance,
- burn resistance (no self-ignition).

Subsequent alloy developments (γ-TiAl) have improved creep resistance and specific strengths such that their potential service temperature can be considered in the range of 700°C to 950°C, Ref. [49-24].

49.5.3 Effect of micro-alloying or doping

49.5.3.1 General

Both the basic TiAl or Ti_3Al compounds are inherently brittle from room temperatures up to approximately 600°C.

Small additions of niobium, tungsten and vanadium (typically 0.5 to 10.0 atomic percent) doped or micro-alloyed with the base compounds induce more usable ductilities.

Table 49.5.2 lists the various titanium aluminide materials under examination, Ref. [49-24].

49.5.3.2 Experimental alloys

Of these, the Ti_3Al + Nb series were the most prominent. Although the niobium additions also assisted in oxidation and creep resistance, interest in the various α-type materials has diminished in favour of the γ-series, Ref. [49-22].

The molybdenum and vanadium additions assist rapid solidification by retaining certain metallurgical phases. Some of these alloys have additions of rare-earth elements. These are added to enhance strength by dispersion hardening.

Table 49.5-2 - Titanium aluminides: Typical compositions

Status	Nominal composition	Company/Organisation
Experimental	Ti$_3$Al-5Nb-1W(at%)	-
[1]	Ti$_3$Al-15Nb(at%)	-
	TiAl-2W(at%)	-
	Ti$_3$Al-1V(at%)	-
	Ti-(17 to 37)Al-1Ru(at%)	Imperial College, UK.
	Ti-(20.5 to 23.7)Al-(5 to 15)Nb-3Zr + (0.3 to 0.9)Er$_2$O$_3$	Marko Materials Inc.
	Ti-24Al-4Nb-4Mo-4V-0.45O	Wright-Patterson AFB/Calspan
	Ti-24Al-4Nb-4Mo-4V-0.2Er-0.2Ce-0.20S-0.2Y-0.45O	Wright-Patterson AFB/Calspan
	Ti-24Al-4Nb-4Mo-4V-0.3Er-0.3Ce-0.30S-0.2Y-0.45O	Wright-Patterson AFB/Calspan
	Ti-47Al-2Cr-0.2Si	FESTIP (protective coatings)
	Ti-47Al-2Cr-2Nb	FESTIP (protective coatings)
Two-phase γ-TiAl	**Ti - 45 to 48 Al - 0 to 3 (Cr, Mn, V) - 0 to 5 (Nb, W, Ta) - 0 to 1 (Si, B)**	**Typical Composition Range (at%)**
[2]	Ti-48Al-2Cr	Plansee GmbH
	GE Alloy: Ti-48Al-2Cr-2Nb	Developed by General Electric, USA. [3] Plansee GmbH

Key: [1] Under investigation in the 1980's. FESTIP evaluation continued in the mid-late 1990s.
[2] Technically advanced and commercially available.
[3] A second-generation alloy for GE90 aircraft engine parts for Boeing 777.

49.5.3.3 Two-phase alloys

Two-phase γ-TiAl based alloys contain both the γ-TiAl phase and the α_2-Ti$_3$Al phase. Their metallurgical composition characteristics can be summarised as, Ref. [49-24], [49-25]:

- The α_2-Ti$_3$Al phase scavenges oxygen, so increases the purity hence ductility of the γ-phase.
- The amount of α_2-phase is controlled by the Al content and additional elements.
- Additions of Cr, Mn and V increase room temperature ductility.
- Additions of Nb, W and, to a lesser extent Ta, improve oxidation resistance and enhance creep properties by significant substitutional solid-solution strengthening.
- Additions of B, Si and C provide effective dispersion or precipitation hardening effects.
- If B or Si exceed certain levels, borides or silicides are present.

- Interstitial elements, such as O, N, C and B reduce ductility if levels exceed ~1000 ppm (by weight).

The characteristics of these alloys are determined by their chemical composition and microstructure. [See: 49.6].

49.6 Titanium aluminides: Properties

49.6.1 General

Data are presented for:

- Experimental alloys (pre-1990): Extracted from various research publications; mainly of US origin. These show the basic characteristics of titanium aluminides and provide a background to the further developments.
- Two-phase alloys (post-1990): These compositions developed from the most promising experimental alloys and are subject to more detailed investigations for aerospace applications. Depending on the composition and condition, the influence of the microstructure on properties can be summarised as, Ref. [49-25]:
    - Coarse-grained, fully-lamella: relatively good fracture toughness, excellent creep resistance but poor tensile ductility and strength especially at RT.
    - Fine-grained, near-◎ and duplex (low volume fractions of lamella grains): low fracture toughness and creep resistance, but moderate tensile ductility and strength at RT and elevated temperatures. An optimised fine-grained lamella microstructure can provide acceptable mechanical performance.
- Orthorhombic phase alloys: Mainly under investigation as matrix phases for intermetallic matrix composites (IMC), [See: 49.10].

49.6.2 Mechanical properties

49.6.2.1 Tensile strength (Yield and UTS)

Table 49.6.1 gives experimental alloy data from various research publications on titanium aluminides, Ref. [49-1], [49-10], [49-11], [49-12], [49-13], [49-24].

Table 49.6-1 - Titanium aluminides: Mechanical properties for materials processed by different techniques

Alloy composition	Temp (°C)	YS (MPa)	UTS (MPa)	Modulus (GPa)	Elong (%)	R of A (%)	Condition	Notes [Reference]
Experimental alloys								
TiAl	-	335*	450	-	0.9	-		Ref. [49-10]
TiAl	-	-	-	176	-	-		$L1_0$ crystal structure,Ref. [49-1]
TiAl	-	-	-	176	-	-		
Ti_3Al	-	-	-	145	-	-		DO_{19} crystal structure, Ref. [49-1]
Ti_3Al	-	-	-	145-110	-	-		Ref. [49-13]
Ti_3Al	-	-	550	-	-	-		Ref. [49-10]
Ti-14.2Al-21.5Nb(wt%) TRW/PWA	20	709	743	-	1.4	0.7	Powder Consolidation by HIP: 927°C/207 MPa/2 hour 1177°C/1 hr/Fan Cool. 760°C/1 hr/Air Cool.	Precision Cast Part Corp. Ref. [49-12]
	"	696	759	-	1.5	1.6		
	"	689	791	-	1.6	2.4		
	204	578	748	-	3.9	4.0		
	"	588	731	-	3.0	3.2		
	"	601	695	-	2.0	2.8		
	649	429	686	-	18.4	23.3		
	"	426	683	-	18.8	27.2		
	"	444	650	-	19.1	17.5		
	20	608	722	-	1.3	1.6	Cast + isoforged at 1068°C + 1093°C/0.5 hr/ Cool 260°C/minute 760°C/1 hr/Air Cool.	Exact composition not stated. Data used for comparison with Powder Met TRW experimental, Ref. [49-12]
	"	608	728	-	1.2	4.3		
	649	385	601	-	13.0	21.5		
	"	385	576	-	16.0	24.8		
Ti_3Al Niobium Modified. Crucible Materials Corp. USA	RT(a)	510	606	-	2	2	1175°C/0.5 hr/Air Cool +760°C/1 hr/AC +595°C/8 hr/Vac Cool.	Powder Production by Plasma Rotating Electrode Process (PREP) consolidated by HIP @ 1065°C, Ref. [49-1] Different Cooling Rates from Solution Treatment Temperature: (a) 50°C/min
	RT(c)	530	592	-	<1	2	1205°C/0.5 hr/Fan Air Cool +760°C.	
	RT(d)	661	772	-	1	3		
	760(d)	303	558	-	14	20	1205°C/0.5 hr/AC +760°C/1 hr/ Vac Cool.	
	425(b)	344	572	-	11	12		

Alloy composition	Temp (°C)	YS (MPa)	UTS (MPa)	Modulus (GPa)	Elong (%)	R of A (%)	Condition	Notes [Reference]
	540(b)	324	517	-	12	15		(b) 60°C/min (c) 120°C/min (d) >280°C/min (e) >17000°C/min
	650(b)	282	468	-	13	20		
	760(b)	248	400	-	18	22	1205°C/0.5 hr/Oil Q + 760°C/1 hr/Vac Cool.	
	760(d)	241	386	-	14	15		
Ti_3Al-5Nb-1W	-	796*	920	-	0.4	-	Not stated.	Ref. [49-10]
Ti_3Al-15Nb	-	-	-	-	4.9	-		
TiAl-2W	-	642*	790	-	0.8	-		
TiAl-1V	-	-	400	-	2.2	-		
Ti-23.75Al-5Nb (at%)	650	270*	587	-	8.3	10.3	As-extruded.	Melt Spun Ribbon-Pulverised-Hot Extruded, Ref. [49-11]
Ti-21.25Al-15Nb (at%)	650	449	840	-	1.8 †	5.2		
Ti-20.50Al-15Nb-3Zr	650	518	962	-	1.6	3.5		
Ti-21.24Al-15Nb-0.3Er_2O_3	650	321	651	-	1.8 †	3.9		
Ti-21.10Al-15Nb-0.6Er_2O_3	650	456	795	-	4.7	8.7		
Ti-21.03Al-15Nb-0.9Er_2O_3	650	388	702	-	9.1	13.8		
Two-phase γ-TiAl alloys								
Ti-48Al-2Cr	-196	-	577	172	-	-	Ingot metallurgy. Near-γ microstructure.	Sheet test specimens,Ref. [49-24]
	25	421*	432	109	2	-		
	600	323*	457	128	4	-		
	700	322*	512	115	31	-		
	700V	350*	562	-	56	-		
	800	292*	357	97	93	-		
Ti-48Al-2Cr	-196	-	559	160	-	-	Ingot metallurgy. Near-γ microstructure. Annealed: 700°C/100hrs.	Sheet test specimens, Ref. [49-24]
	25	-	407	162	0.4	-		
	600	376*	540	145	8	-		
	700	363*	524	112	54	-		
	700V	336*	508	-	66	-		
	800	313*	339	105	65	-		
Ti-48Al-2Cr	-196	625*	622	149	0.2	-	Ingot metallurgy.	Sheet test specimens, Ref. [49-24]

Alloy composition	Temp (°C)	YS (MPa)	UTS (MPa)	Modulus (GPa)	Elong (%)	R of A (%)	Condition	Notes [Reference]
	25	440*	457	150	1	-	PA - Primary annealed (after sheet rolling): 1000°C/2 hrs/vacuum.	
	600	371*	567	136	6	-		
	700	366*	512	120	100	-		
	700V	394*	640	-	65	-		
	800	295*	327	104	89	-		
Ti-48Al-2Cr	-196	-	561	173	-	-	Ingot metallurgy. PA - Primary annealed (after sheet rolling): 1000°C/2 hrs/vacuum. Annealed: 700°C/100hrs.	Sheet test specimens, Ref. [49-24]
	25	450*	453	146	-	-		
	600	345*	546	129	7	-		
	700	368*	487	100	112	-		
	700V	388*	509	-	65	-		
	800	281*	318	90	91	-		
Ti-48Al-2Cr-2Nb	-196	-	617	171	-	-	Powder metallurgy. Near-γ microstructure.	Sheet test specimens, Ref. [49-24]
	25	451*	455	128	1	-		
	600	339*	499	119	4	-		
	700	356*	553	122	15	-		
	700V	375*	620	-	19	-		
	800	337*	406	95	58	-		
Ti-48Al-2Cr-2Nb	-196	-	526	170	-	-	Powder metallurgy. Near-γ microstructure. Annealed: 700°C/100hrs.	Ref. [49-24]
	25	424*	426	153	-	-		
	600	338*	435	120	3	-		
	700	341*	498	93	10	-		
	700V	359*	466	-	3	-		
	800	308*	370	94	71	-		
Ti-48Al-2Cr-2Nb	-196	-	625	169	-	-	Powder metallurgy. PA - Primary annealed (after sheet rolling): 1000°C/2 hrs/vacuum.	Sheet test specimens, Ref. [49-24]
	25	518*	528	101	0.3	-		
	600	439*	632	92	4	-		
	700	392*	558	85	98	-		

Alloy composition	Temp (°C)	YS (MPa)	UTS (MPa)	Modulus (GPa)	Elong (%)	R of A (%)	Condition	Notes [Reference]
	700V							
	420* 693	-	67	-				
800	315* 418	79	80	-				
Ti-48Al-2Cr-2Nb	-196	-	510	149	-	-	Powder metallurgy. PA - Primary annealed (after sheet rolling): 1000°C/2 hrs/vacuum. Annealed: 700°C/100hrs.	Sheet test specimens, Ref. [49-24]
	25	464*	466	119	-	-		
	600	443*	570	122	4	-		
	700	379*	543	102	89	-		
	700V	400*	550	-	66	-		
	800	357*	404	81	83	-		

Key: * : 0.2% Yield Stress † : Specimen failed near gauge clamp. V: Test temp., in vacuum. At room temperature, the base TiAl and Ti_3Al compounds are brittle.

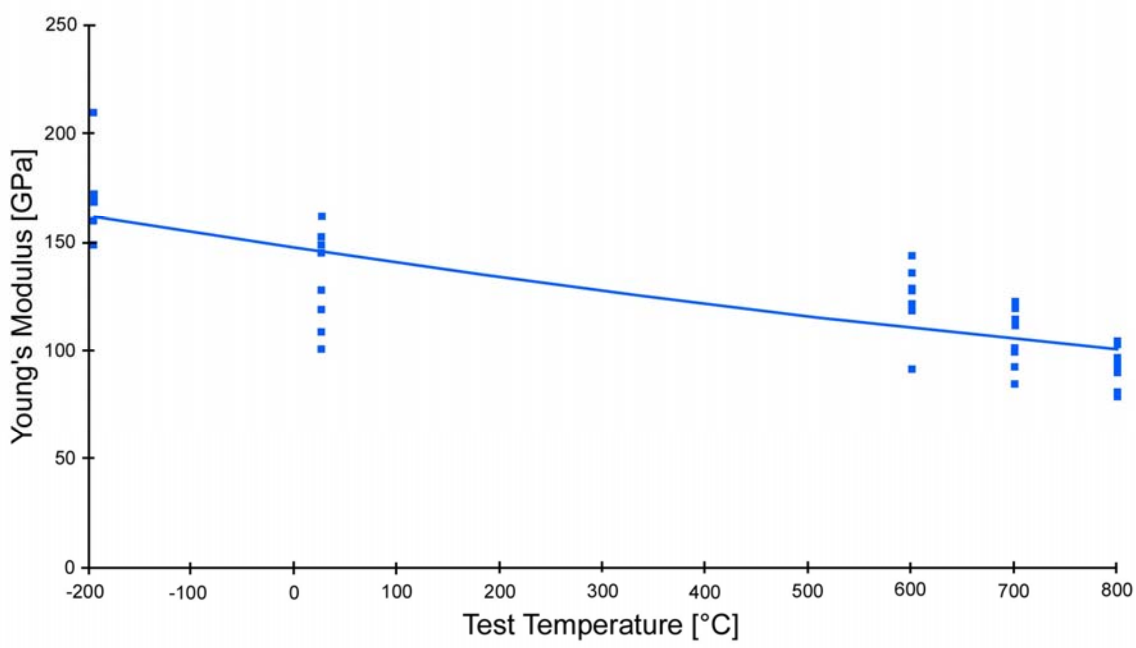
The data for two-phase alloys are mean values taken from a European material characterisation study for potential space applications, Ref. [49-24], [49-25]. Key features include:

- Ultimate tensile strength is temperature dependent. It reduces from -196°C to RT, and then surprisingly increases up to ~600°C to 700°C. Above this temperature, UTS reduces; as seen with conventional metallic materials.
- Yield stress decreases by ~28% between RT and ~800°C This 'softening behaviour' is different to that of conventional metals.

49.6.2.2 Modulus

For the basic intermetallic compounds, TiAl has a higher modulus than Ti_3Al, [See: Table 49.6.1]. For two-phase alloys, Ref. [49-24], [49-25]:

- As expected, the modulus is highest at -196°C.
- Stiffness generally decreases as temperature increases, as shown in Figure 49.6.1, Ref. [49-24]. This trend was determined by mechanical testing (taking into account scatter originating from strain measurements) and confirmed by sonic measurements.



Mean values for PM and IM two-phase γ-Ti Al alloys, all conditions

Figure 49.6-1 - Titanium aluminides: Effect of temperature on Young's modulus

49.6.2.3 Ductility

The experimental alloys have low ductilities at RT and intermediate temperatures, [See: Table 49.6.1].

Two-phase alloys show a ductile-to-brittle transition (DBTT) at about 700°C, as shown in Figure 49.6.2, Ref. [49-24].

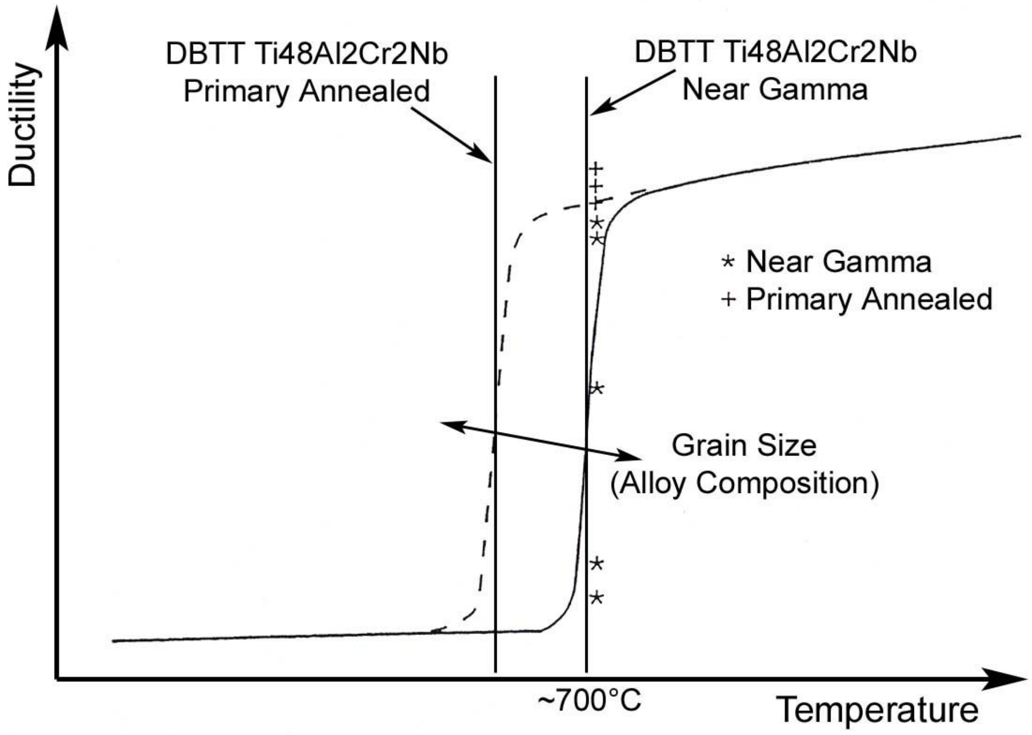


Figure 49.6-2 - Titanium aluminides: Two-phase alloys - Ductility versus temperature

Below the DBTT, both two-phase alloys have low ductilities. Above the DBTT, plastic flow occurs that can result in elongations of 120% or more.

Ductility is also influenced by the processing route (ingot or powder metallurgy) and microstructure (condition heat treatments), e.g. the near-gamma microstructure of PM Ti-48Al-2Cr-2Nb is generally lower than for the primary annealed condition. Likewise the elongation behaviour of the near-γ structure and primary annealed condition differ between 600°C and 800°C.

No significant difference in ductility was seen when tested in air or in vacuum.

A typical elongation value of 1% to 2% at RT and 4% to 6% at 600°C are intrinsic of intermetallic materials and should be taken into account in the design, Ref. [49-24].

49.6.2.4 Fatigue

Limited data have been published on the fatigue behaviour of titanium aluminide materials.

A study on an experimental alloy (Ti-16Al-10Nb wt.%) showed that the fatigue crack growth behaviour at 650°C was independent of the microstructure. An apparent threshold of 6.5MPa√m was determined. When compared with Rene 95 superalloy, as shown in Figure 49.6.1, the shapes of the curves are similar but the crack growth was an order of magnitude higher for the aluminide, Ref. [49-9].

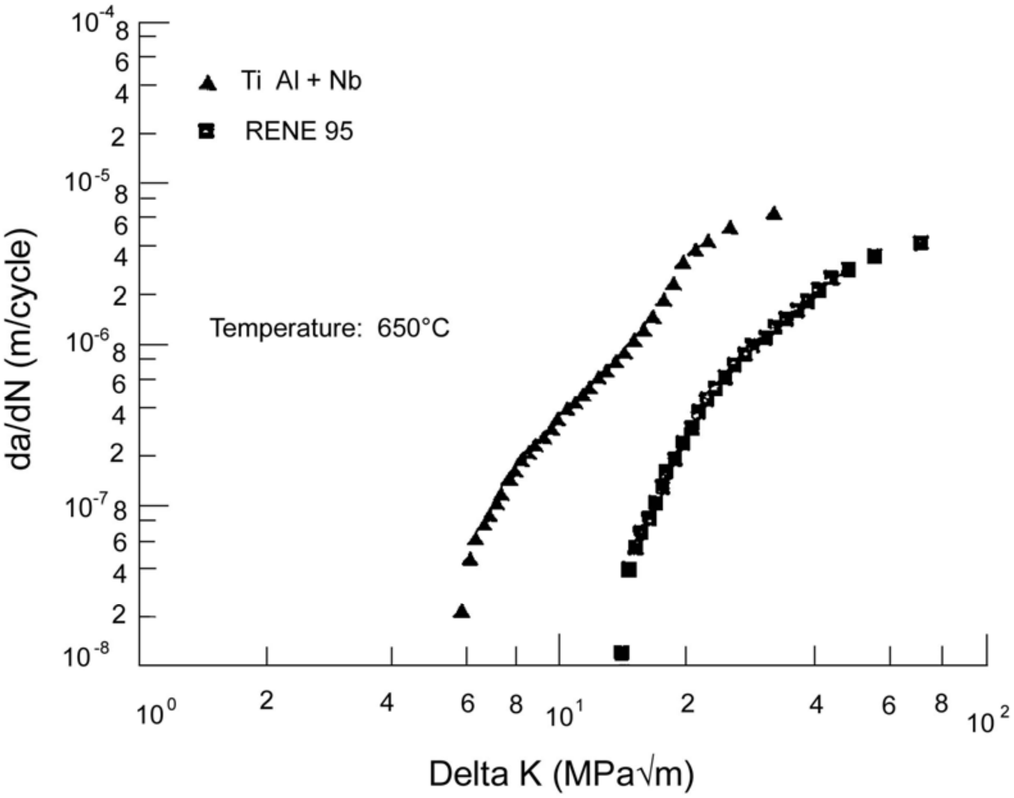


Figure 49.6-3 - Titanium aluminides: Comparison of fatigue characteristics with Rene 95 superalloy

For γ-TiAl materials at both RT and elevated temperatures, fatigue crack growth rates are considerably higher than for superalloys. Fine-grained materials (near-γ and duplex) have considerably higher fatigue crack growth rates (constant amplitude loading) than coarse-grained lamella structures, Ref. [49-25]. [See also: Fracture toughness].

49.6.2.5 Fracture toughness

The γ-TiAl materials exhibit an inverse relationship between tensile ductility and fracture resistance. Consequently, improved ductility does not confer improvements in fracture toughness, Ref. [49-25].

For γ-TiAl materials, fracture toughness is strongly linked to the microstructure and, in particular, the volume fraction of lamella grains present.

For sheet materials, the relationship between fracture toughness and microstructure can be summarised as Ref. [49-25]:

- Near-γ (0% lamella): 12MPa√m
- Duplex (20% lamella): 15MPa√m
- Lamella (95% lamella): 22MPa√m

49.6.2.6 Creep

Table 49.6.2 indicates the creep performance of an experimental Ti_3Al + Nb alloy, Ref. [49-2] and a γ-titanium aluminide (Ti-48Al-2Cr) with a near-γ microstructure, Ref. [49-25].

Table 49.6-2 - Titanium aluminides: Indication of creep properties

Experimental alloy

Alloy	Condition	Stress (MPa)	Plastic deformation (%)		
			23 hour	50 hour	165 hour
Ti_3Al + Nb	PREP Powder HIP @ 1065°C+1205°C/½hr/AgC 760°C/1 hr/Vac.C	138	0.95	1.53	3.55

Key: AgC: Argon cool. Test temperature: 760°C. Vac.C: Vacuum cool

Two-phase γ-TiAl alloy

Alloy	Condition	Max. stress (MPa) (0.2% creep/10hrs)	
		700°C	800°C
Ti-48Al-2Cr	Near-γ microstructure Sheet specimen	~245	~140
Ti 1100	Conventional Ti-alloy [For comparison]	~40	-

49.6.3 Oxidation resistance

In general, the base titanium aluminide compounds offer good oxidation resistance to approximately 650°C. To enhance oxidation resistance of Ti_3Al base experimental alloys, the creation of a $TiAl_3$ surface coating was suggested.

For long-term exposure in an oxidising environment at above 700°C, the mechanical performance of two-phase alloys is likely to deteriorate.

The types of oxidation resistant coatings considered within FESTIP are, Ref. [49-23]:

- pre-oxidation (SiO_2 pack).
- silicide (Si-Cr-B) by pack cementation.
- aluminising (Al-Cr-Nb) by slurry deposition.
- coating (Co-Cr-Al-Y) by plasma spraying.

Coatings reduced the oxidation rate (by about 2 orders of magnitude) compared with the uncoated alloy.

Modified-aluminide coatings showed good resistance under cyclic oxidation tests.

[See also: Chapter 74 – Protective coatings]

49.6.4 Thermophysical properties

49.6.4.1 General

Thermal characteristics have been evaluated with respect to the potential application of titanium aluminides on the external surfaces of spacecraft. Their high thermal conductivity enables higher cooling efficiencies and lower thermal stresses, which is considered an important benefit over ceramic-based materials for similar applications, Ref. [49-23], [49-24].

[See also: Chapter 82]

49.6.4.2 Thermal diffusivity

Figure 49.6.4 compares the thermal diffusivity of two-phase titanium aluminide alloys from RT to 1200°C; mean values measured by laser flash method, Ref. [49-24].

Between RT and ~900°C, the Nb-containing composition shows a 5 to 8% lower thermal diffusivity.

Temp. [°C]	**Ti48A12Cr (IIVI)**	**Ti48Al2Cr2Nb (PM)**	
	Near Gamma	Primary Annealed	Near Gamma
40	6.93	6.51	6.21
100	7.36	6.71	6.50
200	7.72	7.06	6.85
300	7.99	7.46	7.24
400	8.20	7.68	7.49
500	8.52	7.93	7.70
600	8.70	8.16	7.90
700	8.77	8.22	8.02
800	8.81	8.29	8.02
900	8.73	8.26	8.15
1000	7.79	7.33	7.30
1100	7.16	6.88	6.87
1200	6.72	6.44	6.40

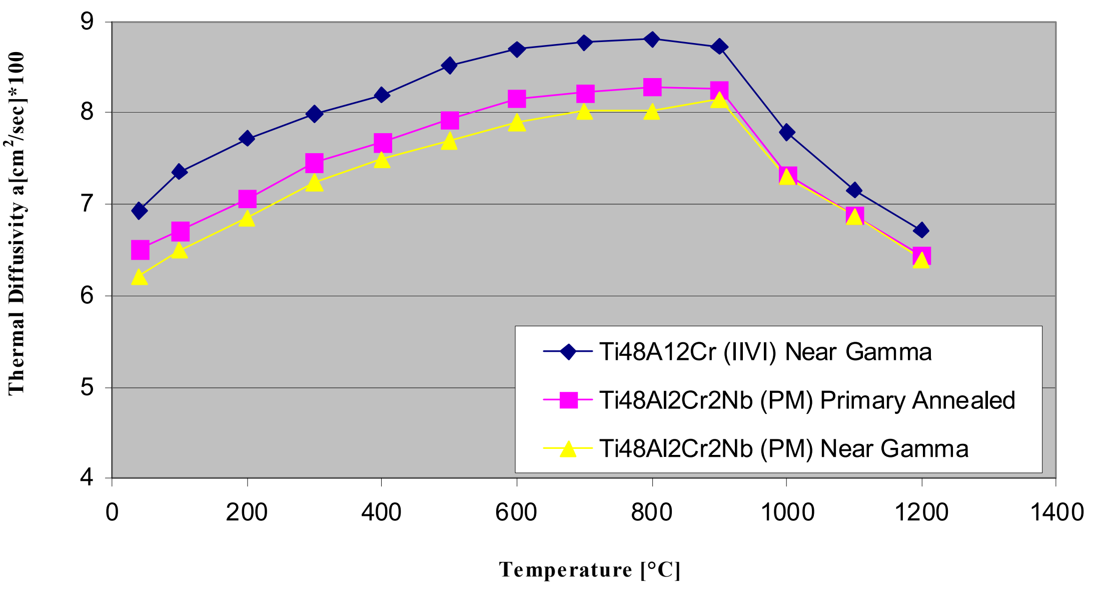


Figure 49.6-4 - Titanium aluminides: Two-phase alloys – Thermal diffusivity versus temperature

49.6.4.3 Specific heat

Figure 49.6.5 compares the specific heat of two-phase titanium aluminide alloys from RT to 1200°C; mean values measured by Differential scanning calorimeter (DSC), Ref. [49-24]. No significant difference in specific heat properties is seen for the two compositions.

Temp. [°C]	**Ti48A12Cr (IM)** Near Gamma	**Ti48Al2Cr2Nb (PM)**	
		Primary Annealed	Near Gamma
50	0.619	0.598	0.609
100	0.640	0.631	0.634
200	0.669	0.655	0.657
300	0.689	0.672	0.673
400	0.704	0.688	0.688
500	0.719	0.701	0.7
600	0.735	0.714	0.713
700	0.779	0.766	0.769
800	0.803	0.791	0.792
900	0.847	0.832	0.829
1000	0.901	0.892	0.884
1100	0.963	0.958	0.945
1200	1.109	1.12	1.072

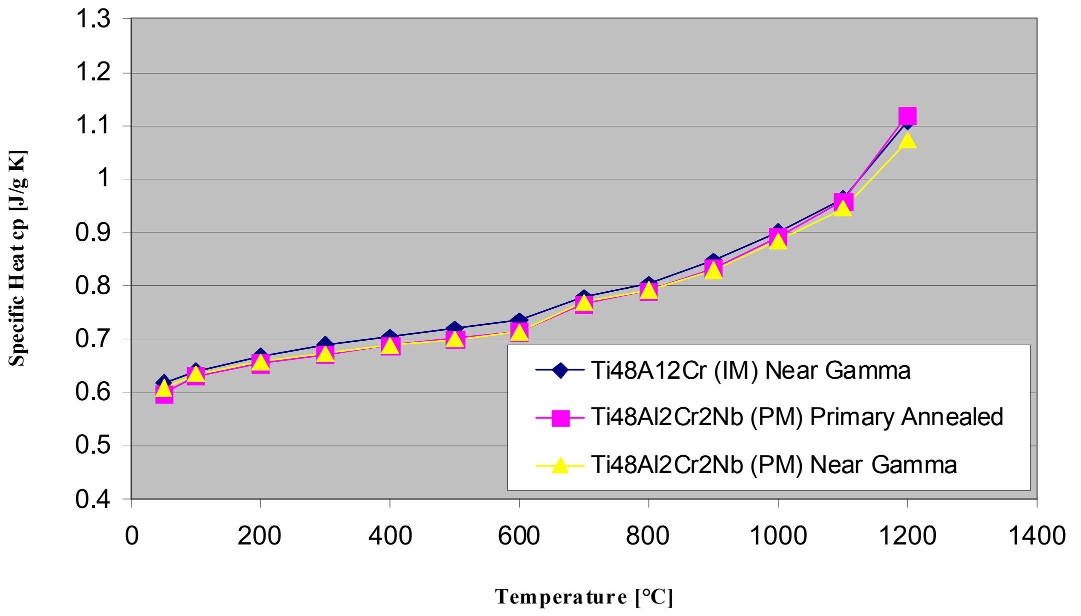


Figure 49.6-5 - Titanium aluminides: Two-phase alloys – Specific heat versus temperature

49.6.4.4 Thermal conductivity

Figure 49.6.6 compares the specific heat of two-phase titanium aluminide alloys from RT to 1200°C, Ref. [49-24].

Temp.	**Ti48Al2Cr (IM)**	**Ti48Al2Cr2Nb (PM)**	
[°C]	Near Gamma	Primary Annealed	Near Gamma
100	17.9	16.6	16.1
200	19.6	18.0	17.5
300	20.8	19.5	18.9
400	21.7	20.5	19.9
500	23.0	21.5	20.8
600	23.9	22.4	21.6
700	25.4	24.1	23.6
800	26.2	25.0	24.2
900	27.3	26.1	25.6
1000	25.8	24.7	24.4
1100	25.2	24.8	24.4
1200	27.1	26.9	25.6

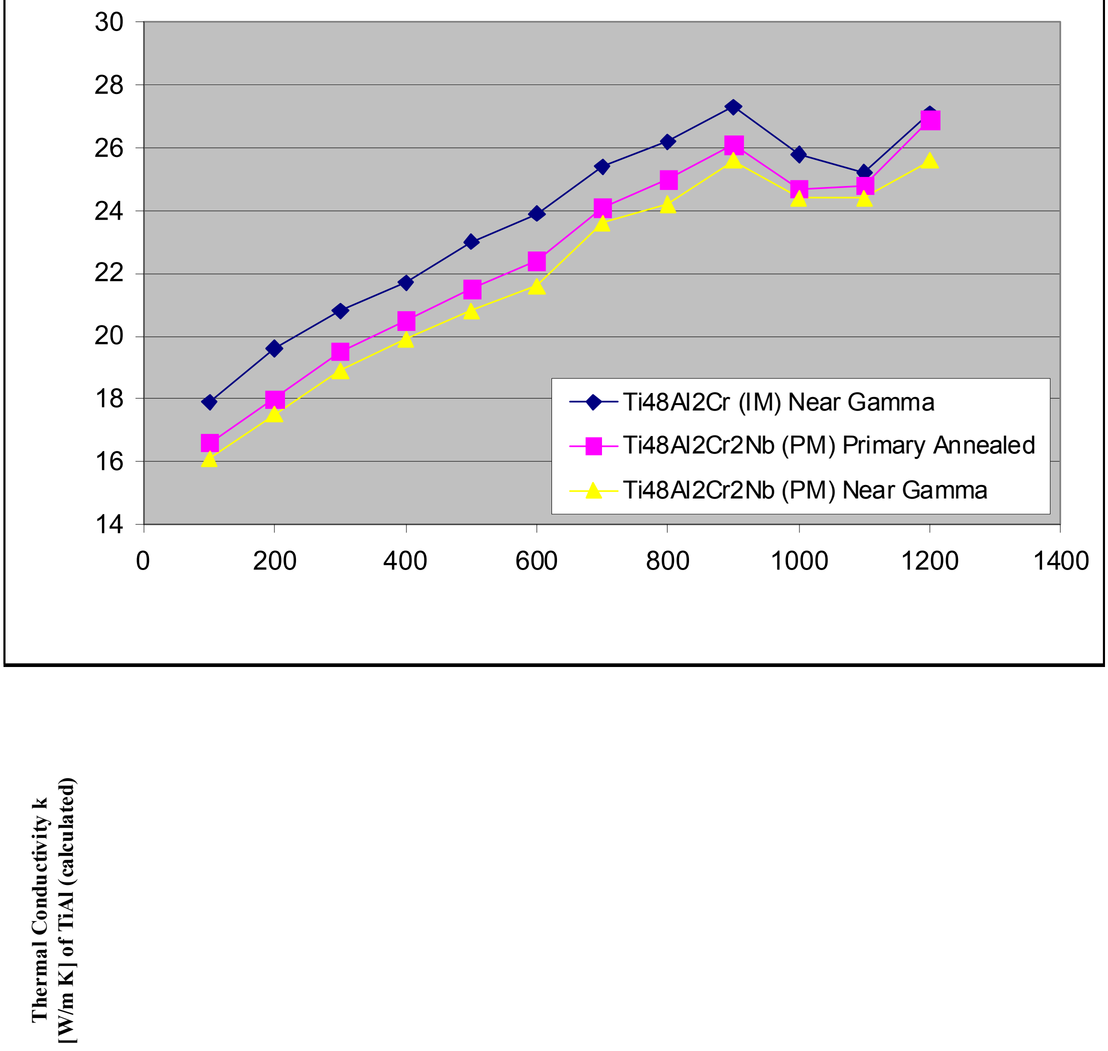


Figure 49.6-6 - Titanium aluminides: Two-phase alloys – Thermal conductivity versus temperature

These values were calculated using the mean measured values for specific heat and density measurements at RT.

The small difference seen between the Nb-containing and the Nb-free composition could be an accuracy artefact (6% to 8%) rather than a real effect.

Changes in the curve shapes with increasing temperature, especially the fall at ~900°C and subsequent increase >1100°C, is related to microstructural phase changes occurring within the materials.

49.6.4.5 Coefficient of thermal expansion

Early work on an experimental alloy (Ti_3Al + Nb) determined a CTE of 10 x 10^{-6} /°C.

Figure 49.6.7 compares the coefficient of thermal expansion of two-phase titanium aluminide alloys from RT to 1200°C. CTE was measured by dilatometer with samples taken parallel to the rolling direction, Ref. [49-24].

No significant difference is seen between the two compositions.

Temp.	**Ti48A12Cr (IM)**	**Ti48Al2Cr2Nb (PM)**	
[°C]	Near Gamma	Primary Annealed	Near Gamma
100	10.67	10.49	10.57
200	10.98	10.80	10.78
300	11.25	11.06	11.00
400	11.51	11.29	11.23
500	11.75	11.52	11.47
600	12.00	11.75	11.73
700	12.27	12.01	12.01
800	12.57	12.31	12.31
900	12.90	12.68	12.65
1000	13.29	13.12	13.02
1100	13.74	13.66	13.42
1200	14.27	14.31	13.87

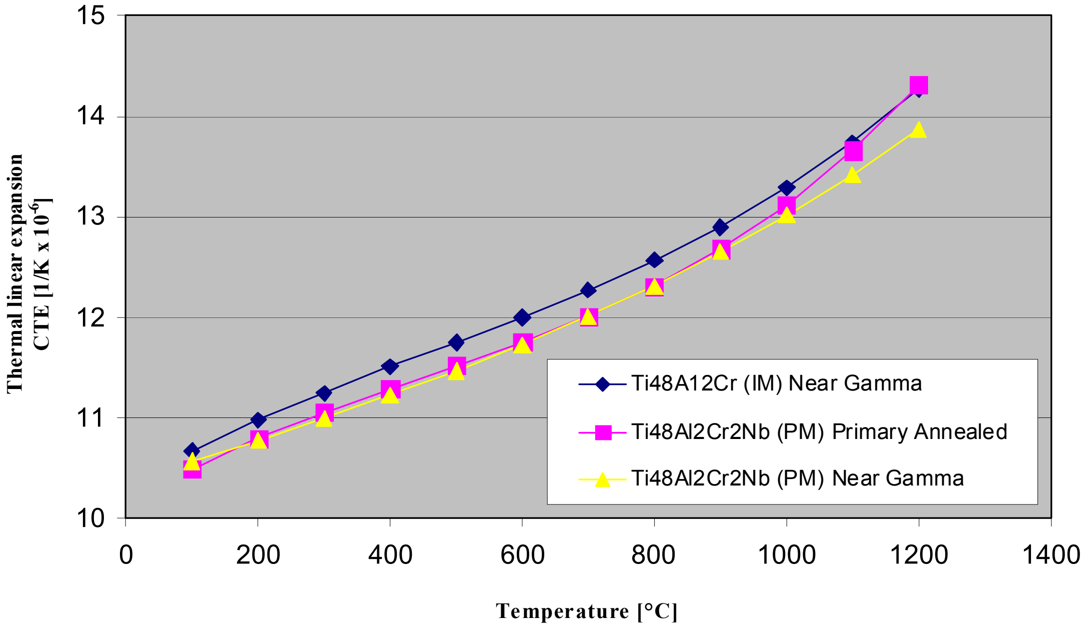


Figure 49.6-7 - Titanium aluminides: Two-phase alloys – Coefficient of thermal expansion versus temperature

49.7 Iron aluminides

49.7.1 Characteristics

49.7.1.1 General

Interest in the iron aluminides largely focused on the FeAl compound. Work on this material and its derivatives has been co-ordinated by NASA, Ref. [49-4].

The FeAl system has a number of beneficial characteristics, notably the level of ductility at room temperature.

Table 49.7.1 compares the advantages and disadvantages of FeAl, Ref. [49-4]. Initial studies concentrated on the Fe-40Al (atomic percent) materials.

Table 49.7-1 - Iron aluminides: Characteristics

Advantage	Disadvantage
Ductility: 3 to 5% at RT †	Melting point: 1340°C
Cyclic oxidation resistance at 1000°C.	Density
Not susceptible to oxygen embrittlement at intermediate temperatures.	Strength and creep resistance decreases significantly at >700°C
Key: †: Fe-40Al (atomic %) is one of the few aluminide compounds with measurable ductility at RT.	

Table 49.7.2 lists some of the alloys undergoing investigation, Ref. [49-4], [49-14]. In general, iron aluminides are considered a possible replacement for some stainless steel components, perhaps also, in non-aerospace applications.

Table 49.7-2 - Iron aluminides: Composition of development materials

Composition	Company	Notes	
Fe-40Al (at.%)	-	-	-
Fe-40Al-0.1Zr-0.2B (at%)	Case Western Uni/NASA-Lewis	Zr (or Hf):	Increase strength to 700°C, typ. & maintain ductility.
		B:	Aid low temperature ductility.
Fe-40Al-0.1Zr-0.2B + 1vol%Y_2O_3	Case Western Uni/NASA-Lewis	Y_2O_3:	Improve high temperature strength by ODS, but maintain ductility.
Key: at.% - Atomic percent; vol% - Volume percent; ODS - Oxide dispersion strengthened.			

49.7.1.2 Material properties

Figure 49.7.1 shows the room temperature behaviour of Fe-40Al (atomic percent) with boron additions and in different conditions, Ref. [49-3].

For comparative purposes, Figure 49.7.2 shows the effect of conditioning and elevated temperature on the strength of Y_2O_3 oxide dispersion hardened alloy systems, Ref. [49-14].

Attempting to enhance mechanical properties above 700°C by further alloy modifications can seriously affect the other beneficial properties of the FeAl system.

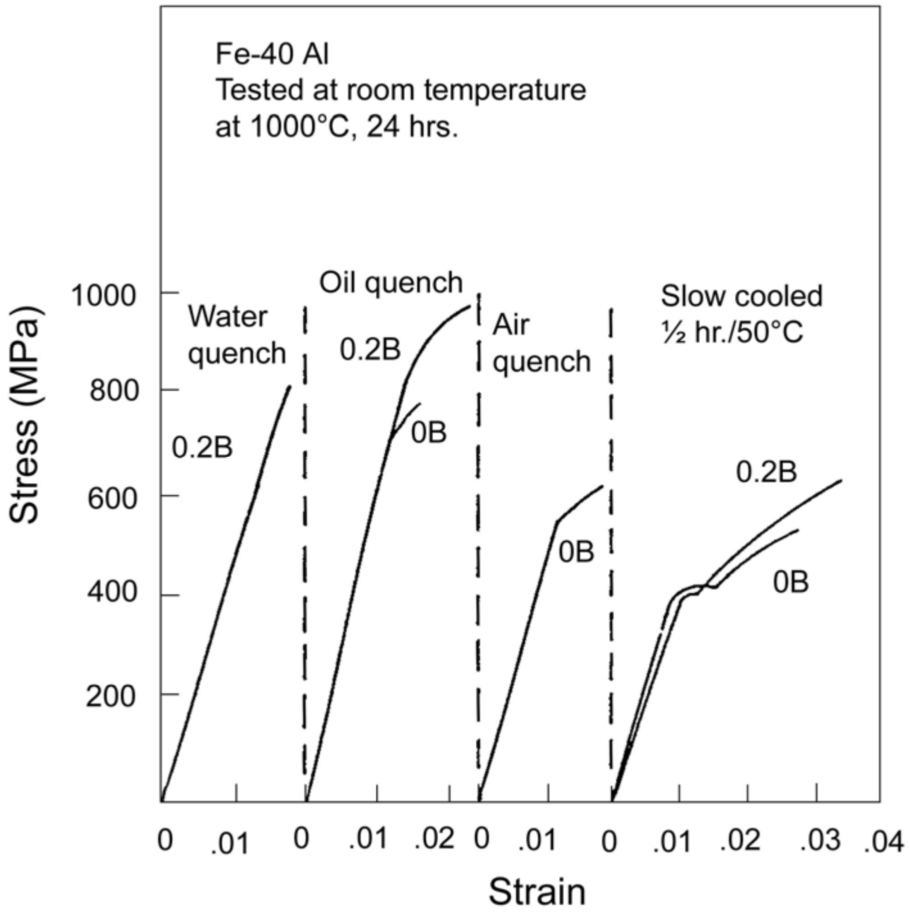


Figure 49.7-1 - Iron aluminides: Room temperature behaviour of Fe-40Al(at. %) + boron additions in different conditions

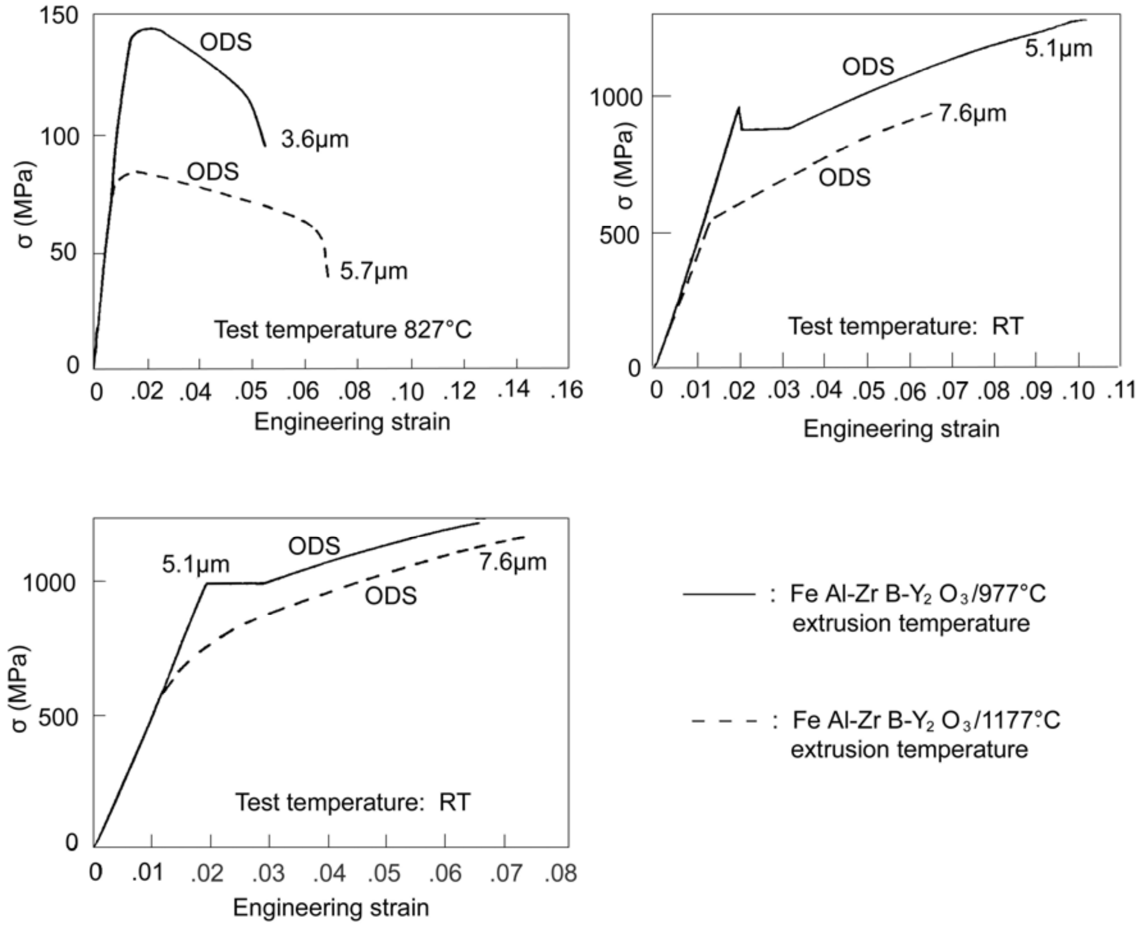


Figure 49.7-2 - Iron aluminides: Effect of conditioning and elevated temperature on strength of Yttria ODS alloy system

49.8 Processing

49.8.1 Development

The development of intermetallic materials has been coupled with a significant effort devoted to their processing technology. This has partly been in an effort to find a method which did not cause a deleterious effect on the properties achieved by doping or micro-alloying, and partly with the aim of finding a cost-effective method of processing materials with high melting points.

Experience of processing conventional high-temperature materials, such as superalloys, has been applied to intermetallics.

49.8.2 Material processing

49.8.2.1 General

Many techniques have been considered, including:

- conventional metal processing methods.

- standard powder metallurgy techniques.
- rapid solidification.

Table 49.8.1 shows general guidelines as to the material processing methods applicable to the aluminides, plus any obvious problems encountered, Ref. [49-1], [49-7], [49-15], [49-16], [49-24], [49-25]. Each method has its own pros and cons. Most of the processing routes investigated require optimising, e.g. temperatures and times, coupled with a full evaluation of the mechanical properties attained from a material processed in a particular way. Processing of γ-TiAl materials has undergone significant levels of evaluation, Ref. [49-25].

Table 49.8-1 - Aluminides: Summary of manufacture and consolidation techniques

Manufacture	Consolidation	Notes
Nickel aluminides		
Ingot by conventional casting in air, vacuum & argon. Melt spinning for rapid solidification ribbons. Spray or plasma deposition for near-net shapes. Conventional powder metallurgy processes. Reactive sintering.	Hot extrusion, if canned. HIP. Difficult to hot work due to low ductility at high temperatures + oxygen embrittlement. Cold work + anneal.	Materials produced by rapid solidification/powder routes tend to have significant levels of oxygen (surface:volume effect) compared with those produced by conventional casting. Material embrittlement by residual oxygen has been noted. Rapidly work hardens.
Titanium aluminides		
Conventional casting (to 815kg ingot). Conventional powder metallurgy processes. PREP powder route. Melt spinning for rapidly solidified ribbons.	Hot extrusion, if canned. HIP. Hot pressing.	Wrought material processing (rolling to thin sheet and foil). Sheet forming: conventional & superplastic forming.
Iron aluminides		
Conventional casting. Powder metallurgy (also ODS alloys).	Hot workable. Hot extrusion.	These materials are usually easier to fabricate.

49.8.2.2 Conventional techniques

The γ-TiAl materials can be processed by, Ref. [49-25]:

- Ingot metallurgy: using techniques that provide ingots with low interstitial impurity concentrations, such as skull melting, vacuum arc melting, plasma melting.
- Casting: ingots, investment casting, permanent die moulding casting (gravity or centrifugal methods) to produce demonstrator near-net shape components, such as compressor or turbine blades, turbochargers, automobile exhaust valves. Porosity in castings is often consolidated by hot isostatic pressing (HIP).

- Hot working: either as single- or, more recently, multi-step processes:
    - forging: 'gatorising', isothermal or quasi-isothermal.
    - extrusion.
    - die forging.
- Hot working of cast products to provide wrought materials and semi-products is usually carried out between 1100°C and 1300°C to give a fine grain structure that can then be optimised by further heat treatment.
- Heat treatment: used to create a variety of microstructures and therefore mechanical properties, [See also: 49.6].
- Rolling:
    - sheet (<2mm thick)
    - foils (~100μm thick).
- Optimising rolling processes is imperative in order to produce sheet and foil of adequate sizes and quality (crack-free, reliable mechanical performance) for the intended structural components for hot surfaces of space vehicles.

49.8.2.3 Powder metallurgy (PM) techniques

Production of γ-TiAl materials by PM techniques is an attractive alternative to the ingot route, provided that the levels of interstitial elements (O, N, C, H) is strictly controlled. This has meant the use of clean room type facilities and improved consolidation techniques. The starting materials can be either, Ref. [49-25]:

- Prealloyed powders: produced by:
    - PREP (Plasma Rotating Electrode Process).
    - TGA (Ti Gas Atomisation Process).
- Blended elemental powders.

Processing techniques used to produce intermetallic phases are, Ref. [49-25]:

- Reactive sintering: prior to the consolidation process.
- Reactive hot isostatic pressing (HIP): during the consolidation process.

Hot working processes used for ingot metallurgy are also applied to HIPped prealloyed powders.

49.8.2.4 Sheet forming

Conventional metal forming techniques can be applied to γ-TiAl materials, provided that their deformation characteristics are fully considered. One-step sheet bending operations have been used to produce 500mm long 'hat' stiffener components in Ti-48Al-2Cr (near-γ) alloy, Ref. [49-25].

Depending on their composition, grain size and strain-rate, γ-TiAl materials exhibit superplasticity in the temperature range 800°C to 1300°C. Investigation of Ti-48Al-2Cr alloy sheets has shown that it can be superplastically formed (SPF) at temperatures <1000°C. This means that SPF facilities used for conventional titanium alloys can also be used for certain γ-TiAl materials, Ref. [49-25].

49.8.3 Joining

49.8.3.1 General

Since the intermetallics are intended for high-temperature service, joining techniques such as welding or diffusion bonding are more appropriate than adhesive bonding. Significant effort is being applied to developing techniques that can produce reliable, acceptable quality, durable joints. This is seen key to these material, especially aluminides, finding applications.

[See also: Chapter 58 for joining of high-temperature materials]

49.8.3.2 Welding

For γ-TiAl materials, methods that provide reliable joints exhibiting good mechanical performance, especially below the ductile-to-brittle transistion temperature (DBTT) have been evaluated, Ref. [49-25].

Owing to the relatively low ductility of the alloys, methods that minimise heat input, and therefore residual stresses are appropriate, such as 'CO_2 Laser Welding'. Preheating the work piece to above the DBTT is also required to obtain sufficient material ductility to accommodate thermal loads without cracking on cooling.

Other possible welding techniques that could prove suitable for TiAl are electron-beam (EB) and friction welding.

49.8.3.3 Brazing

High-temperature brazing can be an appropriate joining technique provided that the ductility of γ-TiAl materials is taken into account in the selection of a suitable processing temperature, Ref. [49-25].

49.8.3.4 Diffusion bonding

The ability to diffusion bond materials during SPF is as important for intermetallics as it is for all other materials. A γ-TiAl alloy (Ti-47Al-2Cr-0.2Si) has been successfully diffusion bonded at its SPF temperature, Ref. [49-25].

49.9 Further developments

49.9.1 Intermetallic compounds

49.9.1.1 General

Table 49.9.1 summarises some other intermetallic compounds, Ref. [49-14]. Refractory metal silicides ($MoSi_2$, $NbSi_2$) were not considered under the FESTIP programme due to their limited development, Ref. [49-23].

Table 49.9-1 - Further development: Intermetallic compounds

Group	Compound	Advantages	Disadvantages †
Aluminide	Nb_3Al	Melting point	Brittle Oxidation
	$NbAl_3$	Melting point Density	Brittle Oxidation
	$TiAl_3$	Density	Brittle
	Ti_2AlNb *	Oxidation $^{(1)}$ Creep $^{(1)}$ Ductility $^{(2)}$	[Not stated]
	$MoAl_3$	Melting point	Brittle Oxidation
Silicide	Ti_5Si_3	Density	Brittle
	Nb_5Si_3	Melting point	Brittle Oxidation
Berylide	Nb_2Be_{17}	Melting point	Brittle Oxidation
	$ZrBe_{13}$	Melting point	Brittle Oxidation

Key:
† Oxidation indicates modest resistance to oxygen.
* Orthorhombic phase
(1) compared with conventional near-α titanium alloys.
(2) compared with γ-TiAl.

49.9.1.2 Titanium aluminides

Of the aluminides, titanium-based compositions are undergoing significant further developments in chemical composition, processing and property characterisation, Ref. [49-23].

The main disadvantage of intermetallics is their brittleness. The orthorhombic titanium aluminides (based on the Ti_2AlNb compound) offer improved ductility at ambient temperatures, e.g. ~16%, depending on their microstructure, Ref. [49-19].

Oxidation resistance remains an important characteristic for the applications currently under consideration for intermetallics, i.e. in engines and spaceplanes. Those materials having ‘modest’ oxidation resistance require development of suitable protective coatings if they are to be used.

49.9.2 Intermetallic matrix composites (IMC)

Mainly owing to their ductility at ambient temperatures, orthorhombic titanium aluminides, based on Ti_2AlNb, are being considered for the matrix phase of SiC reinforced composite materials, Ref. [49-19].

[See: 49.10 – Intermetallic Matrix Composites]

49.9.3 Protective coatings

Multi-layer titanium aluminide coatings are under development for titanium-based materials. The aim is to improve the oxidation resistance of either conventional alloys or titanium matrix composites (TMC), Ref. [49-19]. These multi-layer coatings are applied by a magnetron sputtering technique, developed by DLR. They consist of, Ref. [49-19]:

- single layers: sequence of Ti_3Al, TiAl and $TiAl_3$,
- gradient coatings: continuously increasing Al-content towards the coating-environment interface.

Multi-layer coatings have demonstrated their effectiveness as oxidation protection for short-term high temperatures and long-term applications at temperatures up to 600°C, Ref. [49-19].

For high temperature applications (between 600°C and ~900°C), coatings based on τ-phase ($Ti_{25}Al_{67}Cr_8$) and two-phase γ-TiAl+Laves phase compositions were investigated. Of these, the chromium-containing coatings are undergoing further evaluation, Ref. [49-19].

49.10 Intermetallic matrix composites

49.10.1 General

The IMC materials could provide opportunities to save weight on components destined for high-temperature applications. Their potential role is:

- replacing conventional metals, which tend to be comparatively dense, such superalloys.
- extending the operational service temperatures, e.g. titanium-based materials.

There are on-going research and development studies aimed at establishing whether it is technically and economically viable.

49.10.2 Development

Higher specific properties can be obtained from intermetallic compounds if they are combined with a reinforcement to produce an intermetallic matrix composite (IMC).

Table 49.10.1 summarises the reinforcements and matrix material combinations, Ref. [49-4], [49-17], [49-18], [49-19], [49-26].

Table 49.10-1 - Intermetallic matrix composites: Summary of compounds and reinforcements

Matrix		Reinforcements
Nickel aluminides: [1]	NiAl Ni_3Al	SiC TiB_2 TiC C Al_2O_3
Titanium aluminides: **[2, 3]**	TiAl Ti_3Al	
	Ti_2AlNb **[4]**	**SiC [SCS-6]** **SiC [Sigma SM1140+]**
Iron aluminides:	FeAl	-
Niobium aluminides:	Nb_3Al $NbAl_3$	-

Key: [1] IC221/TiC particulate reinforcement. IC221/Al_2O_3 fibre reinforcement, Ref. [49-17].
[2] Ti_3Al + Nb/Al_2O_3 fibre reinforcement. These materials have comparable CTE values of $10x10^{-6}$, typically. Ref. [49-4].
[3] Ti_3Al + Nb/SiC fibre reinforcement, Ref. [49-18].
[4] Orthorhombic phase: Composition Ti-22Al-25Nb, Ref. [49-19] or Ti-25Al-25Nb, Ref. [49-26].

Of these, titanium aluminides are considered the most promising options. Initial studies covered TiAl and Ti3Al compounds which suffered from a number of problems, including, Ref. [49-26]:

- low ductility and toughness at RT.
- lack of ductility at the fibre-matrix interface.
- embrittlement when exposed to air at elevated temperatures.

More recent European work has concentrated on the Ti_2AlNb compound which offers improved property combinations at RT and elevated temperatures, Ref. [49-19], [49-26].

Table 49.10.2 lists the perceived requirements of a reinforcement for IMC materials, Ref. [49-4], [49-17]. These are very exacting, e.g. CTE matching between fibre and matrix, and it is likely that a compromise is needed to be reached in developing such fibres.

Table 49.10-2 - Intermetallic matrix composites: Requirements for a reinforcement fibre

Mechanical	High stiffness. High temperature.
Physical	High melting point. Low density. CTE to match matrix. Chemical compatibility. Good oxidation resistance.
Other	Ease of handling (spoolability). Capable of mass production.

49.10.3 High temperature Ti-based IMC

49.10.3.1 General

Long-term operation at temperatures >500°C cannot be achieved by conventional near-alpha titanium alloy MMC. For temperatures up to 700°C (long-term) or 1000°C (short-term) the key characteristics are, Ref. [49-19]:

- matrix high temperature properties,
- oxidation resistance,
- fibre-matrix interface stability,
- creep resistance of the matrix.

Additionally, the matrix requires a level of ductility at ambient temperatures in order the exploit the potential reinforcement strength. A brittle matrix phase, or brittle surface layers, drastically reduces the composite tensile properties, Ref. [49-19].

49.10.3.2 Matrix

In general terms, TiAl and Ti_3Al compounds exhibit a high modulus, ductilities <3% at ambient temperatures and high CTE. The composites produced with these matrices have high residual stresses that negate the benefit of the matrix oxidation resistance, Ref. [49-19].

Depending on the microstructure, orthorhombic phase Ti_2AlNb compounds can provide ductilities of up to 16% at RT, i.e. comparable with conventional near-α titanium alloys, but with improved oxidation and creep resistance, as shown in Figure 49.10.1, Ref. [49-19].

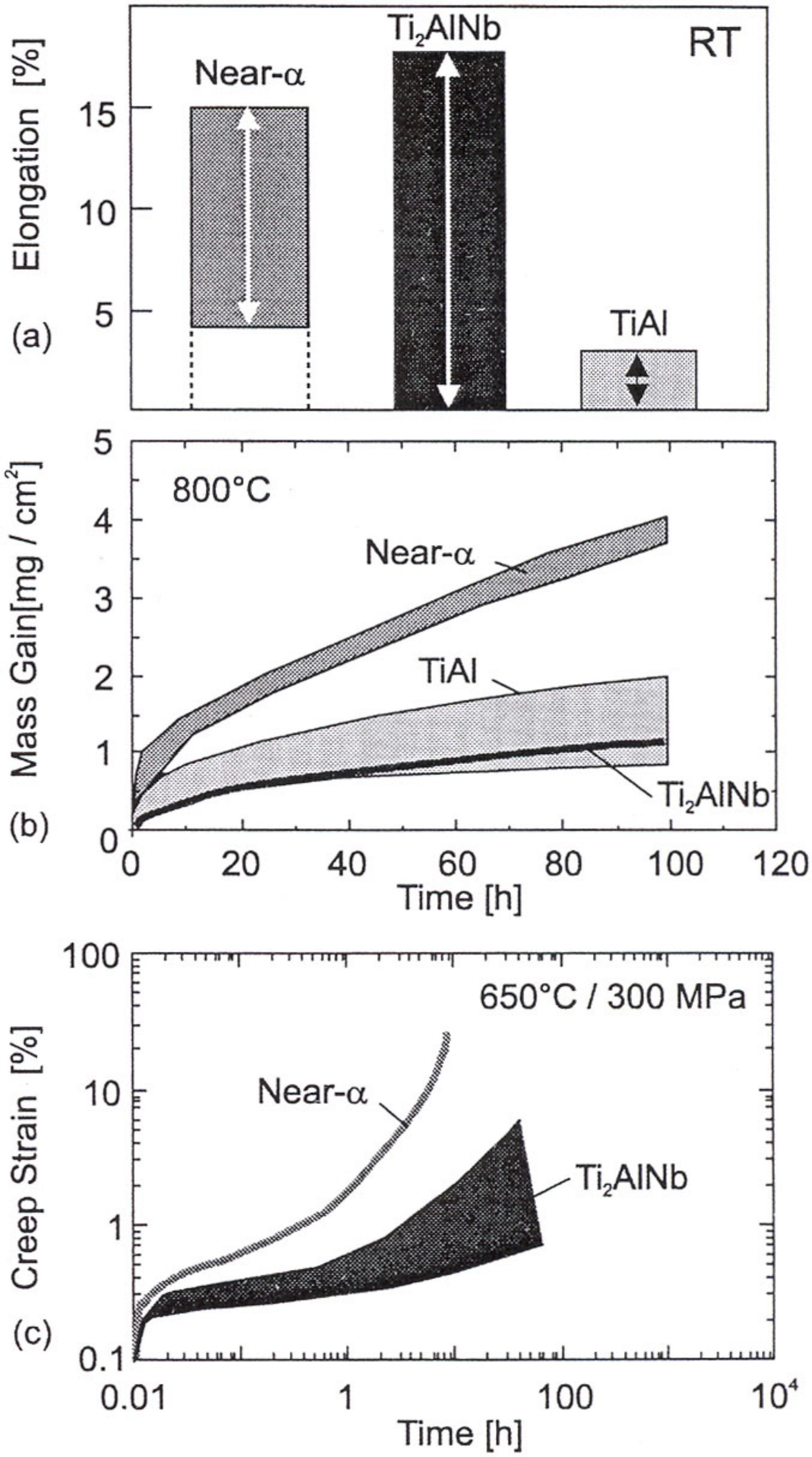


Figure 49.10-1 - Intermetallic matrix composites: Characteristics of orthorhombic phase titanium aluminide matrix

49.10.3.3 Reinforcement fibre

The development of orthorhombic TiAl matrix IMC has used SiC monofilaments, mainly because these have better chemical compatibility for Ti-based intermetallic matrices:

- 'standard grade' SCS-6 silicon carbide monofilament (140μm dia.). This fibre has also been evaluated in conventional titanium alloy matrix composites (TMC), Ref. [49-19].
- carbon-coated (4.5μm thick) Sigma SM1140+ SiC monofilament (100μm dia.), Ref. [49-26].

The inclusion of the reinforcement generally reduces the matrix ductility. This effect has been seen to be more severe for high monofilament diameters. The monofilament protective coating can be consumed during processing. Use of a thicker coating is seen to protect the fibre without strength loss, Ref. [49-26].

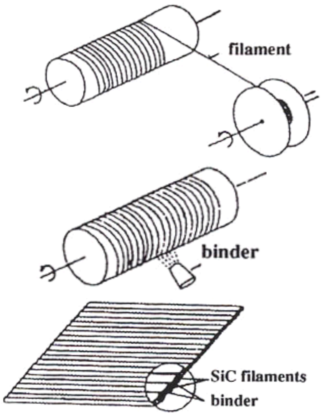
49.10.3.4 Processing

A magnetron sputtering method, developed as a fibre coating technique by DLR, was used to deposit the matrix. The as-processed matrix contains three ordered phases (α_2, β and orthorhombic), Ref. [49-19].

A 'foil-fibre-foil' technique, developed by Insamet, was used to produce lay-ups with 5 matrix foils (125μm thick) and 4 unidirectional reinforcement plies. These were then consolidated by hot pressing under vacuum.

Figure 49.10.2 summarises the various manufacturing steps, Ref. [49-26]. The consolidated composite contained three matrix phases (α_2, β_0 and orthorhombic), plus some unwanted carbides attributed to incomplete binder removal.

Monofilament winding



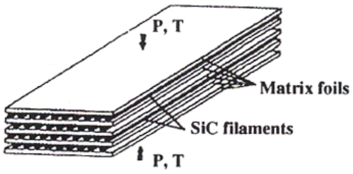
- Filament wound onto a mandrel.
- Winding pitch to give 35% volume fraction (taking into account foil thickness & monofilament diameter).

- Spray-applied polystyrene-based.
- Used to maintain monofilament spacing during ply cutting and lay-up stages.

Binder removed before consolidation, by typical heat-treatment: 400°C for 2 hrs.

⇩

Lay-up

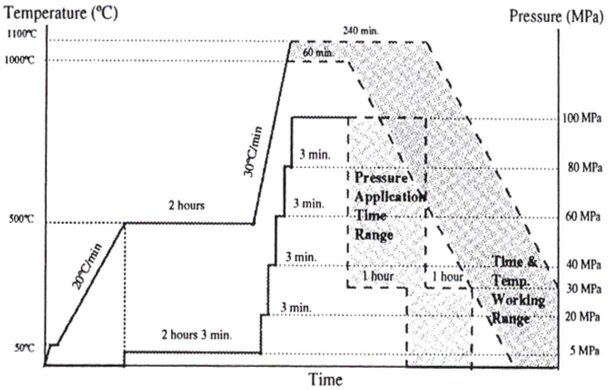


- Matrix foils cleaned and degreased.
- Chemical pickling (Kroll's reagent) to promote bonding.
- Alternate plies of reinforcement and matrix foils: 4-ply $[0]_4$ SM1140+/Ti-25Al-25Nb (35% volume fraction).

Reinforcemnt direction corresponds to rolling direction of matrix foil.

⇩

Consolidation



- Graphite mould (lower cost, easily machined & less reactive with matrix than Ni-, Cr- or Co-based high-temperature mould materials).
- Thin boron nitride layer applied to mould surface (to prevent chemical reaction between matrix and mould).
- Typical processing conditions for 'acceptable' composite: 1050°C, 100MPa, 2 hrs.
- Post-consolidation slow cooling (5°C/min) to 650°C to relax residual stresses forming at the reinforcement/matrix interface.

'Acceptable' composite: fully densified, good bonding with <0.5μm matrix/reinforcement reaction zone.

Figure 49.10-2 - Intermetallic matrix composites: TiAl/SiC composite - Insamet 'foil-fibre-foil' processing steps

The effect of processing parameters (temperature, pressure, time) on composite consolidation were investigated and can be summarised as, Ref. [49-26]:

- Temperature: Between 1000 to 1100°C (under β-transus) was selected to be high enough to produce acceptable matrix flow, but as low as possible to limit oxygen contamination and deleterious chemical reactions.
- A reaction zone ≥1μm can seriously affect mechanical performance, whereas >0.5μm can be beneficial. Highly reactive matrix phases could require lower thickness reaction zones.

- Pressure: 100MPa is high enough to enable acceptable matrix flow, but low enough to limit reinforcement damage and movement of the reinforcement.
- A gradual pressure increase was used to prevent damage to the reinforcement or graphite mould.
- Time: Between 1 to 4 hrs, related to temperature and pressure including a 2hr isothermal (400°C or 500°C) binder removal step. Post-consolidation slow cooling enables relaxation of residual stresses (at the filament-matrix interface).

Proper binder removal is essential to avoid incorrect composite consolidation or formation of brittle phases at reinforcement-matrix interfaces.

49.10.3.5 Composite properties

A tensile strength at RT of up to 2080MPa gives a broad indication of the mechanical performance possible for SCS-6/Ti-22Al-25Nb composite, produced by the sputtering method, Ref. [49-19].

For 4-ply $[0]_4$ SM1140+/Ti-25Al-25Nb composites (35% volume fraction), three-point bend tests provided some preliminary values from the processing study, Ref. [49-26]:

- Flexural modulus: 120 GPa
- Maximum stress: 1700 MPa

The flexural modulus was considered to be lower than expected due to the incomplete binder removal causing formation of carbides and reducing load transfer from the matrix to the reinforcement.

Published mechanical property data is limited.

49.11 Intermetallics: Potential applications

49.11.1 General

Of the original groups of intermetallics (Ni-, Fe- and Ti-based), titanium aluminides are approaching the position where they can compete with superalloys by offering weight reductions, and titanium for elevated temperature applications.

The temperature ranges in which Ti-based intermetallics can compete with conventional materials on specific strength is shown in Figure 49.11.1, Ref. [49-19].

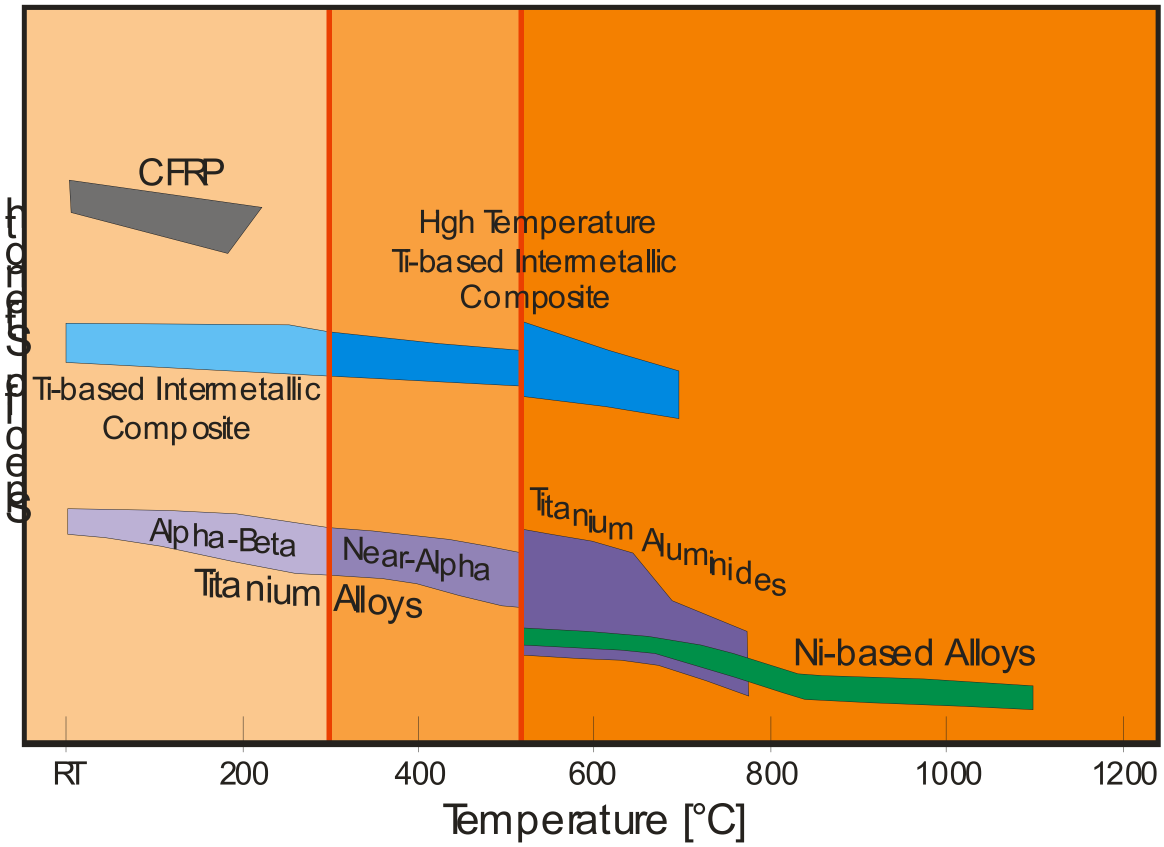


Figure 49.11-1 - Intermetallics: Potential applications - Elevated temperature specific strengths of materials

The specific strength advantages of TiAl could replace some superalloys in compressor components, and their high-temperature properties could have similar results in other engine parts. For example, Ref. [49-22]:

- A demonstrator centrifugal compressor diffuser made of Ti-48Al-2Nb-2Cr to replace IN718 provided a 45% weight saving.
- The US Joint Technology Advanced Gas Generator (JTAGG) included a γ-TiAl diffuser.
- In other US programmes, a target 80% increase in power-to-weight ratio and a 30% reduction in specific fuel consumption, implies the use of titanium aluminides if this is to be achieved
- The increase the operating speed and temperature of turbine disks at both the rim and the bore continues. The major US and European engine manufacturers are conducting independent assessments of titanium aluminides for such uses, Ref. [49-20].

Orthorhombic titanium aluminide could prove to be a significant material for these applications.

49.11.2 Spaceplanes

Initially, the majority of intermetallic developments were in the USA. This largely used NASP development programmes to progress the technology of these materials. Work continues under the various X-programme vehicles.

In Europe, international and national-based spaceplane development studies, including FESTIP, have also concentrated on the group of titanium aluminides for high temperature applications. For example:

- γ-TiAl Alloys: for outer skin structures (up to 800°C). Demonstrator components, as shown in Figure 49.11.2 have been manufactured by Plansee (Austria), Ref. [49-21].
- TiAl matrix composites: SiC filament reinforced orthorhombic titanium aluminide, Ref. [49-19], [49-25].
- Multi-layer TiAl protective coatings: on conventional titanium alloys and TMCs, Ref. [49-19].

Figure 49.11-2 - Intermetallics: Potential applications - Outer skin structures for space applications

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50 Refractory and precious metals

50.1 Introduction

This chapter provides a basic description of the 'Refractory Metals' and 'Precious Metal Group' (PMG). They all have high melting points (1800°C to 3500°C) and are of primary interest for propulsion systems and thin film protective coatings.

[See also: Chapter 74 for protective coatings]

50.2 Materials

50.2.1 General

The key materials are:

- Platinum
- Rhodium
- Iridium
- Rhenium
- Molybdenum
- Tungsten
- Tantalum
- Niobium

50.2.2 Characteristics

The materials are of interest for such characteristics as:

- very high thermal stability.
- inertness.
- oxidation resistance.
- corrosion resistance.

The materials listed have these characteristics to varying degrees, with some being better than others. They all have high densities. Table 50.2.1 identifies their main features.

Table 50.2-1 - Refractory and precious metals: Attributes and disadvantages

Metal	Attributes	Disadvantages
Niobium (Nb)	Ductile High melting point	Modest oxidation resistance
Molybdenum (Mo)	Ductile High melting point	Modest oxidation resistance
Tantalum (Ta)	Ductile Very high melting point Good thermal conductivity	Modest oxidation resistance
Rhenium (Re)	Ductile Very high melting point High strength	Modest oxidation resistance High density
Tungsten (W)	Ductile Very high melting point High thermal conductivity High strength	Brittle below 400°C High density
Platinum (Pt)	Ductile Very oxidation resistant	Expensive High density
Rhodium (Rh)	High thermal conductivity High strength	Very expensive
Iridium (Ir)	Very oxidation resistant Ductile High strength High melting point	Expensive High density

50.2.3 Basic properties

Table 50.2.2 lists the basic properties of the refractory and precious metals group. Pt-Rh compositions are used for thermocouples.

Table 50.2-2 - Refractory and precious metals: Basic physical properties

Metal	Density $(kg\ m^{-3})$	Melting Point (°C)	CTE $(10^{-6}\,°C^{-1})$	Thermal Conductivity † $(W\ m^{-1}\,°C^{-1})$
Niobium (Nb)	8570	2468	7.2	53.7
Molybdenum (Mo)	10220	2617	5.1	138
Tantalum (Ta)	16600	2996	6.5	57.4
Rhenium (Re)	21000	3180	6.6	48.0
Tungsten (W)	19300	3410	4.5	173
Platinum (Pt) ‡	21450	1772	9.0	71.6
Rhodium (Rh) ‡	12400	1965	8.5	150
Iridium (Ir) ‡	22400	2410	6.8	147

Key †: Indicative properties at room temperature.
‡: Precious Metals Group

50.2.4 Alloys

The metals are used in alloy form. Common examples are shown in Table 50.2.3.

Table 50.2-3 - Refractory metal alloys: Examples

Composition	Alloy
Nb-10Hf-1Ti	C-103 for Thrusters
Nb-10W-10Hf-0.1Y	C-129Y
Mo-0.5Ti-0.02C	Alloy 362
Mo-1Ti-0.3Zr	TZC
Mo-0.5Ti-0.1Zr	TZM
Ta-2.5W	Tantaloy 63
Ta-7.5W	Tantaloy 61
Ta-10W	Tantaloy 60

50.3 Applications

For space applications, refractory and precious metals are principally used for:

- Propulsion system items (hot gas environment), and
- Thin films, i.e. protective and inert coatings.

The combination of good thermal conductivity and very high temperature stability continues to dictate the use of these materials in close proximity to hot gas streams within propulsion systems. Their very high densities remain a restricting factor and so precludes them from structures.

[See: Chapter 48 for coatings applied to superalloys; Chapter 74 for protective coatings]

51 Beryllium

51.1 Introduction

As a structural material, beryllium has a number of highly desirable characteristics. These are, however, offset by some significant disadvantages. This has left beryllium as an under-utilised material requiring specialist expertise and facilities.

This chapter describes the characteristics of the various beryllium grades, along with typical property data. The effect of temperature on both mechanical and physical properties is given.

Comments on the safety aspects of working with beryllium are summarised, along with a list of European organisations with expertise in the fabrication of beryllium structures.

For design data, refer to MIL-HDBK-5, Ref. [51-4].

51.2 Characteristics

51.2.1 Features

Table 51.2.1 summarises the advantages and problems associated with using beryllium.

Table 51.2-1 - Beryllium: Characteristics

Attributes	Limitations
Low density: 1860 kg/m^3 Exceptional strength & stiffness: E = 303 GPa. High temperature stability Excellent electrical & thermal conductivity Low coefficient of thermal expansion	Brittleness Notch sensitivity Modest fracture toughness Toxicity of beryllium oxide

51.2.2 Applications

The attributes indicate suitability for applications requiring:

- dimensional stability,
- rigidity, and
- thermal resistance.

The limitations imply:

- damage intolerance,
- joining problems, and
- uncertainty on structural integrity.

Successful applications show that these disadvantages can be overcome. The toxicity issue is resolved by using dedicated machining facilities.

51.3 Products and facilities

51.3.1 Source

All beryllium material products originate from a single source: Brush Wellman Inc., USA.

51.3.2 Materials

51.3.2.1 Processes

- Hot-pressed powders: The majority of grades can be subsequently worked.
- Casting from melts is also feasible.
- Metal working, to achieve the required final product form, e.g.:
    - rolling,
    - extrusion,
    - forging,
    - forming, or
    - machining.

51.3.3 Grades

Table 51.3.1 shows available beryllium grades, optimised for specific applications.

Table 51.3-1 – Beryllium: Grades

Grade	Quality	Production
S-200-E	Standard	Hot pressed
S-200-F		Vacuum hot pressed (VHP)
S-200-FH		Hot isostatic pressed (HIP)
SR-200-E	Sheet	VHP & Hot rolled
S-65	Structural (ductility)	Hot pressed
O-50	Optical (isotropic)	HIP (high density)
I-70		Hot pressed
I-220	Instrument (stability)	Hot pressed
I-400		Hot pressed
PF-10	Foil (purity)	Hot pressed & rolled to <3mm
PF-60	Foil	Hot pressed & rolled to <3mm
B-26-D	Casting	Vacuum melted
SP-200F	Structural †	Impact grinding
SP-65	High purity †	
IP-70	Optical †	
Beryl-coat	Corrosion resistance	Coating of Be

Key † Powder

Certain properties can be selectively enhanced, e.g.:

- ductility,
- isotropy,
- stiffness,
- purity,
- thermal or dimensional stability.

51.3.4 Fabrication

51.3.4.1 General

Various points can be made to clarify aspects of beryllium technology:

- The properties of powder-based beryllium are influenced by particle size, oxide content and impurities.
- Vacuum hot pressing is the principal form of powder consolidation with hot isostatic pressing (HIP) used for high-purity grades to minimise porosity.
- Machining of beryllium requires precision and sharp cutting tools to avoid surface damage.
- Machining is undertaken in a clean environment to avoid material contamination and to restrict the toxic material.
- To avoid mechanical damage, electrical discharge machining (EDM) or electro-chemical milling (ECM) can be used for cutting.

- Machined beryllium is always etched to remove a surface layer (0.1 to 0.25 mm) to eliminate surface defects.
- Beryllium can be worked by hot forming, preferably by bending and rolling, which utilise compressive rather than tensile stresses.
- Brazing is an accepted form of joining, with aluminium as the principal braze material. Zinc and silver can also be used.
- A completed beryllium assembly can be coated (Beryl-coat) to provide corrosion protection and seal the surface oxide.
- A size restriction of 1.2 m^2 exists on material obtainable in hot pressed form.
- Beryllium products are sensitive to machining induced surface damage, i.e. possible sources of fracture initiation.

51.3.4.2 Facilities

In the USA, the major source is Brush Wellman. Within Europe, organisations with expertise in Beryllium are:

- W. C. Heraeus (D):
- SAGEM (F):

51.3.4.3 Joining

Mechanical fastening can be used for joining despite the weaknesses that machined holes induce in the material. Brazing and adhesive bonding have been successfully applied.

51.4 Properties

51.4.1 Influence of microstructure

The properties of beryllium grades are principally determined by the microstructure, in particular:

- grain size,
- oxide content

Two parameters dominate:

- Yield strength and elongation (ductility) increase as grain size diminishes, with dependence on $(\text{grain size})^{-½}$
- Increased dispersed oxide content improves the micro-yield strength, i.e. the stress required to produce the first permanent strain of 1×10^{-6} or 1×10^{-4} %.

51.4.2 Grades

There are three basic grades of beryllium:

- Structural.
- Optical.
- Instrument.

51.4.3 Mechanical properties

Table 51.4.1 provides mechanical data on a range of beryllium grades.

- Structural grades: S200-E, S200-F and S-65 are widely used. Sheet grade SR-200-E exhibits high strengths and ductility.
- Instrument grades: Use both fine grain and highly dispersed oxide content to ensure high micro-yield strengths. I-220 and I-400 are the most recognised grades.
- Optical grades: e.g. I-70, are a high purity composition and hot pressed to give an isotropic material.

Table 51.4-1 - Beryllium grades: Composition and tensile properties

Grade	**Composition**			**Tensile Properties**			**Note**
	Be (min)	BeO (max)	Bal.	UTS (MPa)	YS (MPa)	Elong (%)	
S-200-E	98.0	2.0	<0.2	276	207	1	-
S-200-F	98.5	1.5	<0.2	325	242	2	Standard Quality
S-65	99.0	1.0	<0.1	290	207	3	High ductility
I-70	99.0	0.7	<0.2	242	173	2	High purity
I-220	98.0	2.2	<0.2	380	276	2	High stability
I-400	94.0	4.3	<0.3	346	-	-	Regular or selected grade
SR-200-E	98.0	2.0	<0.2	484	346	10	Sheet ≤7mm

51.4.4 Effect of temperature

51.4.4.1 General

Beryllium has a melting point of 1285°C, which is not particularly high, but despite this it is used in high-temperature (to 760°C) applications for its excellent thermal conductivity and heat capacity.

51.4.4.2 Mechanical properties

For high-temperature applications, the residual mechanical properties of beryllium should be established. As with all metals, properties are also dependent on the thermal and mechanical working history. Table 51.4.2 and Figure 51.4.1, Figure 51.4.2 and Figure 51.4.3 indicate mechanical property changes over the temperature range -200°C to +800°C.

Table 51.4-2 - Beryllium grades S-200-F and SR-200-E: Mechanical properties at various temperatures

Temp	YS	TS	D	Creep Strength (MPa)		
(°C)	(MPa)	(MPa)	(%)	0.2%/3min	0.5%/3min	1.0%/3min
-200	240 [345]	324 [483]	0.5 [0.5]	- [-]	- [-]	- [-]
-150	240 [345]	324 [483]	1.2 [1.2]	- [-]	- [-]	- [-]
-100	240 [345]	324 [483]	2 [2]	- [-]	- [-]	- [-]
-50	240 [345]	324 [483]	2 [5]	- [-]	- [-]	- [-]
0	240 [345]	324 [483]	2 [5]	- [-]	- [-]	- [-]
RT	240 [345]	324 [483]	2 [10]	- [-]	- [-]	- [-]
100	237 [-]	308 [-]	- [-]	- [-]	- [-]	- [-]
200	230 [310]	290 [420]	- [-]	- [-]	- [-]	- [-]
300	208 [-]	248 [-]	- [-]	- [-]	- [-]	- [-]
400	178 [240]	210 [305]	- [-]	- [-]	- [-]	- [-]
500	142 [-]	168 [-]	- [-]	- [-]	- [-]	160 [-]
550	124 [-]	144 [-]	- [-]	- [-]	- [-]	105 [-]
600	102 [140]	115 [170]	- [-]	40 [-]	55 [-]	80 [-]
650	80 [-]	95 [-]	- [-]	30 [-]	38 [-]	50 [-]
700	58 [-]	60 [-]	- [-]	16 [-]	22 [-]	32 [-]
750	30 [-]	30 [-]	- [-]	8 [-]	10 [-]	18 [-]
800	<10 [-]	<10 [-]	- [-]	- [-]	- [-]	5 [-]

Key YS: Yield Strength; TS: Tensile Strength; D: Ductility
Data for SR-200-F; [Data for SR-200-E]

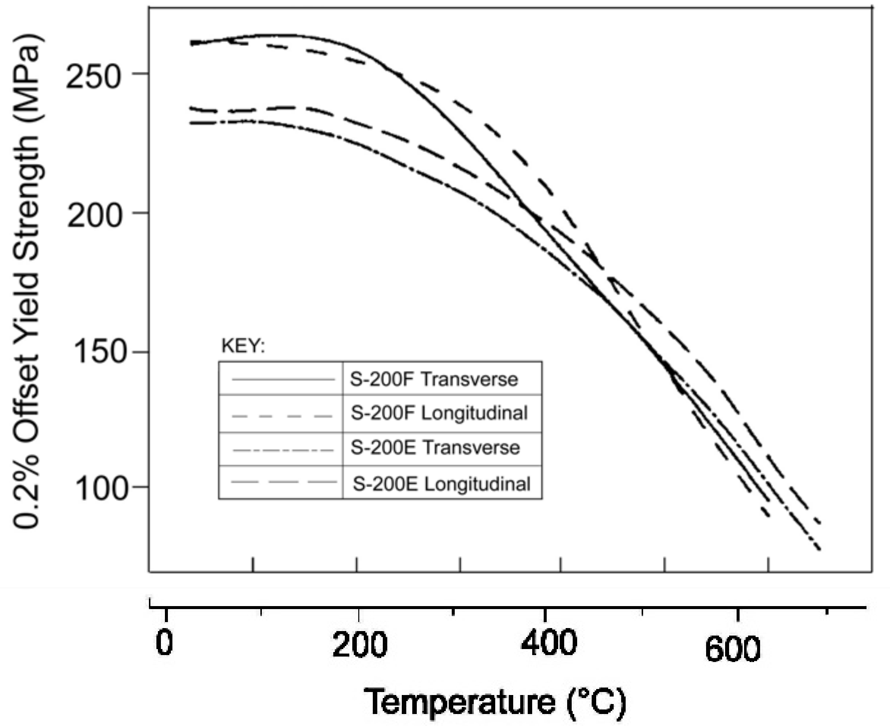


Figure 51.4-1 - Beryllium S-200 grades: Effect of temperature on 0.2% yield strength

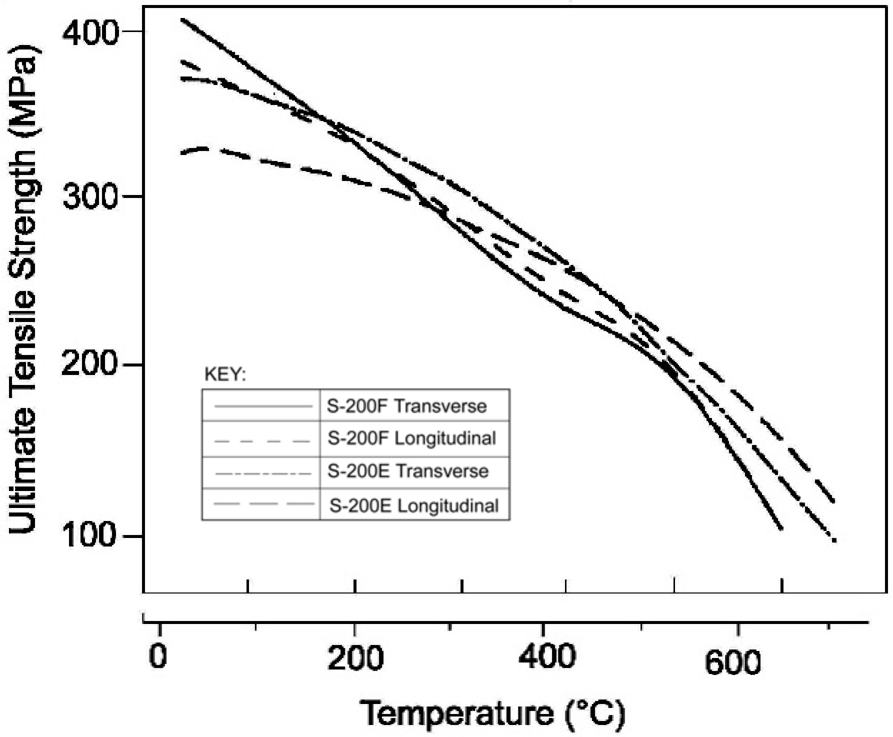


Figure 51.4-2 - Beryllium S-200 grades: Effect of temperature on ultimate tensile strength

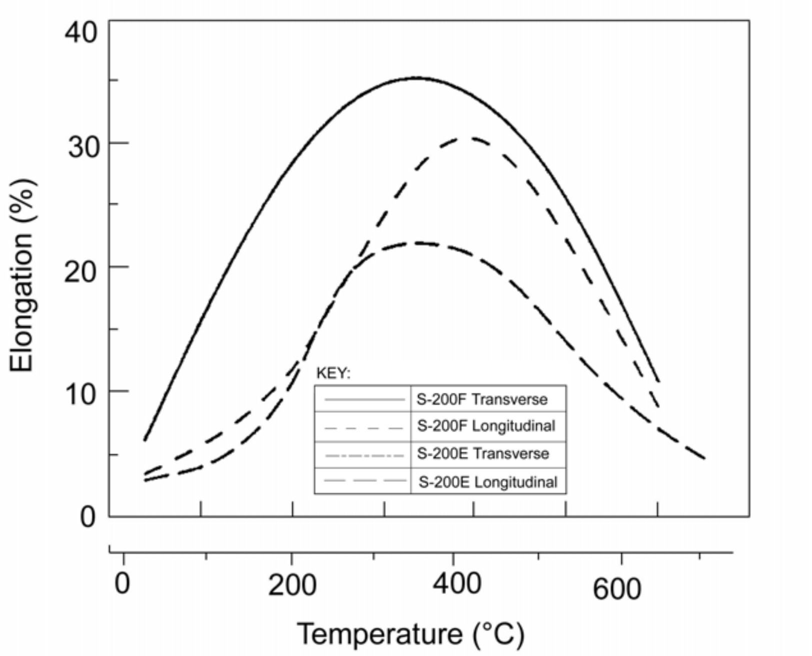


Figure 51.4-3 - Beryllium S-200 grades: Effect of temperature on elongation

51.4.4.3 Physical properties

Table 51.4.3, Figure 51.4.4, Figure 51.4.5, Figure 51.4.6 and Figure 51.4.7 show how the physical properties vary with temperature, which are important for thermal management.

Table 51.4-3 - Beryllium: Effect of temperature on modulus and physical properties

Temp (°C)	**Property**					
	CTE (10^{-6}/°C)		**Specific Heat** (J/kg/°C)	**Thermal Conductivity** (W/m/°C)	**Thermal Diffusivity** (m^2/s)	**Tensile Modulus** (GPa)
	Differential	Linear				
-200	0.2	5089	293	1500	-	300
-150	1.9	7.32	419	830	-	300
-100	4.5	7.74	1004	480	-	300
-50	7.5	8.98	1298	310	-	300
0	10.0	9.95	1694	240	-	300
RT	10.2	-	2009	200	-	300
100	11.6	-	2135	163	0.15	297
200	12.75	-	2386	141	0.12	291
300	13.6	-	2553	127	0.10	283
400	14.3	-	2679	116	0.09	268
500	14.8	-	2763	107	0.08	242
600	15.25	-	2846	98	0.07	180
700	15.55	-	2930	89	0.06	(80)
800	15.8	-	3014	80	0.05	(40)

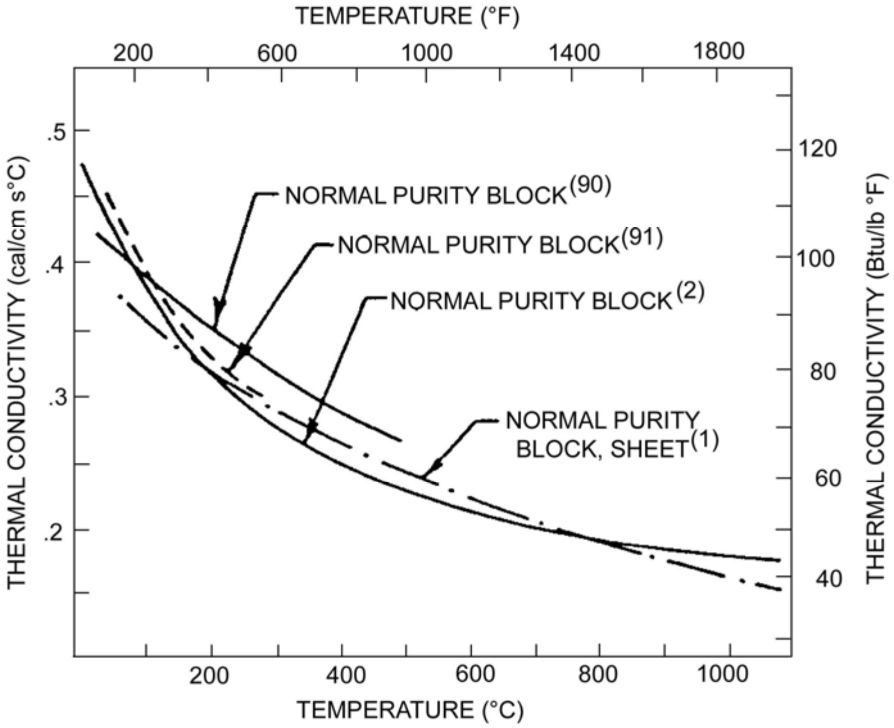


Figure 51.4-4 - Beryllium: Effect of temperature on thermal conductivity

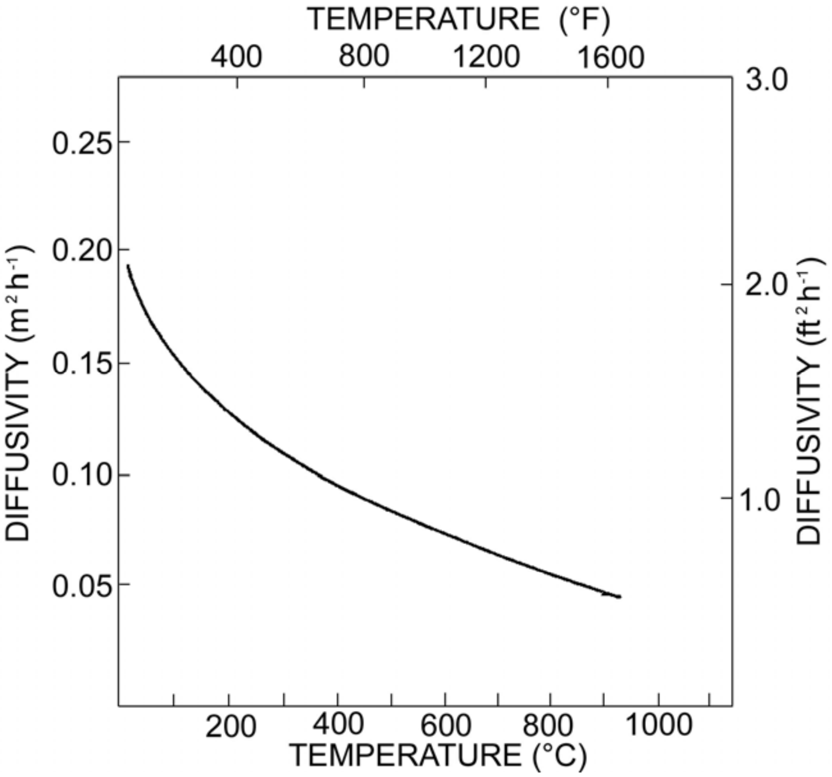


Figure 51.4-5 - Beryllium: Effect of temperature on diffusivity

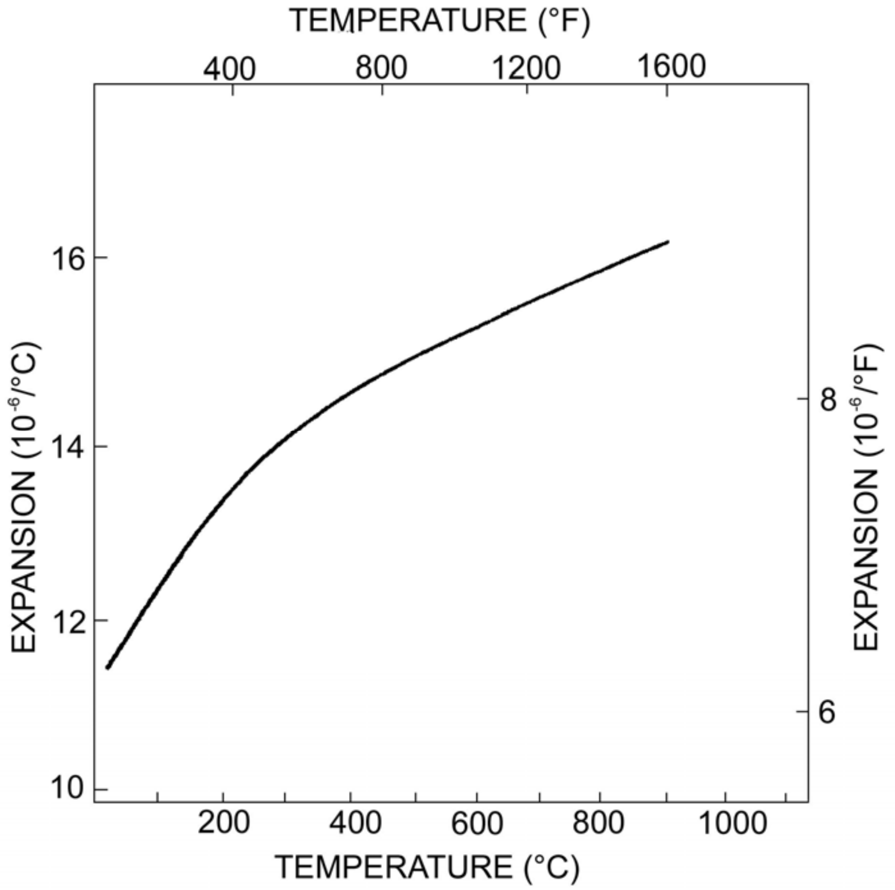


Figure 51.4-6 - Beryllium: Effect of temperature on expansion

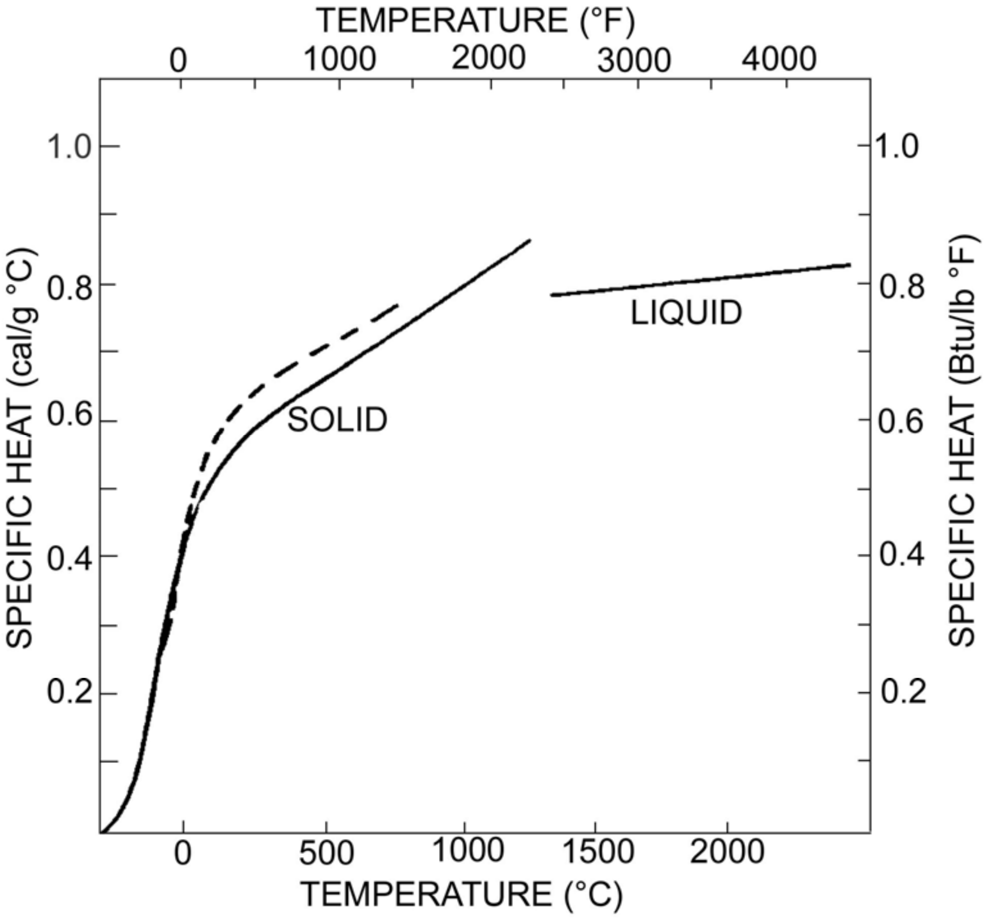


Figure 51.4-7 - Beryllium: Effect of temperature on specific heat capacity

51.4.4.4 Corrosion

Finished beryllium components are normally varnished to seal the surface. This provides corrosion protection and a moisture barrier.

51.5 Health and safety

51.5.1 Facilities

The machining and handling of beryllium needs to be undertaken in dedicated facilities and with protection for personnel against beryllium oxide, which is a hazardous, toxic material.

51.5.2 Health aspects

Long-term exposure increases the risk of contracting `berylliosis'. Inhalation of beryllium and beryllium oxide dust is the most hazardous form of contact. Handling beryllium parts is safe, providing direct contact with the skin is avoided through the use of gloves.

51.5.3 Extraction

Machine shops require separate ventilation and filtering systems with localised extraction to capture aerosols and fumes. Machining is generally performed under wet conditions, to minimise powder particles entering the air. Regulatory exposure limits are defined for operatives working with beryllium.

51.6 Potential applications

51.6.1 Resumé

Beryllium is under-utilised despite its obvious stiffness-to-weight advantage over other materials. The necessity for dedicated manufacturing capabilities to contain the perceived health hazard remains an inhibiting factor. However, the expanding use of so-called 'brittle' materials can help in overcoming its traditionally perceived weakness of being a damage intolerant engineering material.

51.7 References

51.7.1 General

[51-1] D.P. Bashford
'Guidelines for the Use of Beryllium in Spacecraft Applications'
Fulmer Research Report R878/4A/January 1982
ESTEC Contract 4389/80/NL/AK(SC)

[51-2] Interatom
'Beryllium - Thermal Protection Technology (TPT)'
Final Report. May 1991. ESTEC Contract 8824/90/NL/PP

[51-3] T.E.H. Leman & W.R. Newell
'A Study on the Structural Applications of Beryllium'
British Aircraft Corporation, 1974
ESRO Contractor Report CR-209. ESTEC Contract No. 1553/71

[51-4] MIL-HDBK-5F: Metallic Materials and Elements for Aerospace Vehicle Structures
Vol. 1 & 2. November 1990

52 Ceramic matrix composites

52.1 Introduction

Ceramic matrix composites form two main groups:

- Continuous fibre reinforcements.
- Whisker reinforced.

Various combinations of reinforcement and matrix have been assessed, and continue to be studied. This chapter summarises the materials under development, along with a discussion of the properties and how these are influenced by the high-temperature, often oxidising, operational conditions.

The manufacturing processes used are presented because they influence the material characteristics. Whilst silicon carbide fibre reinforced silicon carbide composite (SiC-SiC) were the first group to become commercially available, interest has moved to carbon fibre reinforced silicon carbide (C-SiC) composites. This is largely due to their potential applications for the hot structures of reuseable launch vehicles (RLVs) in areas where the temperature exceeds 1200°C, i.e. with carbon-carbon (C-C) materials, [See: Chapter 54]. SiC-SiC remains an option for lower temperatures, Ref. [52-61].

The characteristics of development materials are likely to change.

52.2 Continuous fibre composites

52.2.1 Matrix groups

52.2.1.1 General

The prospective matrices are described by generic groups which define the principal constituent, but do not take into account any modifying elements or compounds. The main options are:

- carbides.
- nitrides.
- oxides.

Oxides appear to be preferable for use in oxidising environments.

[See also: Chapter 54 for carbon fibre reinforced carbon matrix (C-C) composites]

52.2.1.2 Silicon carbide

SiC is attractive for the thermal stability offered and is, in theory, capable of operating to 1650°C whilst retaining strength. The carbide forms a thin protective oxide layer in oxidising environments to prevent further gross oxidation. It is very hard, and has excellent erosion and corrosion resistance. Its thermal conductivity is greater than that of Si_3N_4 or Al_2O_3.

Technology studies have examined the technical feasibility and cost effectiveness of various processing methods compared with previously used CVI technique.

The main processing methods can be grouped as, Ref. [52-61]:

- gas phase infiltration.
- liquid phase infiltration (prepreg technology).
- liquid silicon impregnation.
- solid state processing (sintering).

[See: 52.3]

52.2.1.3 Silicon nitride

Si_3N_4 possesses marginally poorer thermal stability than SiC. However, unreinforced powder-based Si_3N_4 shows greater strength and toughness than its powder-based SiC counterpart. In addition, its thermal shock resistance is better than that of SiC, not least because the coefficient of thermal expansion is lower. That said, the issue is somewhat confused in the case of composites, as continuous reinforced Si_3N_4 has been made by three routes. These are:

- Pressureless Reaction Bonded (RBSN)
- Hot Pressed Powder (Si3N4, with sintering aids)
- CVI/CVD

The RSBN can be formed at 1450°C by nitriding silicon powder, whilst the hot pressed Si_3N_4 requires 1750°C. The RSBN tends to pose problems with excessive porosity if fibres are present, and the hot pressed powder gives poorer thermal stability as sintering aids are added. This leaves Si_3N_4 prepared by chemical vapour reactions as offering a matrix with reasonable stability provided by compositional control.

52.2.1.4 Alumina

Alumina is promoted on the grounds that it is an oxide with good thermal stability. The main drawback of alumina as a matrix is brittleness and the difficulties in toughening the material with reinforcements, such that thermal shock does not result in catastrophic failure. The tendency has been to include additional compounds, such as silica, to provide better fracture characteristics but which reduce thermal capabilities. To date, alumina matrices with continuous fibres have been prepared by CVI and Sol Gel technology. The amount of work done on these routes has been modest.

52.2.1.5 Zirconia

Only a modest amount of work has been devoted to composites prepared by Sol Gel and Hot Pressing routes. In the powder-based monolithic form, zirconia is noted for its toughness in the partially stabilised (PSZ) and transformation toughened (TTZ) forms. The toughness is modest at temperatures up to 1000°C. This is a matrix with potential, rather than proven, capabilities beyond 1000°C.

52.2.1.6 Other nitrides and carbides

BN, TiC, B_4C and AlN have been tried as matrices, but not developed. They may have supporting roles as:

- BN: Soft ceramic fibre coatings
- TiC and B_4C: Very hard ceramics with good abrasion and erosion resistance.
- AlN: Hard ceramic with good thermal conductivity and the ability to form a stable surface oxide.

52.2.2 Composite development

The development of continuous fibre Ceramic Matrix Composites (CMC) has centred on the groups shown in Figure 52.2.1.

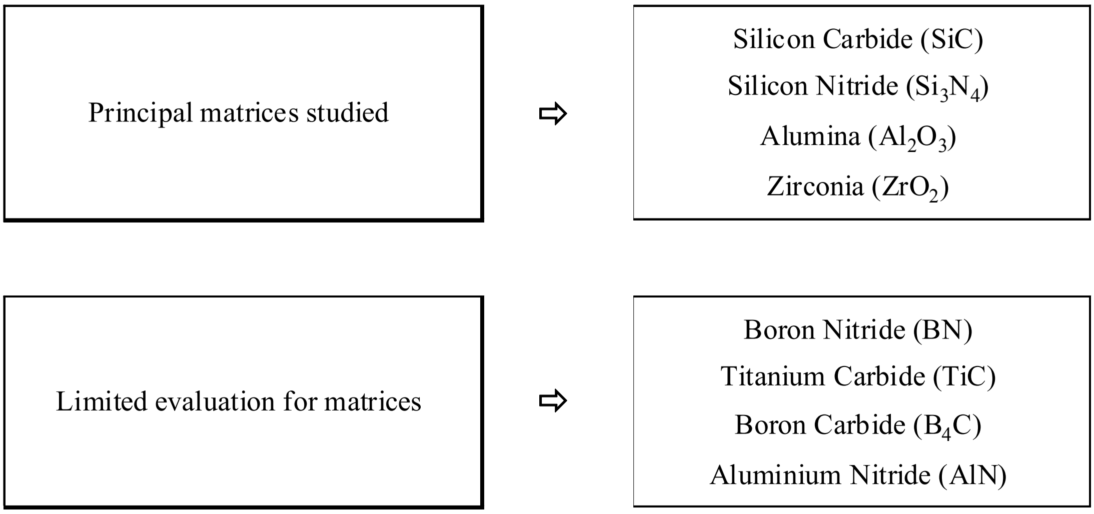


Figure 52.2-1 - CMC composite development

As a resumé of the work undertaken on continuous fibre composites, Table 52.2.1 identifies the main fibre/matrix combinations and those organisations undertaking the work.

Table 52.2-1 - Ceramic matrix composites: Fibre and matrix combinations with sources of development/investigation

Reinforcement	Matrix	Source [Ref.]	Comments
Carbon fibres SiC fibres	SiC	SEP, France. Ref. 52 [1 to 10]	C-SiC & SiC-SiC traded as SEPCARBINOX & CERASEP. Produced by CVI techniques. SEP has the most advanced production capability in the world. Their ceramic matrix composites are applied to a wide range of propulsion units & thermal protection systems for space vehicles. Reasonable property data available. Technology licensed to DuPont.
SiC (Nicalon yarns)	SiC	ORNL, USA. Ref. 52 [11 to 20]	CVI techniques for infiltrating SiC into Nicalon fabrics. Work has concentrated on reducing processing times. Limited mechanical property data available. Pyrolytic graphite coating on fibres prevalent. There is a commercial link with Babcock & Wilcox. Proposed uses in heat exchangers, turbine engines & Space Power Systems (SDI).
Carbon, Nicalon, Alumina fibres (Saffil)	SiC	Refractory Composites Inc., USA. Ref. 52 [21,22]	RECOMP-201 for the C-SiC version. Nicalon fabrics form the principle SiC reinforcement. Published papers by RCI are scarce. Work supported by USA Department of Energy.
Carbon, Nicalon, Nextel 312	SiC	Thermo Electron Corp., USA. Ref. 52 [23,24]	A range of composites prepared by CVI/CVD, including SICONEX ™3M, with Nextel fibres. Intended use in a combustion environment at 1450°C. Tungsten coating included.
Nextel 312	SiC	3M Co & Amercom, USA. Ref. 52 [25]	SICONEX composite produced by CVI/CVD. Amercom have interests in Thermal Protection Systems for space vehicles.
SiC monofilament	Si_3N_4 or RSBN	NASA-Lewis Research Center, USA. Ref. 52 [26]	AVCO SCS-6 derivative fibre used. Composites formed by reaction bonding (nitriding) silicon powder/fibre compacts; giving composites of high porosity (30 to 40% of matrix). Fibre volume fractions up to 40% possible.
SiC monofilament	RSBN	Norton Co., USA. Ref. 52 [27]	AVCO SCS-2 & SCS-6 monofilaments used. SCS-6 with the thicker carbon-rich SiC outer coating gave the highest strength. Processed at 1450°C.
SiC monofilament	Si_3N_4 direct from powder	Battelle Columbus, USA. Ref. 52 [28]	Commercial grade Si_3N_4 powder with 8wt.% Y_2O_3 & 4wt.% Al_2O_3 as sintering aids. Slurry coating & filament winding used followed by hot pressing at 1750°C, under vacuum.
SiC (Nicalon yarn fabric)	Si_3N_4	ORNL, USA. Ref. 52 [14]	Initial work on CVI processing.

Reinforcement	Matrix	Source [Ref.]	Comments
Alumina-based fibres: AB-312 [3M], Saffil [ICI], FP [DuPont], α-Al_2O_3	Alumina (Al_2O_3)	SEP, France. Ref. 52 [29]	CVI processing route. α-Al_2O_3 fibres gave the best results. Brittleness proved a problem, owing to good fibre:matrix bonding. Interface modifications needed to improve toughness.
Nicalon fabric Alumina (Saffil) Zirconia fibres (ZrO_2)	Al_2O_3	University of Florida, Ceramics Division, USA. Ref. 52 [30]	Preliminary processing by Sol-Gel route with high temperature densification at 1200°C.
Alumina (FP), Nicalon	Al_2O_3	Aerospatiale Aquitaine, France. Ref. 52 [31]	Preliminary processing by Sol-Gel route. Problems noted with fibre wetting, fibre degradation & matrix cracking on cooling.
SiC monofilament [AVCO]	Zirconia (ZrO_2)		Composites achieved by colloidal infiltration & pressureless sintering at 1235°C. Theoretical densities of 70% achieved with 20% by volume of fibre.
Nicalon	Al_2O_3	ONERA, France. Ref. 52 [32]	-
Nicalon fibres, with & without BN coatings	Zirconia: ZrO_2 + 50mol%SiO_2 (Zircon) ZrO_2 + 50mol%TiO_2 (Titanate)	Naval Research Labs, USA. Ref. 52 [33]	Initial work noted problems in thermal expansion mis-match between pure Zirconia matrix & fibre. Processing by vacuum hot-pressing & nitrogen hot pressing at 1200 to 1600°C. Significant improvements noted with coated fibres and Zircon & Titanate matrices.
Carbon fibres	Boron Nitride(BN) Titanium Carbide (TiC) Boron Carbide(B_4C)	SEP, France. Ref. 52 [4,5,34] University of Bordeaux, France. Ref. 52 [35]	Porous preforms of 2-D Carbon-Carbon densified by CVI. The preforms consisted of carbon fibre fabric held together with a small quantity of carbon (pyrolysed methane). The three matrices were evaluated, along with SiC; the last became the eventual choice.
Carbon fibres	SiC	MAN Technologie, Germany. Ref. 52 [60] DASA, Germany. DLR, Germany.	**European FESTIP study:** Material and technology development for reusable launch vehicle (RLV) hot structures. Comparison of materials produced by different processing routes. Includes internal oxidation protection methods for applications >500°C in oxidising atmospheres, Ref.52 [61].

52.2.3 Technology status

Figure 52.2.2 summarises the technology and related commercial developments of various composites.

Of these, complex hot structural components have been produced in C-SiC composites. Developed and manufactured in Europe, these items have undergone extensive evaluation and qualification for the X-programme vehicles, i.e. X-38 and CRV, Ref. [52-62], [52-63].

Primary systems	
Matrix	Fibre
SiC	Carbon
SiC	SiC

Secondary developments	
Matrix	Fibre
Si_3N_4	SiC
Al_2O_3	SiC
ZrO_2	SiC

Figure 52.2-2 - CMC composite development: Material combinations

52.2.4 Characteristics

Table 52.2.2 summarises the typical properties of a number of composites.

[See: 53.3 for characteristics of C-SiC materials evaluated under FESTIP]

Table 52.2-2 - Development continuous fibre reinforced ceramic matrix composites: Typical properties

Fibre [Source]	**Matrix [Process]**	**Fibre Vol.% [Type]**	**Mechanical Properties [Reference]**
SiC [N]	SiC [CVI]	45 [U]	σ_{flex} @ RT: 500MPa σ_{flex} @ 1000°C: 280MPa. Ref. [52-11], [52-16]
SiC [N]	SiC [CVI]	40 [B]	σ_{flex} @ RT: 310MPa σ_{flex} @ 1000°C: 140MPa (in air) σ_{tens} @ RT: 230MPa ε_{tens}: 0.75%. Ref. [52-12]
SiC [N]	SiC [CVI]	40 [B]	σ_{flex} @ RT: 350MPa Fracture Toughness (max): 10MPa√m. Ref. [52-22]
SiC [A]	Si_3N_4 [RSBN]	40 [U]	σ_{flex} @ RT: 900MPa σ_{tens} @ RT: 530MPa
SiC [A]	Si_3N_4 [RSBN]	50-60 [U]	σ_{flex} @ RT: 750MPa Ref. [52-27]
SiC [A]	Si_3N_4 [HP]	44 [U]	σ_{flex} @ RT: 900MPa σ_{flex} @ RT: 400MPa Ref. [52-28] Fracture Toughness: 7MPa√m (unchanged)
Al_2O_3 [FP]	Al_2O_3 [CVI]	40 [U]	σ_{flex} @ RT: 250MPa σ_{flex} @ 1200°C: 100MPa. Ref. [52-29]
SiC [N]	ZrO_2 [HP]	- [-]	σ_{flex} @ RT: <700MPa Ref. [52-33]
Carbon [-]	SiC [Various]	-	[See: 52.3]

Key
N: Nicalon.
A: AVCO (SCS-6).
CVI: Chemical Vapour Infiltration.
RSBN: Reaction Bonded Silicon Nitride.
HP: Hot Pressed.
FP: Fibre FP, DuPont.
U: Uni-directional composite.
B: Bi-directional (fabric) composite.

52.3 Carbon fibre reinforced silicon carbide

52.3.1 General

52.3.1.1 Characteristics

C-SiC aims to provide a strong composite with better oxidation resistance than an all-carbon composite. [See also: Chapter 54 for carbon-carbon]. C-SiC composites are a natural progression from carbon-carbon (C-C) for hot structures and thermal protection systems, [See also: Chapter 70 and

Chapter 71]. The low density combined with a controlled CTE have made C-SiC of interest for high-precision optical structures, Ref. [52-64], [See also: 52.7 for application examples]

52.3.1.2 Product sources

The composite is marketed by SEP (France) as SEPCARBINOX for use in oxidising environments to 1500°C.

In Germany, MAN Technologie, DASA (which became part of EADS) and DLR have expertise in the design-development and manufacture of C-SiC complex hot structure components. These technologies also form the basis for the development of dimensionally stable C-SiC materials for optical structures. The materials produced in Germany use different processing methods.

52.3.2 Fibres

52.3.2.1 General

The advantage of carbon fibres over all others is their capability to retain good tensile strength at temperatures approaching 1200°C. This strength retention is conferred to the composite to a higher level than is possible with, for example, silicon carbide fibres.

52.3.2.2 Preforms and near net-shapes

Carbon fibres can be converted to preforms to produce composites in large, complex shapes either by:

- fabric,
- braiding,
- 3-D,
- filament winding.

Near-net shape components are feasible. Unlike C-C composites, machining of finished C-SiC composites needs careful consideration owing to the hardness of the matrix.

52.3.3 Matrix

52.3.3.1 Processing

In addition to chemical vapour infiltration (CVI), other processing methods developed include:

- infiltration and pyrolysis of silicon polymers process, also described as PPP polymer pyrolysis process, developed by Daimler-Benz Aerospace/DASA, Ref. [52-59], [52-71].
- LPI liquid polymer impregnation, developed by DASA Dornier (now part of EADS ST), Ref. [52-60], [52-71].
- Gradient-CVI, developed by MAN Technologie, Ref. [52-60].
- Combined LPI/CVI method, Ref. [52-61].
- LSI liquid silicon infiltration, developed by DLR, Ref. [52-61].

[See also: 88.21 and 88.22 for descriptions of CVD and CVI]

The processing route selected is largely dependent on the requirements of the part to be produced, including Ref. [52-61]:

- mechanical performance,
- environmental conditions,
- maximum temperature,
- part complexity,
- reusability,
- service intervals.

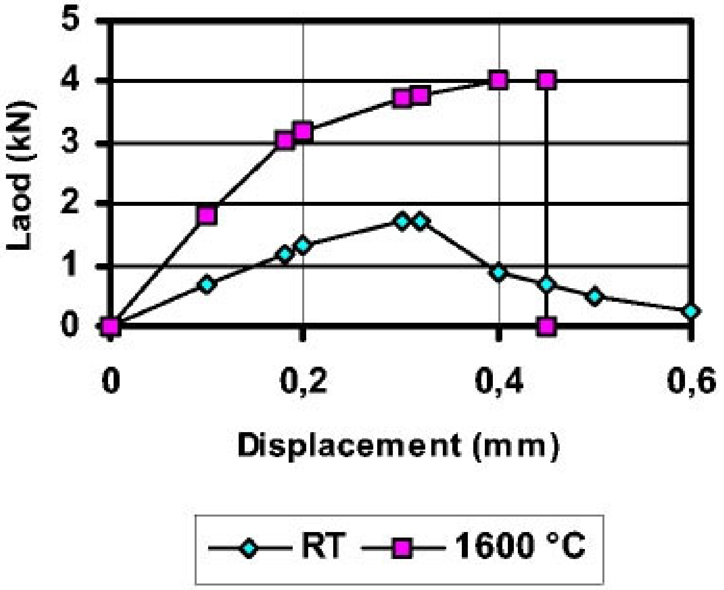
52.3.3.2 Porosity

C-SiC produced by CVI has residual porosity of ~10%. This is not considered unacceptable because the composite possesses sufficient integrity. It can be argued that pores act as crack stoppers, so controlling the fracture characteristics. A higher porosity level leads to a loss of composite integrity through a lack of support by the matrix. It also allows access by the external environment and attack by oxygen of the fibres and fibre/matrix interface, [See: Oxidation].

52.3.4 Characteristics

52.3.4.1 Properties

Figure 52.3.1 shows load-displacement curves for a C-SiC composite at RT and at 1600°C, Ref. [52-63]. These illustrate the composite’s progressive failure characteristic. At high temperature, the material remains elastic at loads exceeding the maximum seen at RT, Ref. [52-63]. C-SiC composite developed for the X-38 body flap by MAN Technologie, Germany, [See also 52.7].



C-SiC composite developed for the X-38 body flap by MAN Technologie, Germany.

Single edge notched beam tests. Crack length to width = 0.45

Figure 52.3-1 - Ceramic matrix composites: C-SiC load versus displacement curves at RT and 1600°C

The processing route selected to create the composite influences the properties. Table 52.3.1 compares the characteristics of C-SiC composites produced by different processing routes, Ref. [52-59], [52-60], [52-64].

Table 52.3-1 - Ceramic matrix composites: Typical properties of C-SiC composites produced by different processing methods

Property		SiC Matrix processing method				
		LPI	Gradient CVI	LSI	PPP †	
					RT	1500°C
Fibre volume fraction	Vol.%	40	42 - 47	-	-	-
Porosity	Vol.%	23	10 - 15	3.5 (open)	-	-
Density	g/cm^3	1.8	2.1 – 2.2	1.9	1.8	1.8
Tensile strength	MPa	260	270 – 330 †	-	270	320
Rupture strain	%	1.2	0.6 – 0.9	-	-	-
Flexural strength	MPa	365	450 - 500	160	530 *	610 *
‖ Compression strength	MPa	365	450 - 570	-	370	470
‖ Shear strength	MPa	30	45 - 55	28 ‡	20 ‡	20 ‡
Young’s modulus	GPa	55	90 - 100	60	60 - 80	60 - 80
‖ CTE	10^{-6} /K	2.3	3	-1.0 / 2.5 (1)	-	-
⊥ CTE	10^{-6} /K	-	-	2.5 / 6.5 (1)	-	-
Key	LPI: Liquid Polymer Impregnation; CVI : Chemical Vapour Infiltration; LSI : Liquid Silicon Infiltration; PPP: Polymer Pyrolysis Process. ‖ : longitudinal; ⊥ : transverse; †: [0°/90°] lay-up; ‡: ILSS; *: 4-point bend; (1): CTE 100°C/1500°C					

52.3.4.2 Oxidation

The inherent weakness of C-SiC lies with poor oxidation performance of the carbon fibre. The SiC matrix provides a degree of encapsulation which inhibits oxidation if excessive matrix microcracking is avoided. This can be difficult, as the matrix is brittle and prone to cracking. The difference in thermal expansion between fibre and matrix hinders the situation under conditions of thermal cycling and shock.

Consequently, C-SiC composites require oxidation protective coatings for applications at temperatures above 500°C, Ref. [52-60], [52-61], [52-63]. Adequate oxidation protection was investigated within FESTIP and hypersonic vehicle programmes. An effective 'multi-component protection system' with self-healing capabilities was developed for LPI and CVI processed C-SiC composites, Ref. [52-60], [52-61], [52-63].

52.3.5 C/SiC LPI liquid polymer infiltration process

52.3.5.1 Description

The material, processing and properties described here are for a grade of LPI C/SiC with T800 6k fibres, which was qualified for the X-38 program and applied for the C/SiC Nose Skirts delivered by EADS ST (formerly DASA- Astrium), Ref. [52-66].

C/SiC material properties differ in thermal and thermo-mechanical properties depending on the type of carbon fibre and the coating applied to the carbon fibre. In general, most types of carbon fibres can be used for LPI prepreg production.

The density of the SiC matrix can be modified by the number of liquid infiltration cycles and subsequent pyrolysis after the first pyrolysis of the green body component.

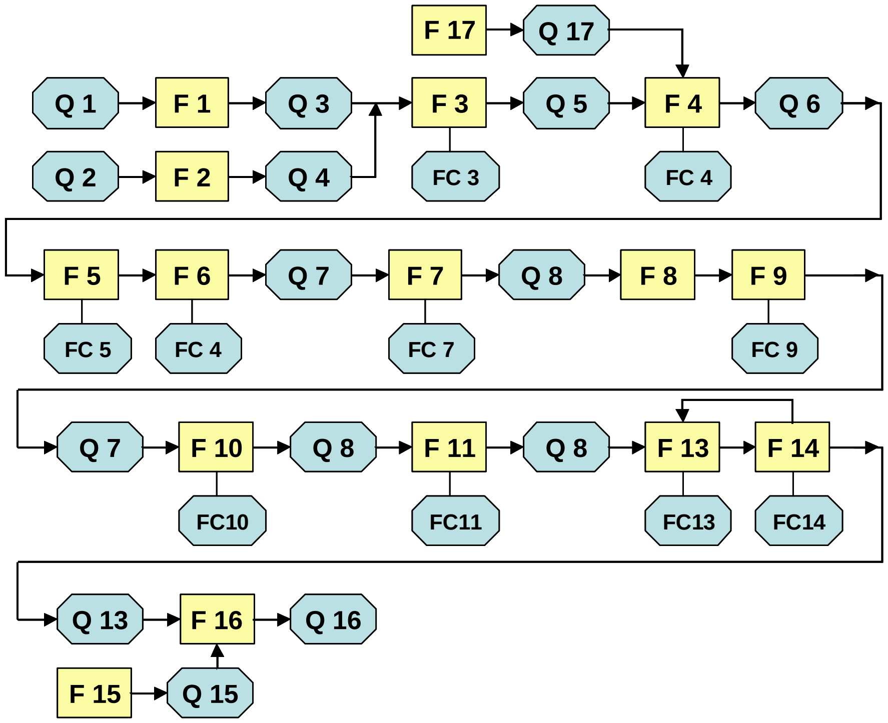
52.3.5.2 Manufacturing and inspection

The LPI route relies to a considerable extent on 'conventional' CFRP processes. Consequently, specific investment and tools costs are reduced because experience and technologies from the CFRP field can be transferred to CMC's.

The manufacturing process for continuous fibre-reinforced C/SiC material produced by the LPI-technique uses a computer-controlled production system. The LPI manufacturing cycle is accompanied by quality assurance, inspection and tests; as shown in Figure 52.03.2 and described in Table 52.3.2. Therefore, non-conformances can be identified at each stage of production, e.g. possible delaminations can be identified very early in the 'green' state of the process by ultrasonic inspection after autoclave curing.

The fabrication steps performed by computer-controlled facilities are also accompanied by quality control activities, e.g. FC 9.

The actual strength properties of the manufactured C/SiC parts are compared with reference coupons (witness samples) to provide confidence in the C/SiC components.



Key: **F** – Fabrication step; **Q** – Inspection step,
[See: Table 52.3.2]

Figure 52.3-2 - C/SiC LPI (EADS-ST): Manufacturing and inspection flow chart

Table 52.3-2 - C/SiC LPI (EADS-ST): Fabrication and inspection steps

Fabrication steps		**Inspection steps**	
	[See: Figure 52.3.2]		
F1	preparing a pre-ceramic slurry consisting of a solvent polymer and a ceramic powder	**Q1**	inspection of incoming raw materials for pre- ceramic slurry
F2	coating of the T 800 fibres with one or two pyrolytic thin C-layer	**Q2**	inspection of incoming T 800 fibres
F3	manufacturing of the prepregs, simultaneously with the infiltration of the continuous carbon fibre rovings with the polymer slurry, prepared under F1	**Q3**	inspection of slurry, prepared under F1
F4	manufacturing of the laminates in accordance with the stipulated prepreg layer-lay-up, shaping the laminates and joining on the mould tool to form the integral structure	**Q4**	inspection of fibre coating
F5	vacuum bagging of laminates on mould tool and curing in autoclave to cross-link the polymer and to form a consolidated fibre-reinforced, powder-filled polymer matrix composite ‘green body’	**Q5**	inspection of prepreg quality, fibre content
F6	preliminary shaping to required outer dimensions	**Q6**	inspection of lay-up of all layers, vacuum bagging of laminates on mould tool
F7	pyrolysis in inert gas to convert the polymer into ceramic matrix material	**Q7**	inspection of curing in autoclave data and dimension control and NDI on ‘green body’
F8	liquid infiltration and re-infiltration of the porous CMC via the polymer route	**Q8**	inspection of CMC parts after first pyrolysis, test of witness coupons

[See: Figure 52.3.2]

Fabrication steps		Inspection steps	
F9	pyrolysis of the re-infiltrated structure, typically 4-6 times, according to density requirements	**Q9**	inspection of re-infiltrated CMC parts after last pyrolysis, test of witness coupons
F10	final machining of structural part to required dimensions taking into account the coating thickness	**Q10**	inspection of CMC parts after final machining, NDI
F11	application of fundamental layer oxidation protection coating by means of Chemical Vapour Deposition (CVD). For re-use and multi mission applications, the coating is improved with multi-layer self healing OPS and final CVD coating (F12-F14)	**Q11**	visual inspection after CVD coating and weight measurement
F12	preparation of slurry for multi-layer coating	**Q12**	inspection of OPS coating slurry
F13	application of multi-layer coating and final erosion resistant layer	**Q13**	visual inspection after OPS coating and final CVD coating, weight control
F14	heat treatment for oxidation protective multi-layer coating for each layer	**Q15**	inspection of transportation container for coated CMC parts
F15	manufacture of transportation boxes and handling fixtures prior first transportation of structural part (green state)	**Q16**	inspection of pre-assembled and final assembled CMC parts, acceptance for delivery
F16	assembling if necessary, packing and transportation		

52.3.5.3 Material characteristics

The material properties of C/SiC differ depending on the application, the type of carbon fibre used and the number of re-infiltration cycles. The material data presented are based on the C/SiC LPI material applied to the X-38 Nose Skirt, which was manufactured by EADS ST (formerly Astrium), Ref. [52-66].

The composite was constructed in quasi-isotropic layers with T800 6k fibres. Each unidirectional layer has a thickness of about 0.2 mm; the angle between the layers was, as far as possible, 45°.

52.3.5.4 Density

The density of the C/SiC components was 1790 kg/m^3. This value was measured on material in a final pyrolysed condition without the CVD coating.

52.3.5.5 Mechanical properties at different temperatures

The values used for linear static analysis margin calculations over the complete temperature range from RT to 1600°C are shown in Table 52.3.3.

Table 52.3-3 - C/SiC LPI (EADS-ST): Mechanical properties at different temperatures

$E_{11} = E_{22} = 47$ GPa	$X_T = Y_T = 157$ MPa
$\nu_{12} = 0.25$	$X_C = Y_C = 291$ MPa
$G_{12} = 19.5$ GPa	$S_{12} = 109$ MPa
$\varrho = 1.83E^{-9}$ Ns²/mm⁴	$S_{13} = S_{13}\ (T)^{2}$ MPa
$\alpha_{11} = \alpha_{22} = CTE(T)^{1}$	
Key: [1]: DASA-C/SiC tested values for $\alpha_{11} = \alpha_{22}$ [2]: DASA-C/SiC tested values for S_{13}	

Temperature-dependent CTE of DASA-C/SiC:					
T (°C)	**20**	**100**	**1000**	**1500**	
$\alpha_{11} = \alpha_{22}$ (10^{-6}/K)	-	0.08	1.45	2.28	DASA-C/SiC test values
Temperature-dependent ILS-allowable of DASA-C/SiC:					
S_{13} (MPa)	12	-	-	17.74	DASA-C/SiC test values

52.3.5.6 Specific heat capacity of C/SiC LPI material

Figure 52.3.3 shows the measurements of specific heat capacity of the EADS ST C/SiC LPI material for the temperature range 100°C to 1500°C.

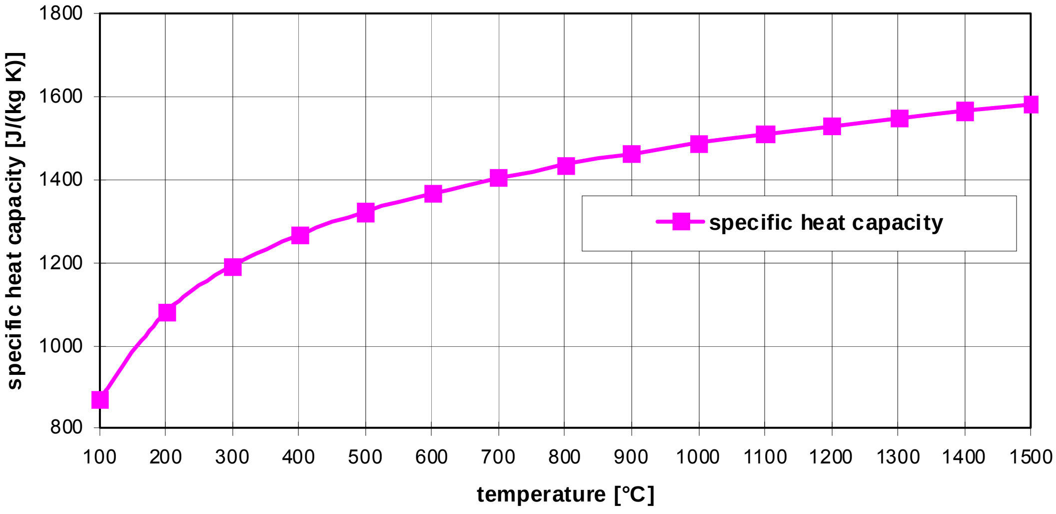


Figure 52.3-3 - C/SiC LPI (EADS-ST): Specific heat capacity

52.3.5.7 Thermal conductivity of C/SiC LPI material

Figure 52.3.4 shows the measurements of thermal conductivity of the EADS ST C/SiC LPI material for the temperature range 100°C to 1500°C. Values for both in-plane and perpendicular to the fibre are given.

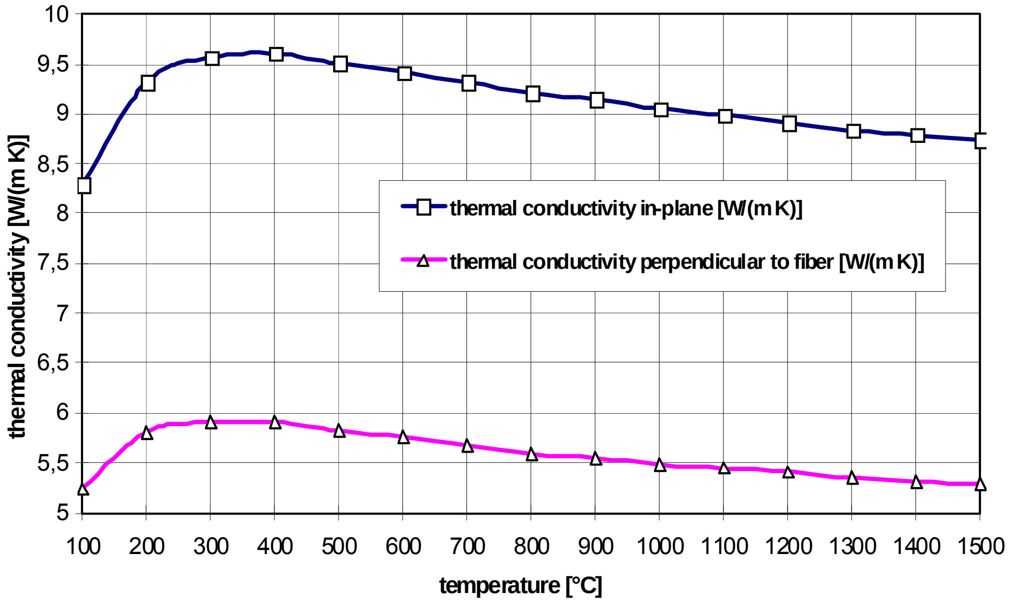


Figure 52.3-4 - C/SiC LPI (EADS-ST): Thermal conductivity

52.3.5.8 Catalycity, plasma erosion and oxidation protection

To avoid plasma erosion and oxidation of the carbon fibres, the C/SiC-panels are covered with an oxidation protection layer system designed for the appropriate temperature regime. Since the outer surface of the C/SiC panels is in contact with the hot boundary layer and since its temperature depends approximately on the difference between convective heat loads and emitted radiation, the characteristic properties of interest are the thermo-optical properties and catalycity.

52.3.5.9 Emissivity

The surface coating is produced by one or more SiC layers applied by CVD chemical vapour deposition. If a multi-layer OPS oxidation protection system is applied, the surface emittance is the same because the top layer of the OPS is the same as the CVD SiC layer. The measured temperature-dependent values of the surface emittance of the anti-oxidation coating system used by EADS ST are shown in Figure 52.3.5 for the temperature range 0°C to 1200°C. For temperatures above the measured range, the emittance value for 1200°C has been assumed.

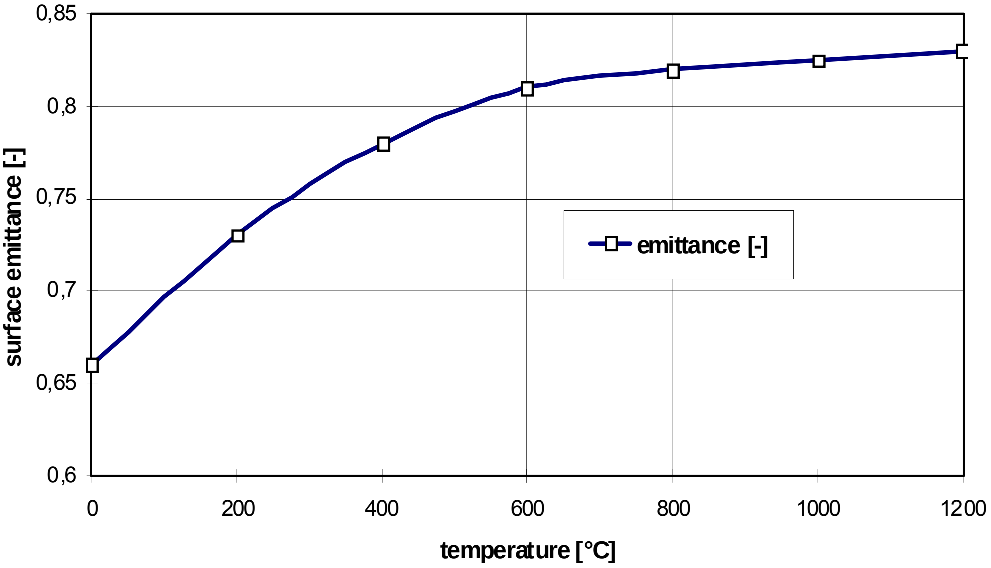


Figure 52.3-5 - C/SiC LPI (EADS-ST): Surface emittance, with anti-oxidation coating

52.3.5.10 OPS oxidation protection system development for reusable applications

The first question is *'why use an OPS oxidation protection system for CMC materials destined for TPS and thermostructural applications, rather than non-oxidising CMC materials, such as SiC/SiC or Nextel/Mullite?'* The main reason is that investigations into CMC over the past ten years have shown that C/SiC components with high strength carbon fibres, e.g. T800, offer the best strength and stiffness at high temperatures up to 2000°C.

For future reusable systems like RLV or CTV, the C/SiC TPS and thermostructural components need an OPS to prevent the carbon fibre reinforcement oxidising. Oxidation occurs with exposure to oxygen at all temperatures above 450°C, so the OPS functions in all applied temperature regimes for reusable C/SiC structures up to 1600°C.

A self-healing, multi-layer OPS, previously developed by EADS, was tested successfully in several investigations, i.e. TPS shingle and panel plasma tests; thermo-mechanical cycles. The main drawbacks of the multi-layer functional coating were:

- highly complex and expensive manufacturing route. Each single OPS layer is pyrolysed separately.
- thermal gradients between the multi- layer coatings, which cause thermal stresses

The OPS has a complex coating architecture. The simplest of which consists of 3 to 5 CVD-SiC layers with a SiO_2 glass sealing on top. However, it proved unreliable during long-term exposure in air and not resistant throughout the whole temperature range from 500°C to 1600°C. Complex systems have bond layers to adjust the thermal expansion coefficient or the chemical compatibility between the substrate and the coating. Even more complex systems consist of more than three layers with different functions so that the system works from 500°C to 1600°C. Self-healing OPS consists of various layers with different functions: a bonding layer, an intermediate functional layer system with self-healing capability and an erosion protection layer. Multilayer oxidation protection coatings are applied to C/SiC composites either by a slurry technique or by CVD.

Figure 52.3.6 summarises a current architecture for a multi-layer, multi-functional, self-healing coating from EADS ST.

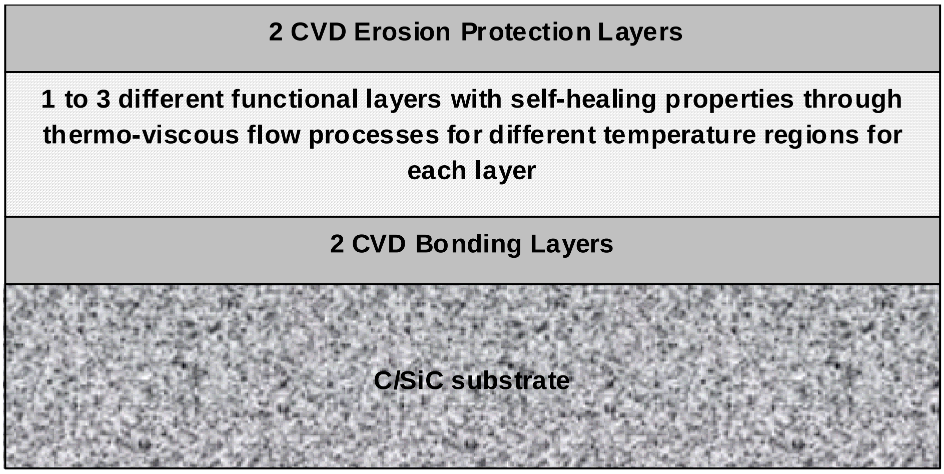


Figure 52.3-6 - C/SiC LPI (EADS-ST): Architecture of multi-layer, self-healing OPS

The function of the different layers summarised in Figure 52.3.7 can be described as:

- Erosion protection layer, which prevents oxygen diffusion to the functional layer and reduces the evaporation of the second viscous layer as well as minimising erosion of the coating. Erosion protection layers like SiC react with oxygen to form silica as an oxygen barrier due to its very low oxygen diffusion coefficient.
- Functional layer with self-healing capability, which is an intermediate layer that seals cracks and prevents oxygen diffusion into the substrate. Best results have been achieved by using combinations of several boron and silicon phases. The boron containing systems are able to react with diffusing oxygen and form lower melting point boron glasses which can seal cracks within the rigid layers by viscous flow processes.
- Bonding layer, which has the main task of accomodating the differences in thermal coefficients between the fibre-reinforced SiC matrix and the second layer. The bonding layer also prevents carbon from diffusing out of the substrate. Normally this layer consists of SiC applied by CVD.

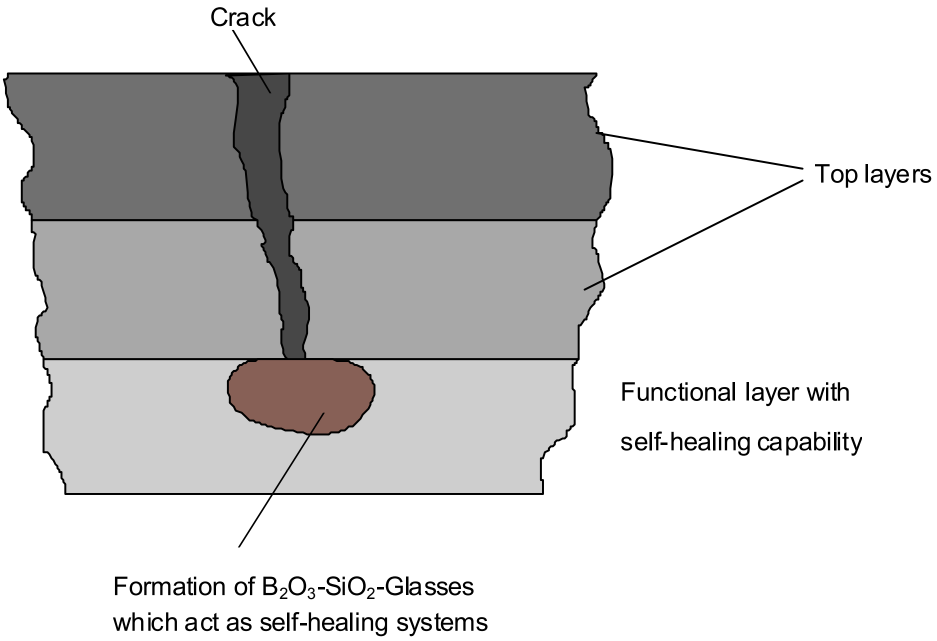


Figure 52.3-7 - C/SiC LPI (EADS-ST): Function of layers in OPS

52.3.5.11 WEPROT and OLCHOS studies on OPS systems

Recent experience in testing of different OPS systems have been gained within the ESA studies 'WEPROT', Ref. [52-67], [52-68], [52-76], and 'OLCHOS', Ref. [52-69]. Both studies investigated different OPS in an extensive life-cycle test programme. The WEPROT program also investigated the lifetime behaviour of the OPS with respect to impacts and erosion caused by low-speed impact, rain drop erosion and hail impacts. Within the OLCHOS programme, the OPS systems applied by EADS ST are given in Table 52.3.4.

Table 52.3-4 - C/SiC LPI (EADS-ST): OPS used in OLCHOS programme

OPS Reference	Architecture	Total layers
E 1.2	2 CVD layers, one multifunctional layer, 2 CVD layers	5
E 2.2	2 CVD layers, two different multifunctional layers, 2 CVD layers	6
E 3.2	2 CVD layers, three different multifunctional layers, 2 CVD layers	7

All three systems survived up to 100 re-entry cycles during the test program. The best result of the three systems was obtained from the OPS with the lowest complexity (E1.2), with the combined self-healing layer.

Within the WEPROT study, the system E2.2 has been applied with excellent results even with OPS samples pre-damaged by low speed impact or rain erosion.

The test results from OLCHOS and WEPROT revealed that at the lower temperature range (about 800°C to 900°C), the self-healing capacity of the OPS could be improved, whereas at higher temperatures (1200°C to 1500°C) the OPS functional layer performance was optimal.

52.3.6 C/C-SiC LSI liquid silicon infiltration process

52.3.6.1 Material characteristics

There are 3 main types of C/C-SiC materials produced by DLR. All of which comprise carbon fibre bundles in surrounding SiC-layers. The manufacturing process parameters and fibre conditioning define the mechanical properties. The LSI (liquid silicon infiltration) process involves making a CFRP part using a special resin with a high carbon content. After pyrolysis at 900°C, the resulting porous C/C preform is infiltrated by liquid silicon at about 1600°C. The silicon partially reacts with the carbon to form SiC.

52.3.6.2 Mechanical properties

Table 52.3.5 summarises the mechanical properties of two grades of DLR C/C-SiC LSI material. These are used for manufacturing TPS and hot structures, e.g. X-38 Nose Cap assembly under the TETRA programme, [See also: 70.24].

DLR LSI materials have also been investigated as part of an ESA-funded study on failure criteria, Ref. [52-70], [See also: 64.5]

Table 52.3-5 - C/C-SiC LSI (DLR): Mechanical properties for different grades

Material grade	$E_x = E_y$ **(MPa)**	G_{xy} **(MPa)**	ν_{xy}	ϱ (g/cm³)	α **(1/K)**	$S_{x,t} = S_{y,t}$	$S_{x,c} = S_{y,c}$	S_{xy}
C/C-SiC XB	60000	15000	0.05	1.9	1×10^{-6}	72	225	54
C/C-SiC XT	60000	15000	0.05	1.9	1×10^{-6}	150	205	60
C/C-SiC XT (1)	60000	15000	0.05	1.9	1×10^{-6}	150	250	60
Key: (1) in-plane bending								

Figure 52.3.8 shows mechanical properties for tests on XB and XT grades of DLR C/C-SiC LSI materials. The average values are for 5 samples cut from one plate, Ref. [52-70].

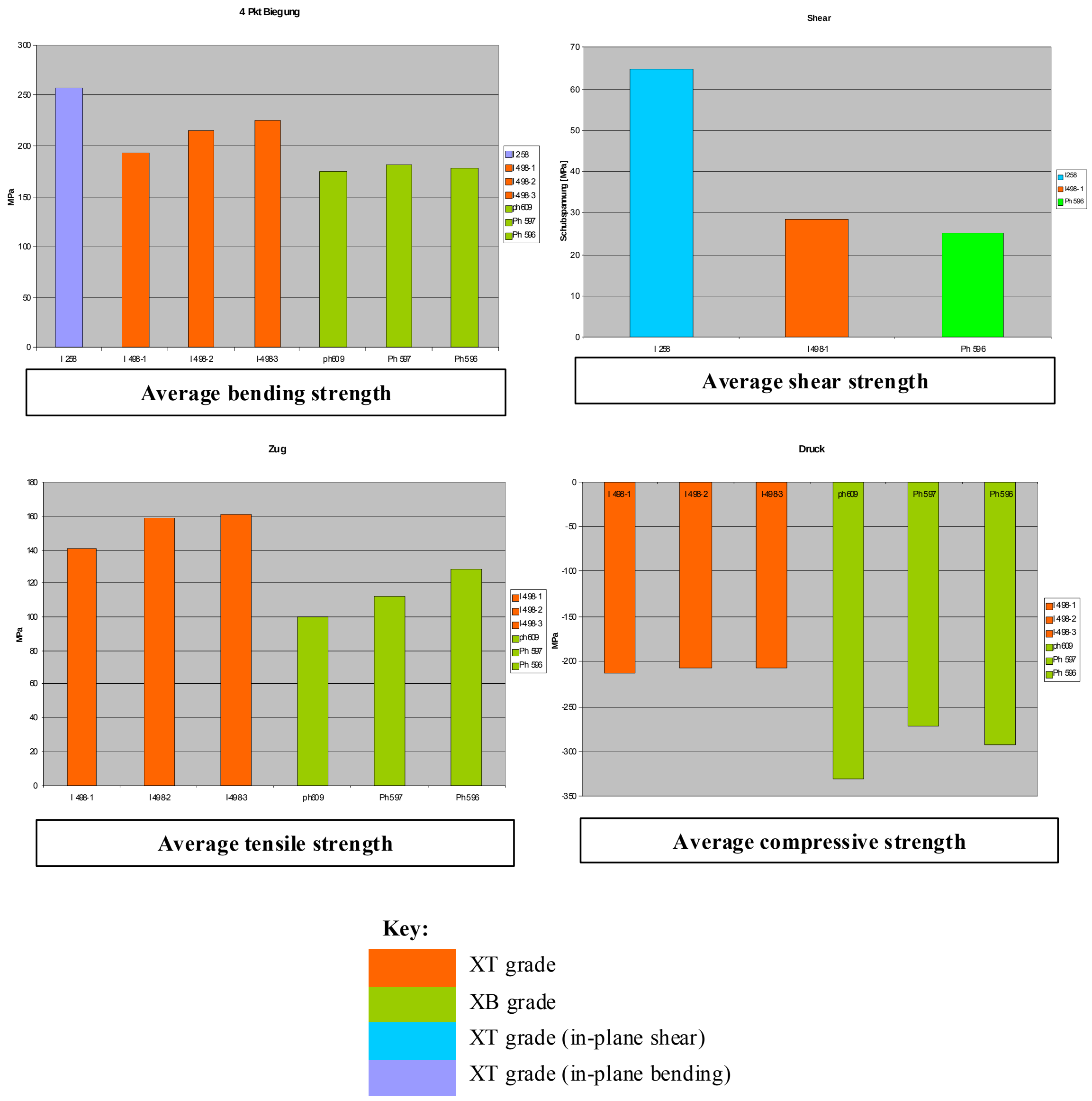


Figure 52.3-8 - C/C-SiC LSI (DLR): Mechanical properties for XT and XB grades

52.4 Silicon carbide fibre reinforced silicon carbide

52.4.1 Technology status

SiC-SiC is by far the most developed of the oxidation resistant ceramic matrix composites. CVI is the preferred manufacturing route.

The key participants are:

- Société Européene de Propulsion (SEP), France; in collaboration with the French government and authoritative universities. A licence for their SiC-SiC CVI production technology has been sold to DuPont with the production capability in the USA (1989/1990). SEP's trade name is CERASEP.

- Oak Ridge National Laboratory, USA; in collaboration with Babcock and Wilcox (USA). The latter is aiming to use the technology of the former for commercial products. The work is supported by the US Department of Energy.
- Nippon Carbon Co; the manufacture of Nicalon fibre is offering SiC-SiC produced by polymer pyrolysis. This material has insulative characteristics but indifferent mechanical strength.
- Refractory Composites Inc., USA.
- Thermo Electron Corp., USA.

52.4.2 Applications

The intended commercial uses for SiC-SiC composites include:

- Rocket and propulsion units, Ref. [52-36].
- Gas turbine engine components, Ref. [52-37].
- Heat exchangers, Ref. [52-38].
- Thermal protection systems, Ref. [52-39].
- Refractory furnace linings, Ref. [52-40].

52.4.3 Characteristics

52.4.3.1 Fibres

The most noticeable disadvantage of SiC-SiC composites is the lack of a fibre which is thermally stable above 1300°C, where progressive degradation occurs to present fibres. Nicalon and Tyranno are, at present, the only practicable options.

52.4.4 Manufacturing of SiC-SiC

The main chemical reaction used is that with methyltrichlorosilane (MTS):

$$CH_3SiCl_3 + xH_2 \longrightarrow SiC + 3HCl + xH_2, @\ 1200°C$$

Excess hydrogen is used as a carrier gas. Deposition times can vary between 30 hrs and 150 hrs, typically. Work has mainly concentrated on producing composites from plain and satin weave fabrics.

There is no limitation on the size of SiC-SiC components that can be produced, but very few facilities exist for dimensions between 1m and 3m.

All deposition occurs within a closed vessel under controlled gas flow conditions and at an evenly distributed temperature. Prior to depositing the SiC matrix, the SiC fibres are pre-coated usually with carbon or pyrolytic graphite to a thickness of <1µm.

52.5 SiC-SiC composite: Properties

52.5.1 General

SiC-SiC composites are the most developed of the CMCs, so published information includes the:

- Stress-strain profile of the composites, with respect to progressive failure.
- Attainable flexural and tensile strengths at room temperature.
- Degrees of strength retention at high temperatures under extreme environments.
- Measured fracture toughness.

52.5.2 Mechanical properties

52.5.2.1 General

The mechanical properties of SiC-SiC composites are dependent on:

- fibre orientations, and
- volume fraction.

Figure 52.5.1 gives strengths for some of the SiC compositions reported. It is noticeable that the higher values are for the SiC filament reinforced SiC and unreinforced hot pressed ceramic.

Filament reinforced materials are not appropriate for structural uses, neither are unreinforced brittle materials. Toughened composites with fibres have 600MPa as very much the upper limit.

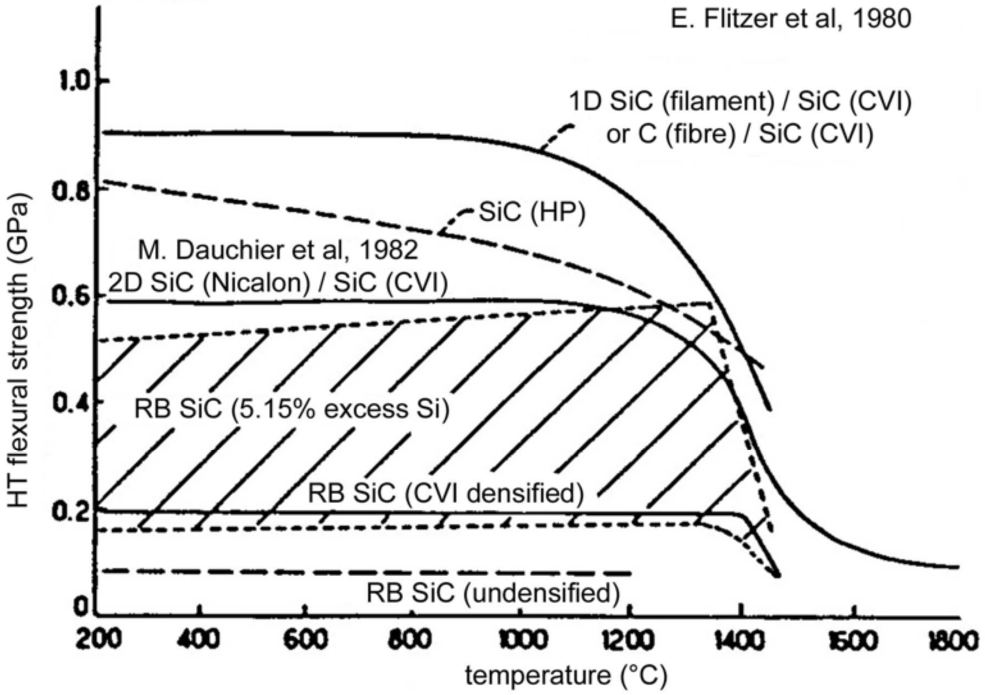


Figure 52.5-1 - SiC-SiC composites: High temperature flexural strength of various compositions

52.5.2.2 Effect of environment

Testing at temperature under inert atmospheres gives greater strength values than similar composites tested in oxidative or corrosive environments, or after thermal cycling.

52.5.2.3 Effect of fibre coating

The fibre coating and its function as the interface between fibre and matrix determines the composite behaviour and properties. The in-situ fibre strength dictates the ultimate strength of the composite and the fracture characteristics.

The fibre size is removed by either solvent or pyrolysis. The coating is then applied, often by the organisation undertaking the matrix CVI. As yet there is no one accepted coating. Usually a carbon or pyrolytic graphite coating is used; thicknesses between 0.01μm and 0.1μm. Pyrolytic boron nitride has also been promoted as the coating, but with less prominence.

52.5.2.4 Stress-strain response

Figure 52.5.2 shows a representative stress-strain profile for a bidirectional fabric SiC-SiC composite with Nicalon reinforcement, Ref. [52-7].

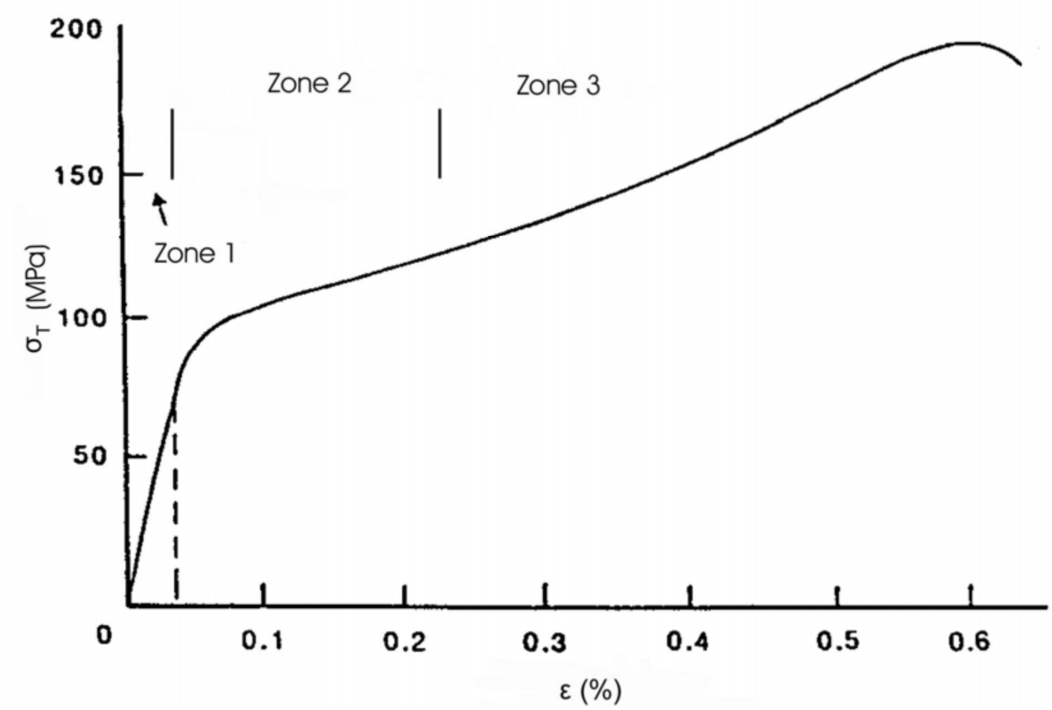


Figure 52.5-2 - SiC-SiC composite (bidirectional): Typical tensile stress-strain curve

Three zones can be seen in the stress-strain curve:

- Zone 1: The behaviour of the composite is elastic to a strain of 0.035%, with fibre and matrix acting in unison.
- Zone 2: The matrix is microcracking and there is a gradual transfer of load to the fibres. This explains the fall in modulus from the original 210GPa.

- Zone 3: The load is entirely sustained by the fibres to 0.6% strain. The 190MPa failure stress should be viewed in the light of the composite being based on bi-directional fabric. This strength level is indicative, and has been improved upon.

In using SiC-SiC composites which possess a very restricted linear elastic response, the mechanical stressing caused by either direct load or thermal shock should not reach such levels as to promote progressive microcracking. The design limits, therefore, are more modest than the maximum attainable strengths, suggesting values of 100MPa for a bi-directional fabric composite.

52.5.2.5 Effects of temperature

The main advantage of SiC-SiC is the strength retention to 1200°C, as shown in Figure 52.5.3, Ref. [52-2]. These strengths were attained in an atmosphere of argon and hydrogen. The higher in-situ strength of carbon fibre with respect to that of Nicalon is also evident.

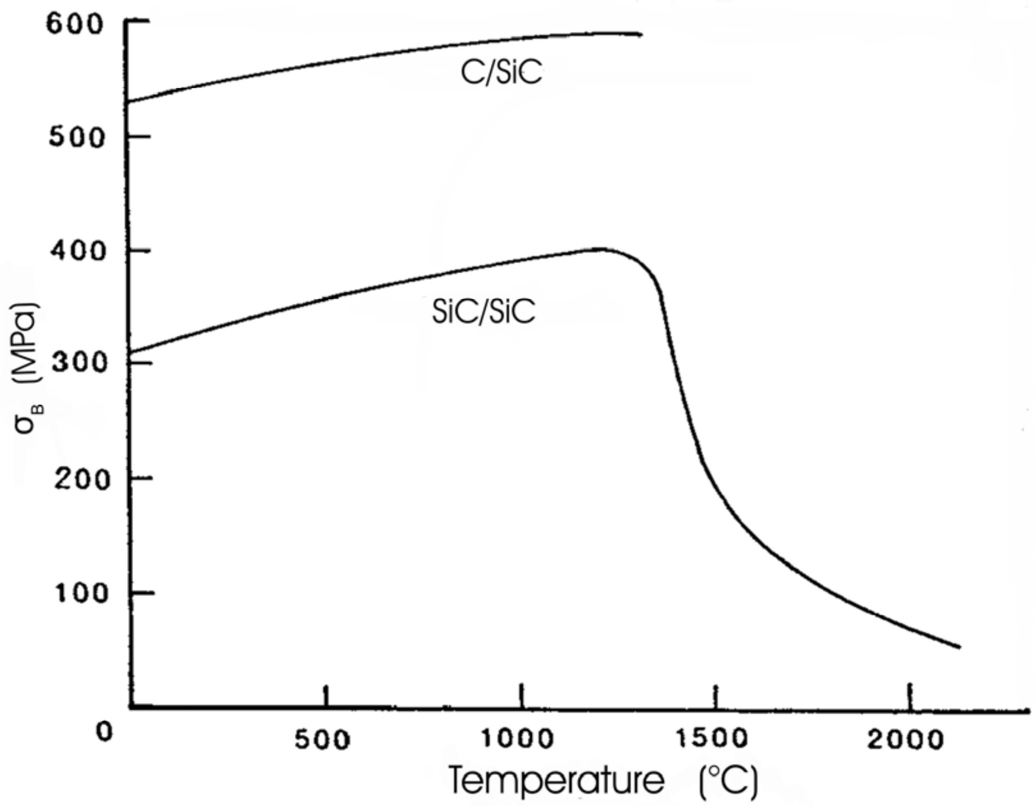


Figure 52.5-3 - SiC-SiC composites: Typical bending strength versus temperature profiles compared with C-SiC composite

The results shown in Figure 52.5.4 and Table 52.5.1 show SiC-SiC capable of sustaining its strength and fracture toughness despite thermal shock and repeated thermal cycling, Ref. [52-2]. Hence, the use of SiC-SiC can be considered for thermal protection systems where the modest mechanical strengths can be accommodated.

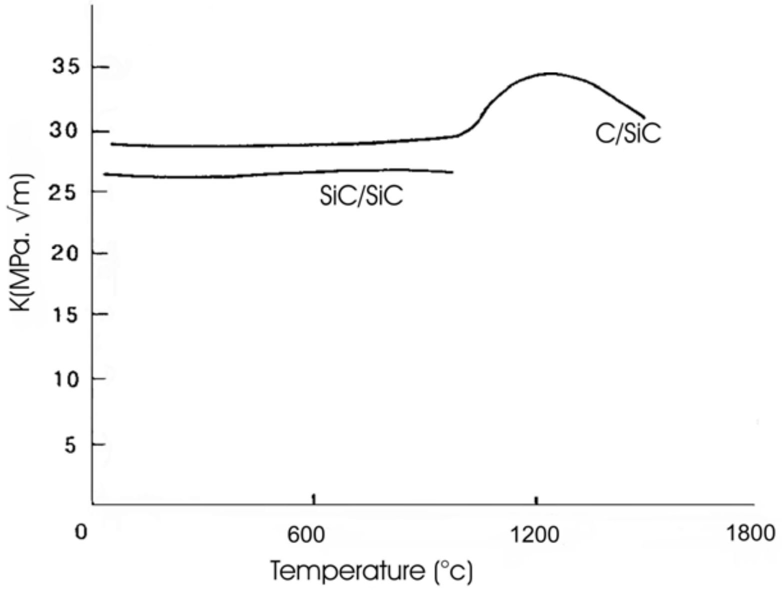


Figure 52.5-4 – SiC-SiC composites: Representative through-thickness fracture toughness versus temperature compared with C-SiC

Table 52.5-1 - SiC-SiC composites: Indicative properties, as measured by SEP (France)

Property	Temperature (°C)					
	RT	1000	1200	1400	1600	2000
Thermal conductivity (Wm^{-1} $°C^{-1}$): Parallel to fibres Perpendicular	25 6	18 5	18 5	- -	- -	- -
Thermal diffusivity ($10^{-6}m^2s^{-1}$): Parallel Perpendicular	12 4.5	4.5 2.2	- 2.2	3.5 2.2	- -	- -
CTE ($10^{-6}°C^{-1}$)	5	-	-	-	-	-
Bending strength (MPa)	300	350	390	200	150	50
Key: Material: 2-D laminates with Nicalon fabric & 10% porosity. No strength loss @ 1000°C in air up to 500 hours. Thermocycling & Thermal Shock to 1200°C caused little or no change to strength characteristics. Fracture Toughness of 25MPa√m constant to 1300°C. No catastrophic failure characteristics.						

52.5.3 Environment

52.5.3.1 Oxidation

Whilst silicon carbide is an oxidation-resistant material, SiC-SiC composites degrade significantly under prolonged use, e.g. in gas turbine applications.

To combat oxygen attack, SEP provide a grade of SiC-SiC which has an applied glaze (glass) to the outer surface to provide additional protection.

52.6 Whisker reinforced composites

52.6.1 Development

52.6.1.1 Reinforcements

The advantages that whiskers have over fibres are:

- high purity, and
- high tensile strength.

Table 52.6.1 indicates very high strengths and moduli. The purity provides a high level of thermal stability.

Table 52.6-1 - Ceramic matrix composites: Ceramic whiskers

Whisker type	**Trade name [Source]**	**Properties**			
		Density (kg/m^3)	Size (μm∅)	UTS (GPa)	Modulus (GPa)
α-SiC	Silar SC-9 [Arco, USA]	3200	0.6	6.9	689
α-SiC	Silar SC-10 [Arco, USA]	3200	-	-	-
β-SiC	Tokamax [Tokai Carbon, Japan]	3190	0.1-1	3-14	400-700
β-SiC	Tateho SCW [Tateho, Japan]	3180	0.1-0.5	20.6	483
-	XPW2 [JM Huber, USA]	-	-	-	-
β-SiC	VLS [Los Alamos]	-	3-10	15.9	580
α-Si_3N_4	Tateho [Japan]	3180	-	-	-
Al_2O_3	Emcor 66 [Engelhard, USA]	-	-	-	-
Al_2O_3	- [Thermokinetics, USA]	-	-	-	-

52.6.1.2 Composites

Whiskers added to ceramics do not retain their very high mechanical properties because it is difficult to:

- achieve bonding between whisker and matrix (to use the whisker strength),
- minimise whisker degradation by chemical interaction.

Table 52.6.2 shows whisker and matrix combinations which have been assessed. The main motivation for studying these materials is for use in internal combustion engines.

Table 52.6-2 - Ceramic matrix composites: Development whisker and matrix combinations

Whisker Reinforcement	Matrix	Source [Reference]	Comments
SiC (ARCO)	Si_3N_4 with Y_2O_3 & CeO_2 sintering aids. Al_2O_3	GTE Laboratories, USA. Ref. [52-41]	20 wt% whisker content. Powder route. Al_2O_3 hot pressed @ 1850°C & Si_3N_4 @ 1725°C.
β-SiC	Si_3N_4 with Y_2O_3 & La_2O_3 sintering aids.	Japanese Government Industrial Research Institute. Ref. [52-42]	Hot pressing @ 1800°C. Up to 50% whisker content. Whiskers modified strength of monolithic ceramic by very small amount to 650 MPa, fracture toughness improved slightly.
SiC (Tokamax)	Si_3N_4 with Y_2O_3 & Al_2O_3 sintering aids.	Swedish Institute for Silicate Research. Ref. [52-43], [52-44]	Cold isostatically pressed. Nitrided @ 1350°C and then Pressureless Sintered @ 1850°C. Neither the flexural strength or the fracture toughness of Si_3N_4 improved. The whisker:matrix bond judged to be too good, causing brittle failure.
SiC (VLS grade)	Si_3N_4 with MgO sintering aid.	Los Alamos National Laboratory, USA. Ref. [52-45]	Whisker volume fractions of 40%. Hot pressing @ 1850°C. Toughness increased by 50% to 10.5 MPa $m^{-1/2}$.
SiC (Silar SC-9, ARCO)	Si_3N_4 with Y_2O_3 & Al_2O_3 sintering aids.	GTE Laboratories, USA. Ref. [52-46]	Hot pressed @ 1800°C. For 30 vol.% whiskers, fracture toughness increased by 40% to 6.4 MPa $m^{-1/2}$ & flexural strength by 25% to 950 MPa.
SiC (SC-9, ARCO)	Al_2O_3 Mullite	ORNL, USA. Ref. [52-47], [52-48], [52-49]	Hot pressed @ 1850°C for alumina matrix. Fracture toughness of both matrices improved two-fold. Al_2O_3 with 20 vol.% whiskers, flexural strength of 805 MPa @ RT & 520 MPa @1200°C obtained.
SiC (SC-9, ARCO)	Al_2O_3	University of Illinois, USA. Ref. [52-50]	30 vol.% whiskers. Hot pressed to 1950°C. Flexural strength of 650 MPa; Fracture toughness 9.5 MPa $m^{-1/2}$.
SiC (SC-9, ARCO)	Al_2O_3	Rockwell Corp., USA. Ref. [52-51]	15 wt.% whiskers. Hot pressed to 1500°C. Flexural strength of 650 MPa; Fracture toughness 4.6 MPa $m^{-1/2}$.
SiC (SC-9, ARCO)	Al_2O_3	University of Southern California, USA. Ref. [52-52]	15 wt.% whiskers. Composite supplied by ARCO. Creep data acquired in air @ 1500°C, where creep is appreciable even at stresses of 48 MPa.
SiC	Al_2O_3 (WG300)	Brown University, USA. Ref. [52-53]	Fracture Toughness & Fatigue Crack Growth study. 60% increase in toughness, K_{IC} values increase by 70 to 150%.
SiC (Silar SC-9, SCW-1)	Mullite ($3Al_2O_3$:$2SiO_2$)	General Electric Co., USA. Ref. [52-54]	Up to 40 wt.% whiskers. Hot pressed @ 1700°C. Flexural strength: 386 MPa; Fracture Toughness 3.52 MPa $m^{-1/2}$. Failure strain: <0.15%.
SiC (SCW-1, Tateho): Also Al_2O_3 & Si_3N_4	Al_2O_3 Corderite Mullite ZrO_2	University of Hamburg/Max-Plank Institute, G. Ref. [52-55], [52-56]	Hot pressing of various matrix:whisker combinations. Thermal expansion mismatch between whiskers & matrix strongly influence strength levels. Fracture Toughness of all ceramics increased.
SiC whiskers (VLS grade)	Molybdenum disilicide ($MoSi_2$)	Los Alamos National Laboratory, USA. Ref. [52-57], [52-58]	20 vol.% whiskers. Hot pressed @ 1640°C. 100% increase in flexural strength; 50% increase in Fracture Toughness.

52.6.1.3 Material processing

A powder processing route is used with whisker additions between 20% and 50% by volume.

Consolidation by hot pressing occurs at pressures of ~25MPa (3500psi). The temperatures are higher than for CVD/CVI; between 1600°C and 1950°C, depending on the matrix. The composites obtained show low porosity.

52.6.2 Properties

52.6.2.1 Composites

Published information indicates that the strength and fracture toughness of the composites are only marginally better than those of the base monolithic ceramics. The base ceramics have flexural strengths between 500MPa and 900MPa, with failure strains to 0.3%.

52.6.3 Applications

For spaceplane structures, continuous fibre composites are likely to be more appropriate than whisker-based systems on the grounds of 'pseudo-plastic' or 'benign' failure characteristics.

52.7 Potential applications

52.7.1 Resumé

CMC materials were developed for high-temperature applications where their low density, compared with metals, and fracture characteristics, compared with monolithic ceramics, made them of interest for reusable and hypervelocity vehicle projects. Various international and national-based programmes have progressed CMC technology such that some materials have been fully characterised for use in specific thermo-structural applications.

The demands for improved data rates and lower power consumption in satellite communications systems means that optical-based systems have advantages over those using radio waves. CMCs are of interest for such applications which need materials with a long-term, very high dimensional stability in the space environment.

52.7.2 High temperature applications

52.7.2.1 General

CMCs were developed for use at temperatures >1000°C. With the onset of degradation at 1200°C, their application is largely dictated by the time-dependent retention of residual properties. At higher temperatures, e.g. 1650°C, oxidation protection of the carbon fibre reinforcement is necessary because potential applications are generally in oxidising environments. The main features of CMCs are their thermal characteristics, including the ability to withstand thermal shock and thermal cycling, coupled with adequate mechanical performance.

52.7.2.2 Thermo-structural systems

Various RLV concept vehicles perceived the use of CMCs for the protective, aerodynamic surfaces of spaceplanes, [See: Chapter 70]. Some examples include, Ref. [52-62], [52-63], [52-65], [52-66], [52-71], [52-73], [52-74], [52-75]:

- X-38 - body flaps, nose cap assembly, [See also: 70.XX]
- X-33 elevon, Ref. [52-73].
- Hopper elevon, Ref. [52-73].
- OPS X-37 elevon, Ref. [52-73].

52.7.2.3 TPS thermal protection systems

Various RLV concept vehicles perceived the use of tiles and shingles in for the TPS, [See: Chapter 71].

52.7.2.4 Deployable hot structures

FOLDHOST is a concept for a deployable decelerator; as shown in Figure 52.7.1, Ref. [52-73], [52-77]. This is based on the requirements for the Mars Mission ISRU in-situ resource unit. The decelerator is completely folded inside the payload container for launch. During ejection the decelerator deploys automatically by a spring-loaded deployment mechanism, [See also: 70.25].

The benefits of considering CMC (C/SiC) for this application can be summarised as, Ref. [52-73]:

- All other hot structures made of metallic materials, e.g. Inconel or high temperature ODS, are limited in temperature compared with C/SiC and are also much heavier.
- C/SiC material is a suitable hot structural material because of its strength (about 200 MPa), stiffness comparable to aluminum but with a lower density than aluminium.
- C/SiC can support higher loads at about 1600°C compared with room temperature performance.
- In other concepts, a deployable decelerator with cold structural panels and additional TPS, e.g. ablator, amount to about double the mass compared with a C/SiC decelerator.

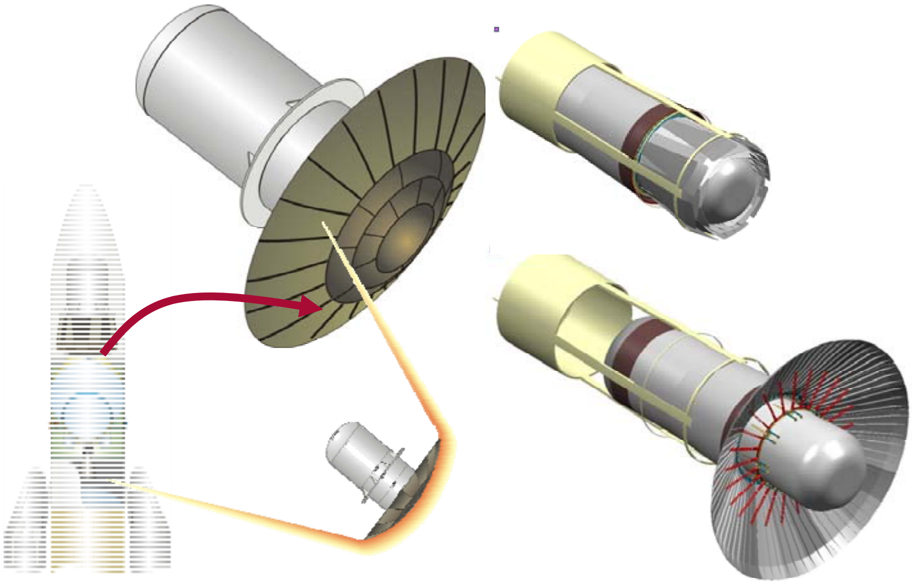


Figure 52.7-1 – Ceramic matrix composites: FOLDHOST concept for deployable decelerator

52.7.2.5 Propulsion systems

Within engines and propulsion systems, CMCs are considered for some static components in order to avoid dynamic mechanical loads.

52.7.2.6 Heat exchangers

CMCs are considered for extreme high-temperature heat exchangers.

52.7.2.7 X-38 body flaps

The X-38 test vehicle design includes two pairs of moveable flight control surfaces (rudders and body flaps) for the intended autonomous, controlled re-entry and parafoil assisted landing.

Each body flap can be moved independently for roll and pitch manoeuvres. For the NASA X-38 experimental vehicle V201, the dimensions of each flap were 1.6m long; 1.6m wide, Ref. [52-63].

A number of comprehensive studies were undertaken on the application of CMC for the body flaps in order to meet the exacting conditions experienced during re-entry (V201 flight conditions; combined thermal, pressure, mechanical loading; 4 re-entry cycles). The studies have resulted in the design, manufacture, testing and flight qualification of C-SiC composite body flaps by MAN Technologie. These are shown in Figure 52.7.2, which also highlights the associated design-developments necessary to make a fully functional, complex all-CMC structure, Ref. [52-63].

Each flap contains about 100 different parts. These are made from a 2D C/SiC composite. A modification to the basic processing method (carbon fibre fabric preforms infiltrated with SiC) was applied depending on the size and shape of the component part to be processing. This resulted in two material 'Types' having slightly different densities, tensile strength and strain to failure, Ref. [52-65].

[See also: 70.23]

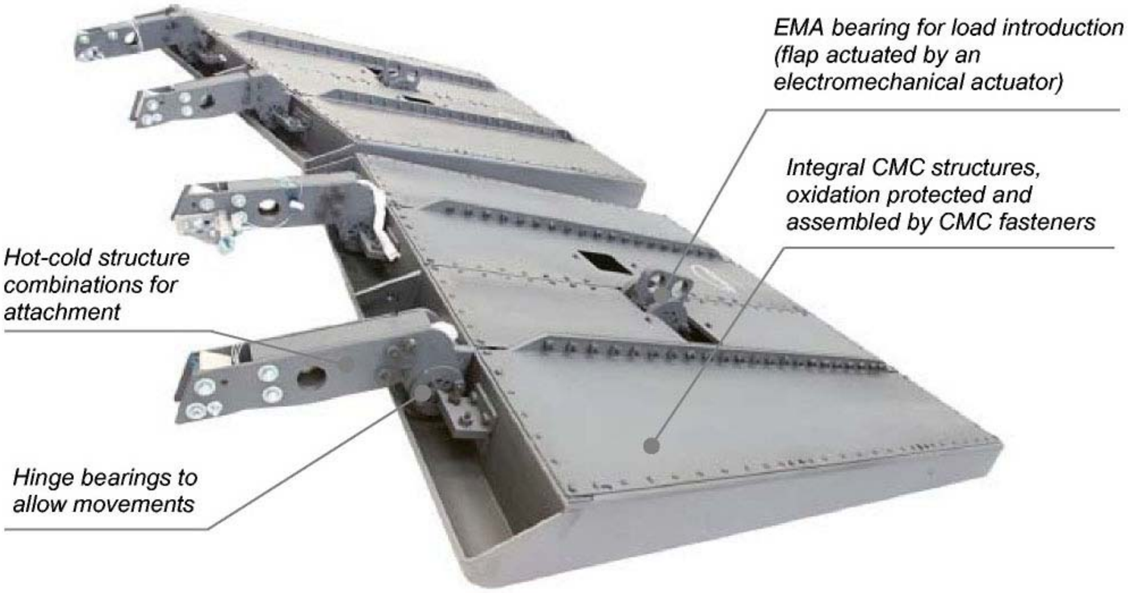


Figure 52.7-2 – Ceramic matrix composites: Applications – X-38 body flaps

52.7.3 High precision optical structures

The development of space-based laser communication optical systems need light-weight materials with long-term thermal and dimensional stability. In addition to material selection, design and manufacturing aspects, such as number of components, production costs for a series of parts, machining and preparation of high-precision optical surfaces and assembly (with provision for accurate alignment) are also key demands, Ref. [52-64].

For optical systems, e.g. Cassegrain or Off-axis Telescope concepts, C/C-SiC CMCs were investigated for the Telescope Tube and Upper Spider components, as shown in Figure 52.7.3, Ref. [52-64].

To achieve the dimensional stability, the thermal behaviour of the component parts needs to be known and controlled, i.e. mismatch in thermal expansion between different materials, such as the support structure and the mirror. In this case, with a Zerodur mirror, a near-zero CTE was necessary for the composite parts.

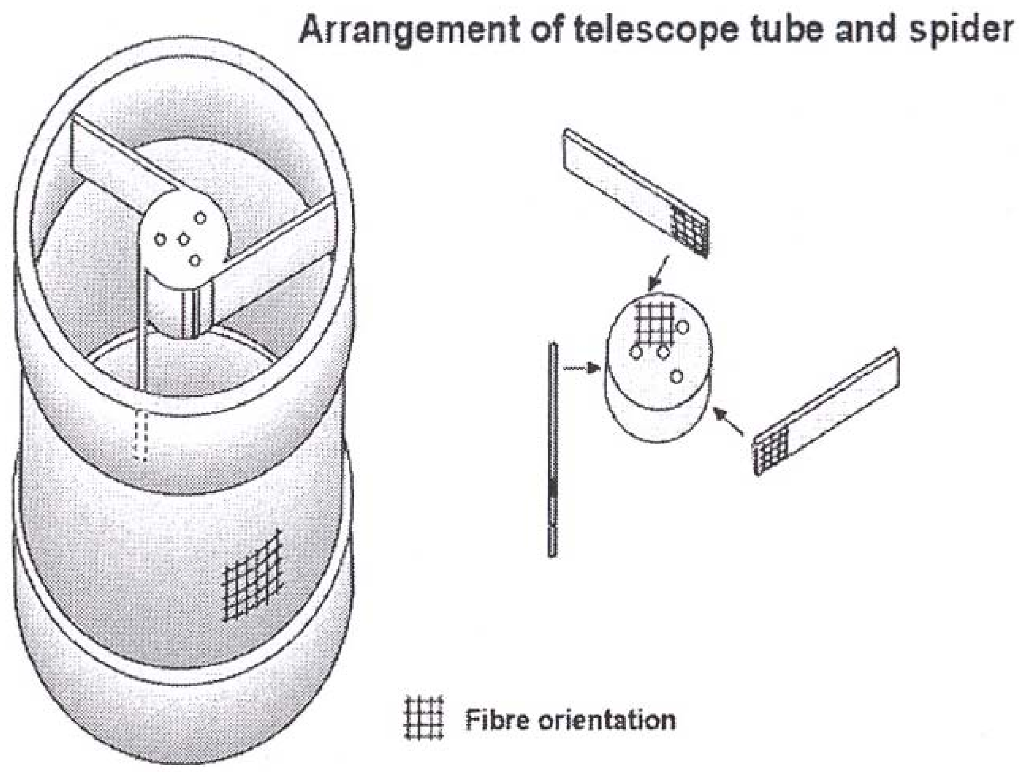


Figure 52.7-3 - Ceramic matrix composites: Applications – Optical communications systems

The characterisation of the thermal behaviour of C/C-SiC composites showed that, Ref. [52-64]:

- In-plane (fibre-axis) composite thermal expansion is affected by the:
  - –ve CTE C/C: $\alpha_{(-35°C)} = -0.7 \times 10^{-6}\ K^{-1}$; $\alpha_{(+50°C)} = -0.5 \times 10^{-6}\ K^{-1}$.
  - larger, +ve CTE of the SiC matrix: CTE $_{SiC}$: $\alpha = <4 \times 10^{-6}\ K^{-1}$.
- Varying the phase content of the composite, by adjusting the SiC content between 30 wt.% and 50 wt.%, affected the composite CTE, e.g. measured in-plane CTEs at RT:
  - low SiC $-0.2 \times 10^{-6}\ K^{-1}$
  - high SiC $+0.8 \times 10^{-6}\ K^{-1}$
- Other means of controlling the CTE of these materials included the choice of reinforcement fibre (HT, HM, IM) and the fibre architecture.

The 'standard' LSI C/C-SiC composite uses HT carbon fibres in a woven fabric, an XP-60 high-yield carbonaceous precursor, resulting in a composite containing ~75%C/C, ~25% SiC, with ~5 wt.% unreacted silicon.

[See: Table 52.3.1 for typical 'standard' LSI material properties]

Prototypes components have been manufactured using the LSI (Liquid Silicon Infiltration) process, developed by DLR for spacecraft thermal protection, Ref. [52-64].

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53 Glass and glass-ceramic matrix composites

53.1 Introduction

The chemical stability and environmental resistance of glass-based materials made them a possible matrix material for temperatures in the range 600°C to 1300°C. Interest has focused on carbon and silicon carbide continuous reinforcements. The matrix can be chemically tailored to be more compatible with the fibre. The most developed materials are described in this Chapter.

Composites are manufactured with the glass in a viscous phase, hence limiting the high-temperature fibre degradation.

For structural use, the mechanical properties determined from development materials are encouraging, but as yet appear to be difficult to reproduce. The mechanical characteristics of the most advanced composites are given.

For aggressive environments, where metals and polymer composites degrade, the glass and glass-ceramic composites can be attractive.

53.2 Continuous fibre composites

53.2.1 Characteristics

Glasses and glass-ceramics offer:

- thermal stability, in the range 600°C to 1300°C,
- oxidation resistance,
- erosion resistance,
- chemical stability.

Without modification by reinforcement, they lack combined strength and fracture toughness for structural use.

53.2.2 Composite development

53.2.2.1 Matrix

Work began with glasses such as borosilicates, having thermal capabilities around 600°C. With modifications to the glass constituents, by gradually introducing a higher ceramic content, thermal stability beyond 1000°C is possible.

Important attributes are:

- Glasses can be created with a broad range of chemistry to control fibre-matrix chemical interaction.
- Glasses can be produced with a wide range of thermal expansion characteristics which can be tailored to nearly match those of reinforcing fibres.
- The modest elastic moduli of glasses (50GPa to 90GPa), and glass-ceramics (80GPa to 110GPa) enable high-modulus fibres to provide true reinforcement.
- The ability to control the viscosity of glasses and then flow them easily under pressure enables the physical densification of composites without mechanical damage to the fibres.
- The composite densification process can be rapid, since glass matrix flow is all that is needed. In this respect, the matrix can be treated as a thermo-formable material which can be melted.

Table 53.2.1 shows the progression of the matrices used. Whilst these are mainly related to developments at United Technology Research Center (UTRC) and Corning Glass (USA), the information is indicative of the group of composites as a whole, Ref. [53-2], [53-3].

Table 53.2-1 - Glass and glass-ceramic matrices

Matrix Type	Major Constituents	Minor Constituents	Max. Use Temp † (°C)
Glasses			
7740 Boro-silicate	B_2O_3, SiO_2	Na_2O, Al_2O_3	600
1723 Alumino-silicate	Al_2O_3, MgO, CaO, SiO_2	B_2O_3, BaO	700
7930 High Silica	SiO_2	B_2O_3	1150
Glass-ceramics			
LAS-I	Li_2O, Al_2O_3, MgO, SiO_2	ZnO, ZrO_2, BaO	100
LAS-II	Li_2O, Al_2O_3, MgO, SiO_2	ZnO, ZrO_2, BaO	1100
LAS-III	Li_2O, Al_2O_3, MgO, SiO_2	ZrO_2	1200
MAS	Al_2O_3, MgO, SiO_2	BaO	1200
BMAS	BaO, Al_2O_3, MgO, SiO_2	-	1250
CAS	CaO, Al_2O_3, SiO2	-	-
Ternary Mullite	BaO, Al_2O_3, SiO_2	-	~1500
Hexacelsian	BaO, Al_2O_3	-	~1700
Key: † : In composite form.			

53.2.2.2 Reinforcements

A number of reinforcements have been considered for GMCs, including:

- Continuous fibres and filaments:
    - Silicon Carbide (SiC)
    - Boron
    - Carbon
    - Alumina
    - Glass
- Whiskers.

By far the greatest effort has centred on fibre yarns of carbon, alumina, and SiC. Composites with carbon fibres came first and exhibited significant strength and stiffness coupled with good fracture toughness and low density (~2000kg/m^3). For potential space use, there is the added benefit of dimensional stability conferred to the composite by the carbon fibres. This can be exploited in applications not requiring high-temperature performance. The major disadvantage of carbon fibres as a reinforcement at high temperatures is that they readily oxidise in air.

The alumina-fibre systems have undergone modest development. Whilst these have been shown to be unaffected by exposure to temperatures up to 1000°C, the overall levels of toughness and strength were lower than for carbon and SiC reinforcements, Ref. [53-1].

SiC yarn reinforced composites are now the main focal point for developments in matrix composition to give improved composites.

53.2.3 Manufacture

53.2.3.1 General

In comparison with other ceramic candidates, the 'glassy' matrix composites offer considerable potential because of their:

- ease of composite densification,
- low cost, and
- performance characteristics.

Whilst process technology was originally developed with glasses, they can be used with glass-ceramics. The key is that composite densification takes place whilst the matrix is in a substantially glassy and viscous form. After full densification, the glass-ceramic can be heat treated to achieve a matrix with superior toughness and high-temperature strength.

Two fabrication techniques dominate for these composites:

- Hot Pressing, and
- Matrix Transfer Moulding.

Both methods exploit the good flow characteristics of glasses at high temperatures and are appropriate for continuous fibre reinforcements.

53.2.3.2 Hot pressing

Unidirectional monolayer tapes are made by winding slurry-impregnated yarns onto a mandrel. The slurry consists of water, a water-soluble resin binder and a glass powder. These tapes are cut to make plies, which are densified by hot pressing. For proper densification to occur, pressing is carried out at a temperature where the glass viscosity is low enough to permit the glass to flow into the interstices between individual fibres of the yarn bundles. Pressure is applied only after the mould temperature reaches the softening point of the matrix. The resulting composites are generally >98% theoretical density. Multi-directional composites made from tapes are possible, as are variants using fabric reinforcements.

53.2.3.3 Matrix transfer moulding

Hot pressing of tapes and woven fabric lay-ups is less suitable for complex external and internal geometry components. In these situations carefully engineered fabric preforms can be used. These are arranged inside a mould cavity, then a fluid glass matrix is transferred at high temperature into the mould cavity to fully impregnate the preform. Whilst thin wall and complex shapes can be produced, the desired fluidity of the glasses can only be achieved by using a substantially higher processing temperature than for hot pressing. This, in turn, can result in excessive fibre-matrix interaction and consequent embrittlement of the composite.

53.3 Carbon fibre reinforced composites

53.3.1 Material

Developments in these materials have centred on borosilicate glass for the matrix. UTRC have used T300, GY-70, P-100 and HMU fibres and Aerospatiale XAS and IM6, Ref. [53-4].

53.3.2 Mechanical properties

53.3.2.1 Tension

Table 53.3.1 and Table 53.3.2 summarise mechanical properties achieved by the composites, Ref. [53-8]. The mechanical properties are respectable for this class of material. Many of the glass matrices are PYREX™ from Corning Glass Works (USA), Ref. [53-8].

Table 53.3-1 - Carbon fibre/borosilicate unidirectional composites: Mechanical properties

Carbon Fibre	Fibre (Vol%)	Properties			
T300	39	UTS	RT	(MPa)	710
		E		(GPa)	127
GY-70	58	UTS	RT	(MPa)	680
		E		(GPa)	322
P-100	54	UTS	RT	(MPa)	680
		E		(GPa)	322
XAS	65	σflex	RT	(MPa)	1240
			500°C †	(MPa)	1237
		E	RT	(GPa)	158
			500°C †	(GPa)	154
		ILSS	RT	(MPa)	38
			500°C †	(MPa)	36
IM6	68	σflex	RT	(MPa)	1030
			500°C †	(MPa)	970
		E	RT	(GPa)	160
			500°C †	(GPa)	160
		ILSS	RT	(MPa)	30
			500°C †	(MPa)	30

Key: Unidirectional composite † Inert Argon environment

Table 53.3-2 - Unidirectional and angle-ply tensile data for Hercules HMU carbon fibre reinforced 7740 borosilicate glass composite

Unidirectional Tensile Data					
Composite	**E (GPa)**	**PL (MPa)**	**UTS (MPa)**	ν	ε_f **(%)**
0°	165	299	787	0.170	0.618
	170	266	856	0.195	0.657
	173	304	711	0.183	0.531
Mean value	169	290	785	0.183	0.602
10°	120	139	170	0.184	0.123
	146	128	175	0.198	0.121
	144	153	168	0.179	0.111
Mean value	140	140	171	0.187	0.118
30°	72	29	50	0.169	0.078
	70	41	50	0.197	0.073
	68	39	41	0.187	0.060
Mean value	70	37	47	0.184	0.070
60°	35	11	18	0.112	0.054
	38	16	18	0.134	0.075
	33	19	24	0.086	0.077
Mean value	35	15	23	0.111	0.069

Angle-Ply Test Data					
Composite	**E (GPa)**	**PL (MPa)**	**UTS (MPa)**	ν	ε_f **(%)**
$[\pm10]_s$	158	170	429	0.286	0.420
	161	160	469	0.269	0.418
	163	224	424	0.295	0.319
Mean value	161	185	441	0.283	0.410
$[\pm30]_s$	81	12	179	0.887	0.399
	70	19	193	0.834	0.524
	77	14	189	0.972	0.594
Mean value	76	15	187	0.898	0.506
$[\pm45]_s$	42	5.6	44	0.696	0.384
	35	5.6	40	0.687	0.249
	36	6.6	48	0.633	0.512
Mean value	38	5.9	44	0.672	0.382
$[\pm60]_s$	24	3.0	25	0.287	0.655
	24	2.8	25	0.313	0.408
	20	4.5	22	0.248	0.459
Mean value	23	3.4	24	0.283	0.507
[0/90]	81	39	252	0.022	0.403
	80	52	317	0.005	0.500
	86	39	331	0.025	0.527
Mean value	82	43	300	0.017	0.477

Key PL indicates proportional limit, as the initial deviation from linearity of σ/ε curve.

Fibre Volume Fraction: 40 to 43.6%, except for 60°UD where V_f = 30%.

53.3.2.2 Notched

The notch sensitivity of HMU carbon fibre reinforced Code 7740 borosilicate glass is shown in Table 53.3.3, Ref. [53-6]. The 0/90° composites are reasonably notch insensitive, Ref. [53-6].

Table 53.3-3 - Mechanical test data for notched 0/90° reinforced HMU/7740 composites

Hole Dia. (mm)	d/b	Fibre Vol.%	Actual UTS (MPa)	Normalised Actual UTS † (MPa)	PL (MPa)	Ultimate Extensometer Strain (%)
Unnotched	0	39	309	1.0	43	0.48
	0	38	320	1.0	81	0.56
	0	40	341	1.0	76	0.57
1.6	0.110	39	324	1.05	121	0.92
	0.113	38	334	1.04	37	1.05
	0.112	40	330	0.97	77	0.97
3.1	0.202	39	296	0.96	16	1.08
6.4	0.431	38	297	0.93	20	1.42
	0.429	40	306	0.90	31	1.52

Key † : Ratio of notched/unnotched tensile strength.
d/b : Ratio of hole diameter to specimen width.

This is in agreement with fracture theory which predicts this response from composites with low values of interfacial (fibre to matrix) shear resistance and high values of in-situ fibre strength. The desirable 'benign' and 'fibre pull-out' characteristics of this glass matrix ceramic are the same as for all brittle matrix composites.

53.3.2.3 Environment

Owing to the inertness of glass matrix composites with respect to vacuum, there is interest in the USA for these materials in structural applications. Material characterisation is proceeding, Ref. [53-6].

53.3.2.4 Thermal expansion

As carbon fibres have a highly negative axial coefficient of thermal expansion (CTE), it is possible to achieve a composite with a CTE close to zero.

53.3.3 Applications

The incorporation of high-modulus carbon fibres, e.g. GY-70 and P-100, into glasses has been exploited in space-related mirrors and reflectors.

One such application is in thermally stable infrared mirrors using UTRC Thermally Stable Composites (TSC). A 300mm diameter frit bonded composite mirror in the form of an 'egg-crate' sandwich construction has been developed, Ref. [53-7]. An added advantage of using these materials is in their ability to be machined, replicated and figured using conventional polishing techniques.

53.4 Silicon carbide fibre reinforced composites

53.4.1 Composite development

53.4.1.1 Matrix

In moving from carbon to SiC fibre reinforcements in search of oxidation resistance, it became clear that borosilicate glasses could not exploit the full potential of SiC fibres, such as Nicalon, Ref. [53-9].

It was therefore necessary to move to glass-ceramics, such as lithium aluminosilicate (LAS) with various modifications. There is a further group of matrices, such as magnesium aluminosilicate (MAS), Ref. [53-10], and Barium magnesium aluminosilicate (BMAS), Ref. [53-11], which offer higher thermal stability than LAS. These could be exploited in the future. The matrix compositions not only contribute to such composite properties as elastic modulus and coefficient of thermal expansion, but more importantly, matrix compositions provide a means of controlling fibre-matrix reactions during composite densification. This reactivity, or lack thereof, determines the nature of the fibre-matrix interface.

53.4.1.2 Fracture

An important feature of these composites is their fracture characteristics, which are fibrous in nature, providing high crack growth resistance and hence toughness. The term fibrous implies significant fibre pull-out rather than a clean fracture through fibre and matrix. In the successful LAS matrix/SiC yarn systems, the fibre-matrix interface has characteristics which provide excellent fracture toughness, Ref. [53-10]. Among these are the formation of niobium carbide (NbC) particles around the fibres and a very thin carbon-rich layer between the fibre and NbC particle. The NbC results from the reaction between Nb_2O_5 from the LAS matrix and the SiC fibres.

53.4.1.3 Thermal stability and toughness

The thermal stability and toughness of glass-ceramics are achieved through microstructural modifications obtained by heat treatments. For the LAS-II/SiC system, the as-pressed matrix is primarily glassy with small amounts of Mullite ($3Al_2O_3.2SiO_2$) and β-quartz-silica solid solution LAS crystals, which form on cooling from the fabrication temperature. By heat-treatment, a matrix is achieved which is highly crystalline, primarily β-spodumene with a small amount (<10 vol. %) of residual glassy phase at the grain boundaries.

Table 53.4.1 gives the properties of various as-pressed and ceramic SiC/LAS composites.

Table 53.4-1 - SiC reinforced glass-ceramic composites: Comparison of RT unidirectional (0°) properties with SiC fibre reinforced epoxy

Property	**Matrix**				
	Epoxy	LAS-I	LAS-I	LAS-II	LAS-II
Matrix state †	-	P	C	P	C
Fibre Vol.%	-	46	46	44	44
	Tension				
Strength (MPa)	875	-	455	670	680
Elastic modulus (GPa)	106	-	133	128	136
Failure strain (%)	0.84	-	0.33	0.90	1.03
	Flexural				
Strength (MPa)	1240	755	758	1380	1050
Ratio flexural to tensile strengths	1042	-	1.67	2.06	1.54
ILSS (MPa)	87	-	34.4	-	-
Key † - P: As-pressed; C: Ceramed					

53.4.1.4 Stress-strain and fracture

The stress-strain and fracture characteristics of glass-ceramic matrix composites are different from those of thermosetting resin composites. This has important consequences when designing with these new materials.

- The stress-strain response of unidirectional (0°) LAS-II/SiC composites is not linear (Hookean) to failure.
- At fairly modest strains of around 0.4%, the matrix starts to crack locally as this reflects the strain capacity of the matrix. The progress of the cracks is inhibited at the fibre-matrix interface, due to decoupling between the two.
- A network of microcracks develops as the strain increases. This microcracking has the effect of lowering the elastic modulus, up to the maximum stress which occurs at around 1% strain.
- Unlike polymer matrices, the glass-ceramic matrices make a significant contribution to stiffness as their moduli are in the range 60GPa to 100GPa, whereas those of polymers are 2GPa to 3GPa. Progressive matrix cracking therefore deprives the composite of some of its stiffness.
- When the highest stress is reached, catastrophic failure is not inevitable because progressive fibre pull-out can occur.
- The maximum stress achieved by the composite is very much determined by the retained in-situ strength of the SiC fibres.

53.4.2 Effect of in-situ fibre strength

The importance of in-situ fibre strength applies to all high-temperature composites because there is a risk of fibre degradation by thermally induced chemical and microstructural modifications.

As an indication of the strength degradation which can occur solely through high temperature processing, SiC fibres have been extracted from composites where their strength has fallen from the original 2070MPa to 1450MPa, i.e. a 30% loss.

53.4.3 Effect of fibre-matrix bonding

Modest fibre-to-matrix bonding ensures the desired strength and toughness characteristics. This has implications for the off-axis composite response, such as 90° ply strain to failure.

For 0/90° constructions, the 90° ply strain to failure is low at around 0.05%; a consideration for designing components with these materials. Therefore fabrics and multi-directional fibre preforms are preferable to unidirectional composites by providing increased fibre integration and avoiding weak matrix dominated planes.

53.5 Silicon carbide reinforced composites: properties

53.5.1 LAS matrix composites

53.5.1.1 General

The LAS matrix versions have undergone the greatest development and are the most appropriate to concentrate on. The progression from LAS-I to LAS-III improved the overall strength and thermal stability of composites.

53.5.1.2 Stress-strain response

- Unidirectional LAS-I composites exhibit Hookean (linear) stress-strain response without significant levels of microcracking prior to the ultimate strength.
- For LAS-II and LAS-III, a significant extension to the stress-strain response occurs beyond the onset of matrix microcracking. This effectively gives a 'Proportional Limit'; see Figure 53.5.1.

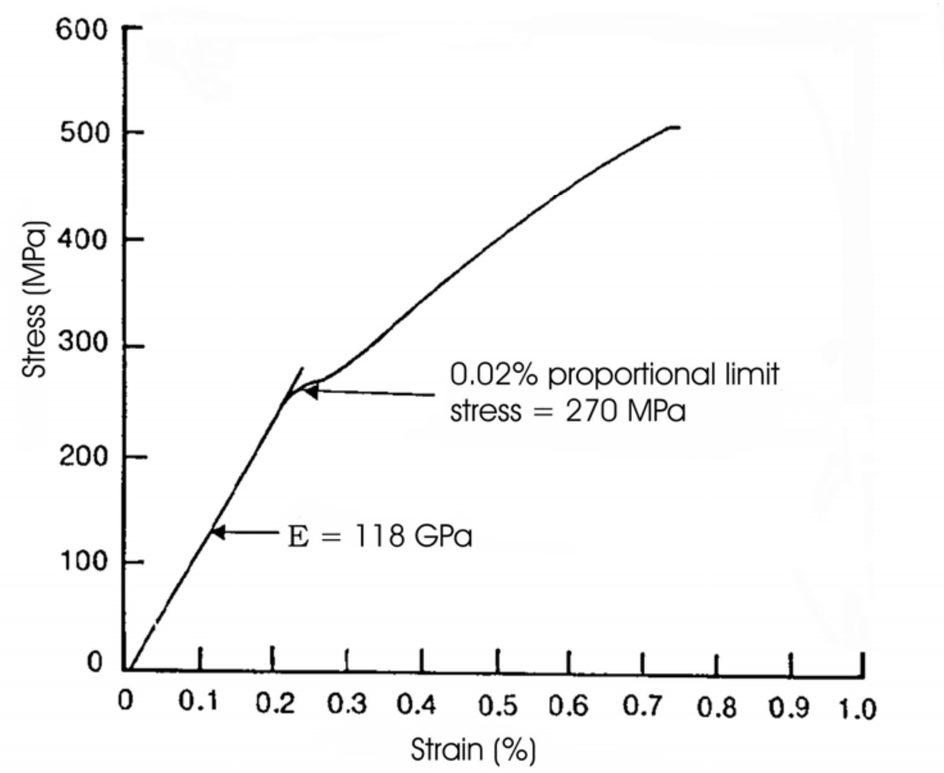
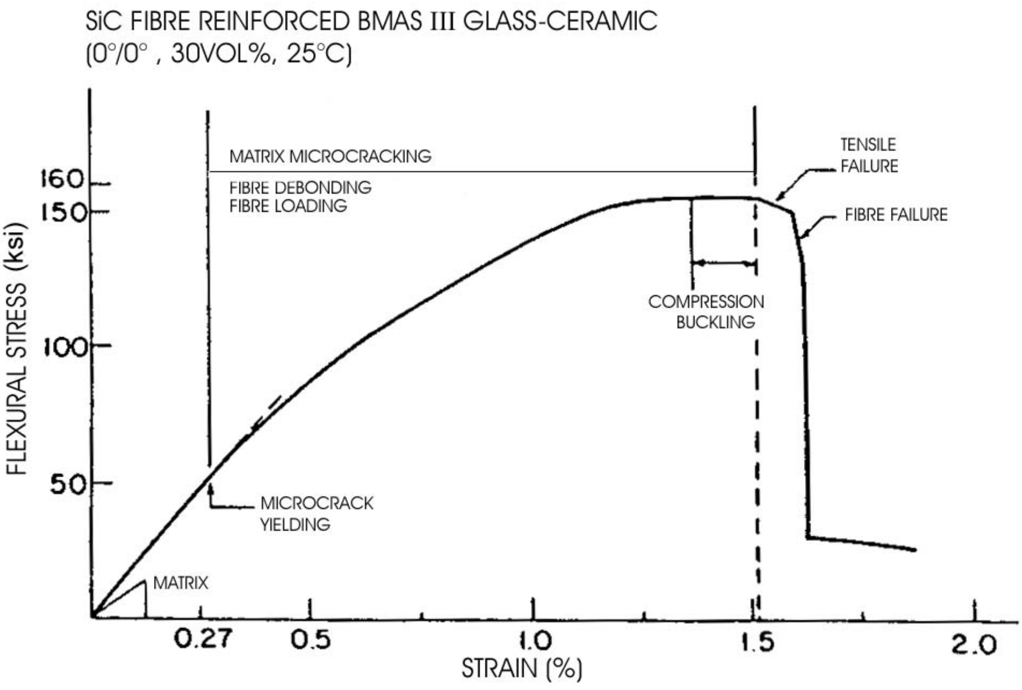


Figure 53.5-1 - Glass-ceramic composites: Tensile stress-strain curve for unidirectional (0°) SiC/LAS-II at room temperature

The 'proportional limit' provides a tenuous comparison with the response of metals and is an indicator of the true strength of the composite in terms of elastic response. All tensile and flexural strength figures stated relate to the ultimate strength of the composite, i.e. the in-situ strength of the fibres, beyond the onset of microcracking.

Figure 53.5.2 provides a better insight into the true stress to strain response of a glass-ceramic matrix composite, Ref. [53-11].



Key: Temperature: 25°C, Strain Rate 5 x 10^{-5} sec^{-1}

Figure 53.5-2 - Glass-ceramic composites: Flexural stress-strain curve for SiC/BMAS-III

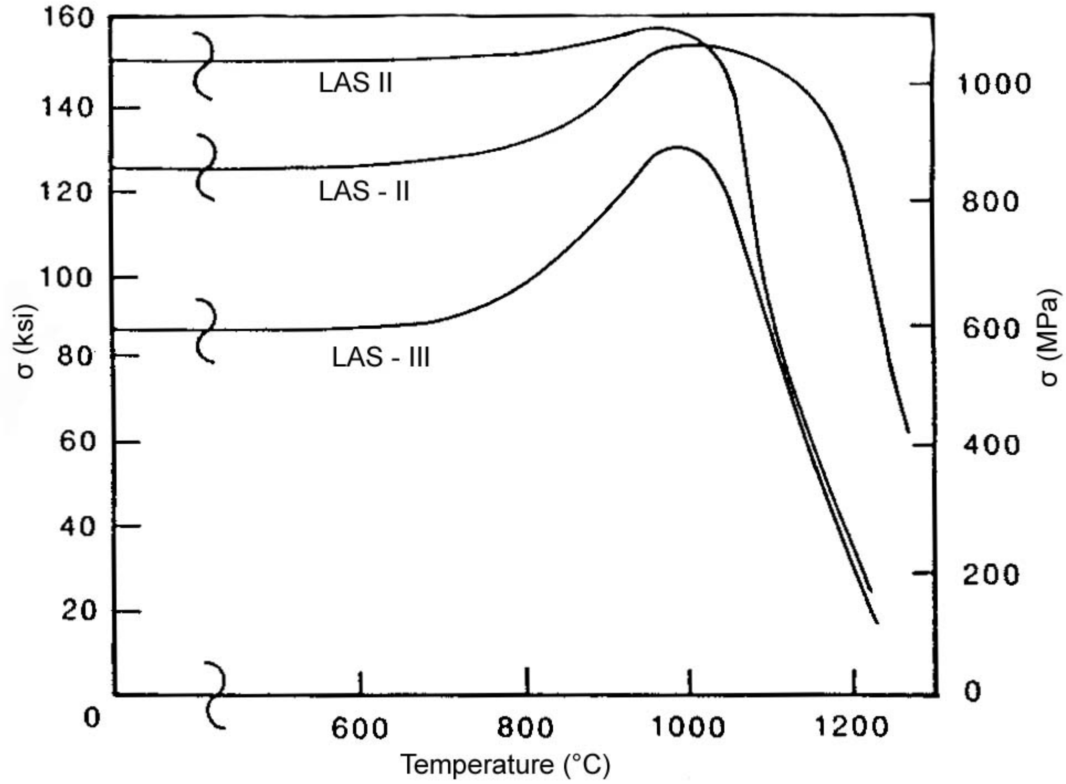
53.5.2 Mechanical properties

53.5.2.1 General

Published literature shows that problems have been encountered in achieving reproducible results with the development materials; not least in relation to in-situ fibre strength. No definitive explanation has been identified.

53.5.2.2 Tensile and flexural

Both the tensile and flexural strengths of SiC/LAS composites have been measured and indicative values are given in Figure 53.5.3, [See also: Table 53.4.1], Ref. [53-13].



Conditions: Three-point bend in Argon

Figure 53.5-3 - SiC reinforced glass-ceramic composite: Flexural strength versus temperature for unidirectional SiC/LAS

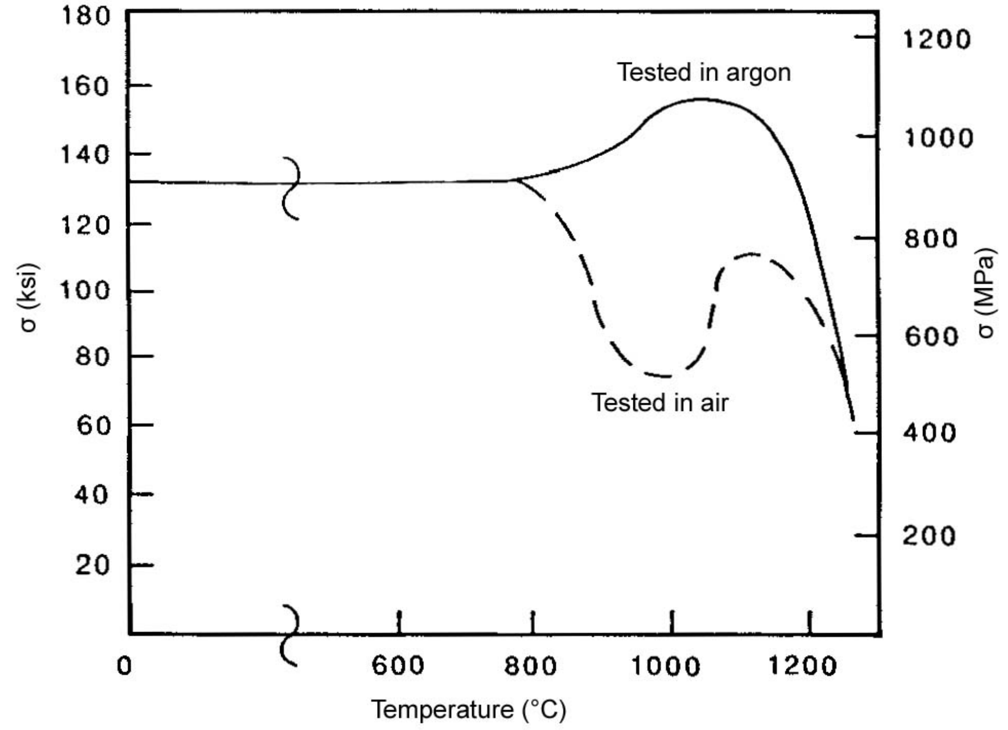
Whilst the tensile mode of failure is fairly well understood, the flexural response is slightly more complex due to the presence of compressive forces within the specimens. This gives rise to a phenomenon where the flexural strengths can actually increase at intermediate temperatures (800°C to 1000°C) just below temperatures where excessive matrix softening leads to a loss in strength, [See: Figure 53.5.3].

The increase in flexural strength at 800°C to 1000°C is thought to result from partial matrix softening enabling localised load redistribution during three-point bending.

Flexural strengths are always higher than tensile strength for a correspondingly similar material. The high temperature bend strengths in Figure 53.5.3 were obtained in an inert atmosphere.

53.5.2.3 Effect of environment

The effect of oxidation is shown in Figure 53.5.4. The bend strengths above 600°C show a dramatic drop and fluctuation indicating oxidative penetration of the composite.



Conditions: Three-point bend, in Argon and Air

Figure 53.5-4 - SiC reinforced glass-ceramic composite: Flexural strength versus temperature for unidirectional SiC/LAS-III

53.5.2.4 Compression

The compressive response of SiC/LAS composites provides a further contrast on failure characteristics, Ref. [53-14]. Matrix microcracking is again present beyond certain strain levels, but fibre buckling and fibre (bundle or yarn) kinking determines ultimate strain levels. Figure 53.5.5 shows compressive strength versus strain responses for LAS-II/SiC composites.

Off-axis plies, such as ±45° and 90°, in composites have low failure strains. This is observed for tensile loading, and coupled with matrix microcracking (proportional limit) makes clear that maximum permissible operating strains, hence stresses, are modest for these composites.

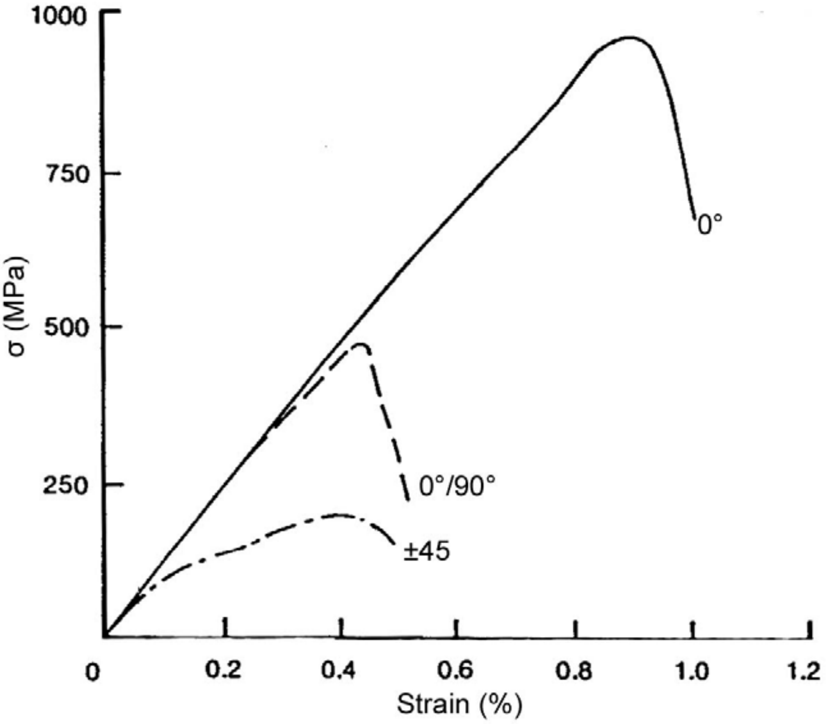


Figure 53.5-5 - SiC reinforced glass-ceramic composite: Compressive stress-strain response of 0°, 0°/90°, and ±45° SiC/LAS-III, at 23°C

Figure 53.5.6 shows the flexural stress-strain response of a 0°/±45°/90° LAS-II/SiC composite at various temperatures. The response of this multi-directional composite has a 'proportional limit' of around 100MPa for all test temperatures.

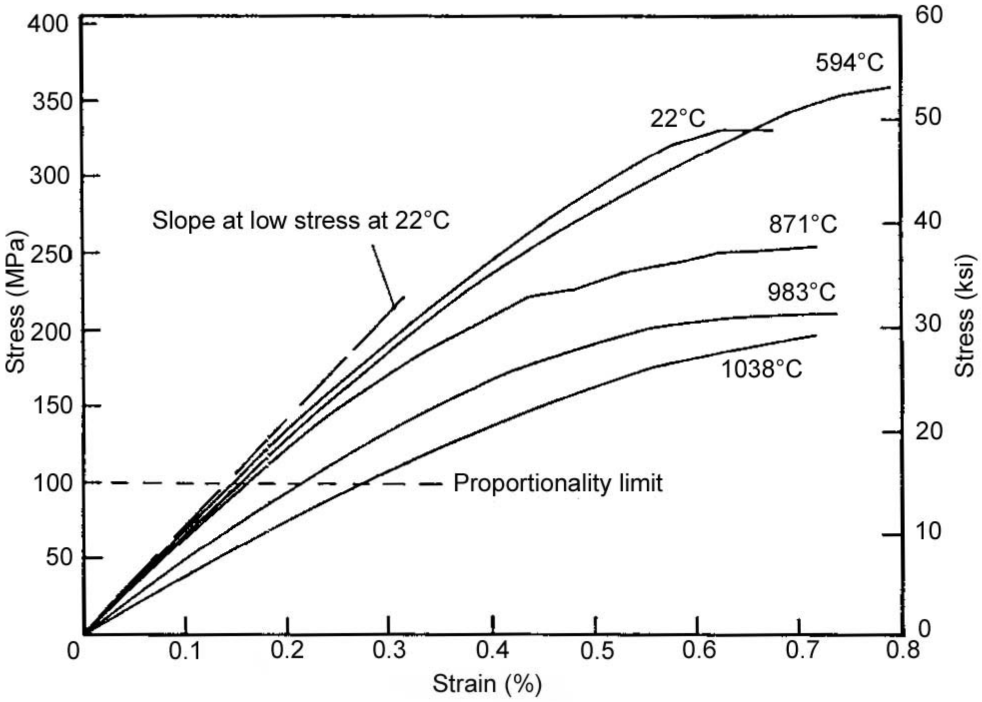


Figure 53.5-6 - SiC reinforced glass-ceramic composite: Flexural stress-strain data for 0°/±45°/90° SiC/LAS for a wide temperature range

Figure 53.5.7 and Figure 53.5.8 provide indicative strength data for SiC/LAS composite against the unreinforced monolithic glass-ceramic, Ref. [53-17].

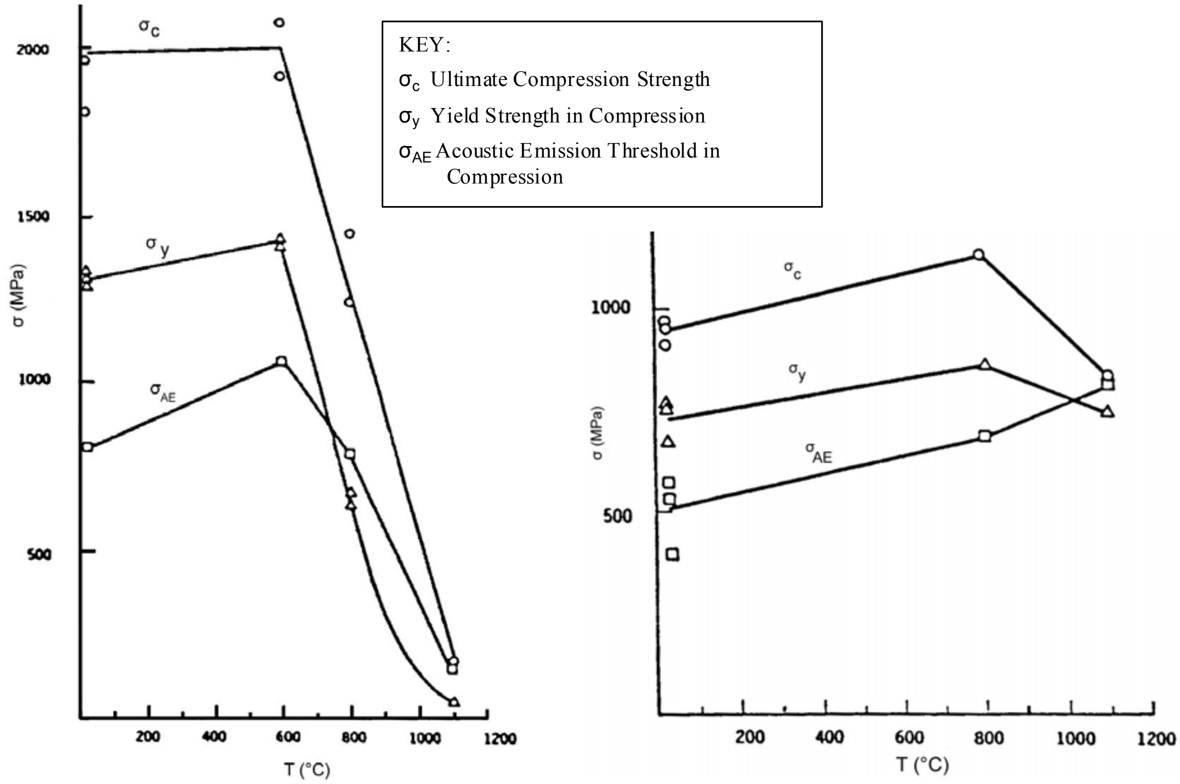
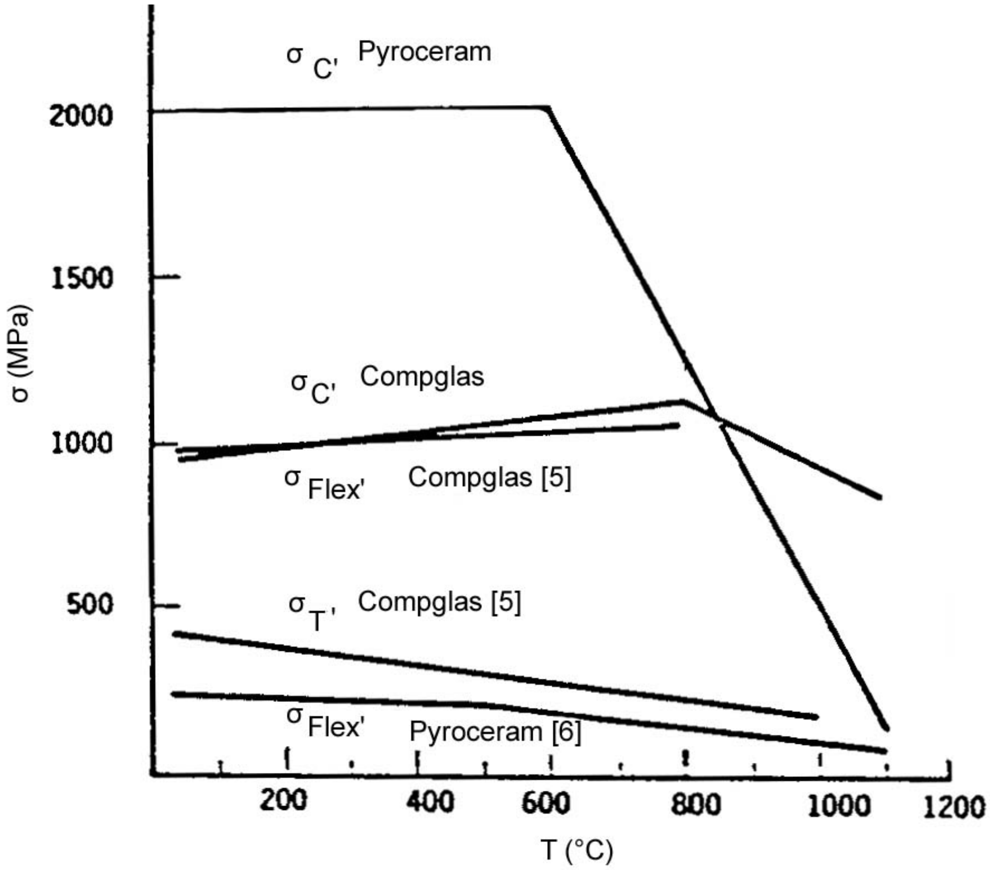


Figure 53.5-7 - SiC reinforced glass-ceramic composite: Strengths versus temperature for monolithic LAS (Pyroceram) and unidirectional LAS/SiC (Compglas)



Key: σ_T Ultimate tensile strength

σ_{flex} Ultimate flexural strength

Figure 53.5-8 - SiC reinforced glass-ceramic composite: Dependence of failure strengths with temperature and loading mode for 0° Compglas and monolithic Pyroceram

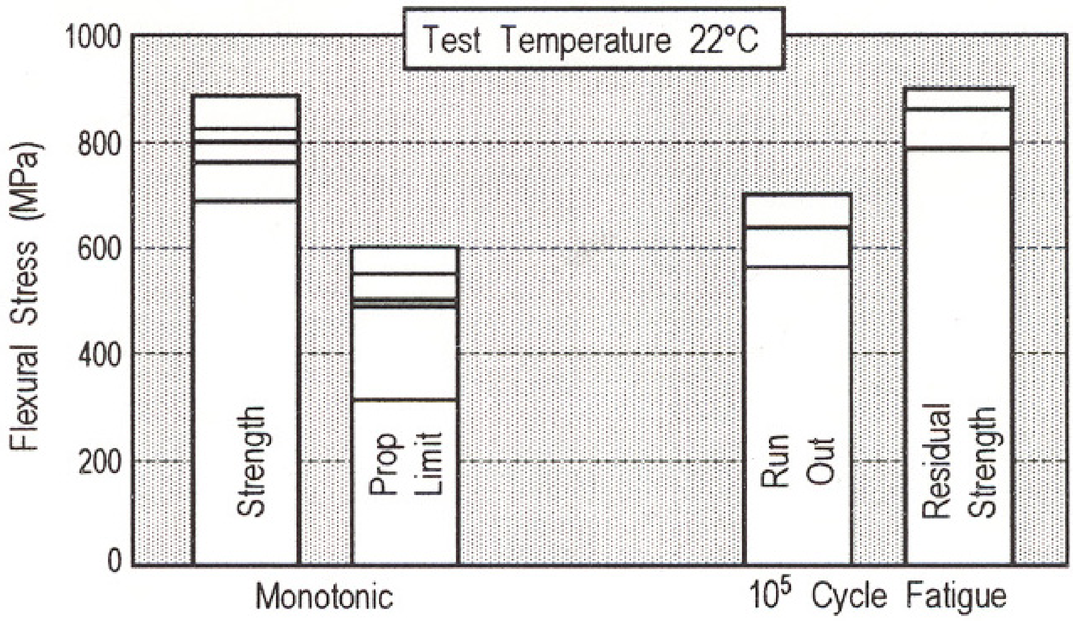
53.5.2.5 Fatigue

The formation of microcracking at modest stress levels, often well below ultimate strength, has important implications for repetitive loading, as in fatigue, Ref. [53-15], [53-16]. Flexural fatigue testing indicates that the use of peak fatigue stresses greater than the 'proportional limit' have the effect of inducing further microcracking. This implies a larger network of microcracks providing greater access for the environment to enter the composite and increase the fibre degradation. The repetitive increase in microcracking effectively lowers the 'proportional limit'. As a result of high tensile stress fatigue the 'proportional limit' stress can be reduced by as much as 60%.

Some preliminary flexural fatigue data has been acquired for UD (0°) LAS-II/SiC composite, see Figure 53.5.9, Figure 53.5.10 and Figure 53.5.11. The main points can be summarised as:

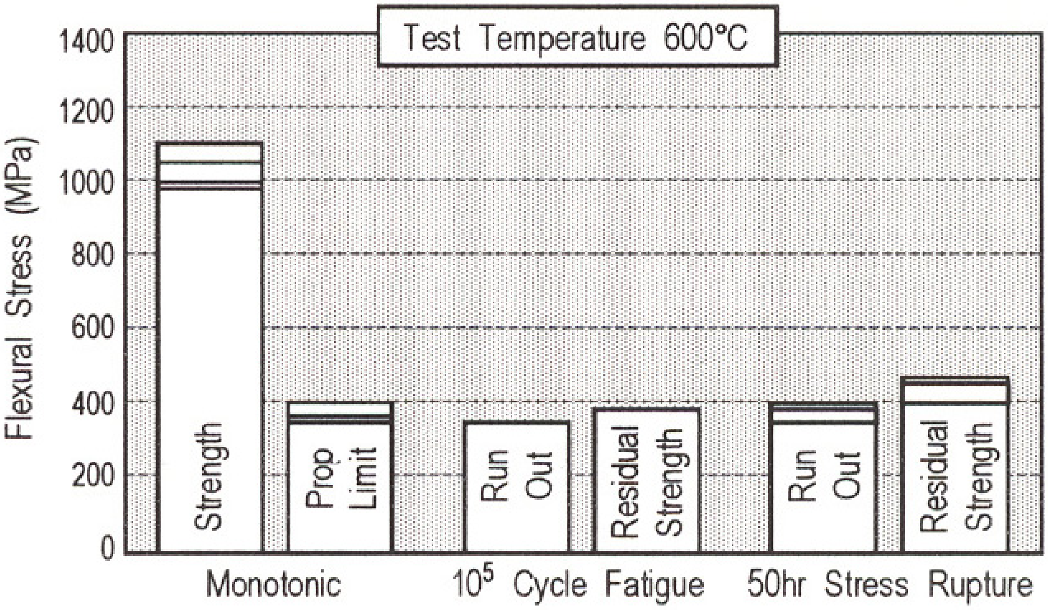
- At 22°C (RT) the ultimate flexural strengths were between 700MPa and 850MPa with a spread in 'proportional limit' of 300MPa to 600MPa.
- Peak flexural stresses less than 650MPa were required to ensure that 105 fatigue cycles are endured and allow run out.
- The residual strengths of specimens surviving 105 cycles were similar to those of as-made specimens.

- When the test temperature was raised to 600°C, the ultimate bend strength of the as-made composite increased reaching 1000MPa to 1100 MPa. The 'proportional limit' was however much lower at around 380MPa.
- Subsequent fatigue tests at this temperature showed that peak fatigue stresses had to be less than 380MPa to achieve 105 cycle run out.
- The residual strength of the composite experiencing 105 cycles was correspondingly low.



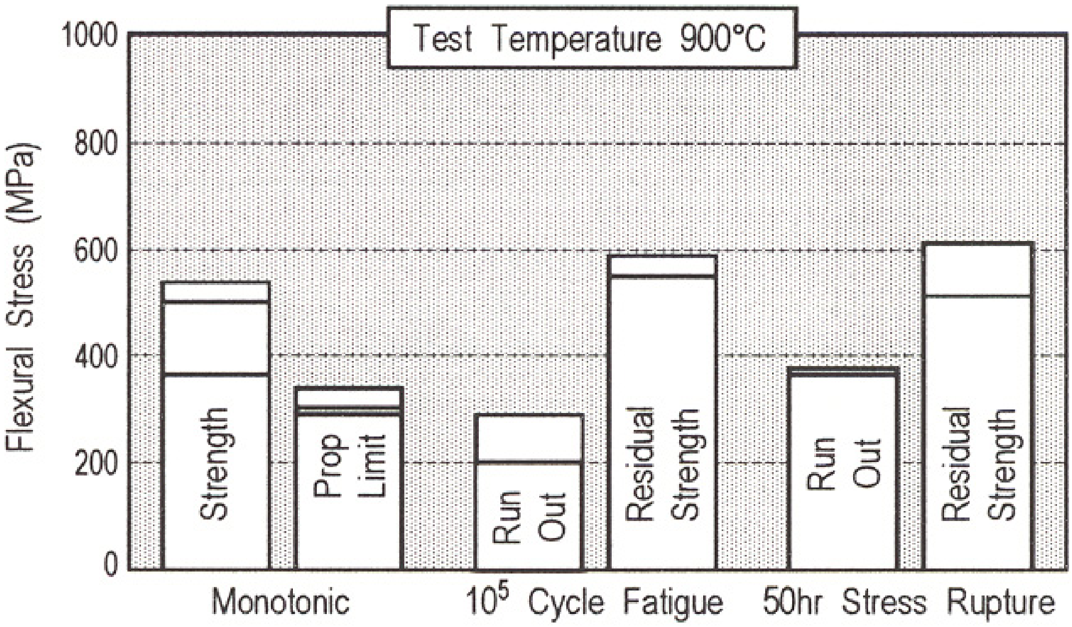
Fibre volume fraction: 45 to 50%

Figure 53.5-9 - SiC reinforced glass-ceramic composite: Comparison of flexural strength under various loading conditions for 0° SiC/LAS at 22°C



Fibre volume fraction: 45 to 50%

Figure 53.5-10 - SiC reinforced glass-ceramic composite: Comparison of flexural strength under various loading conditions for 0° SiC/LAS at 600°C



Fibre volume fraction: 45 to 50%

Figure 53.5-11 - SiC reinforced glass-ceramic composite: Comparison of flexural strength under various loading conditions for 0° SiC/LAS at 900°C

At the same time stress rupture tests lasting 50 hours were conducted to quantify the continuous stress level that the composite could withstand without failure:

- For 50 hours, this was around 380MPa.
- At 900°C, stresses below 300MPa were needed to achieve 105 cycles run out; see Figure 53.5.12, Figure 53.5.13 and Figure 53.5.14, Ref. [53-16].

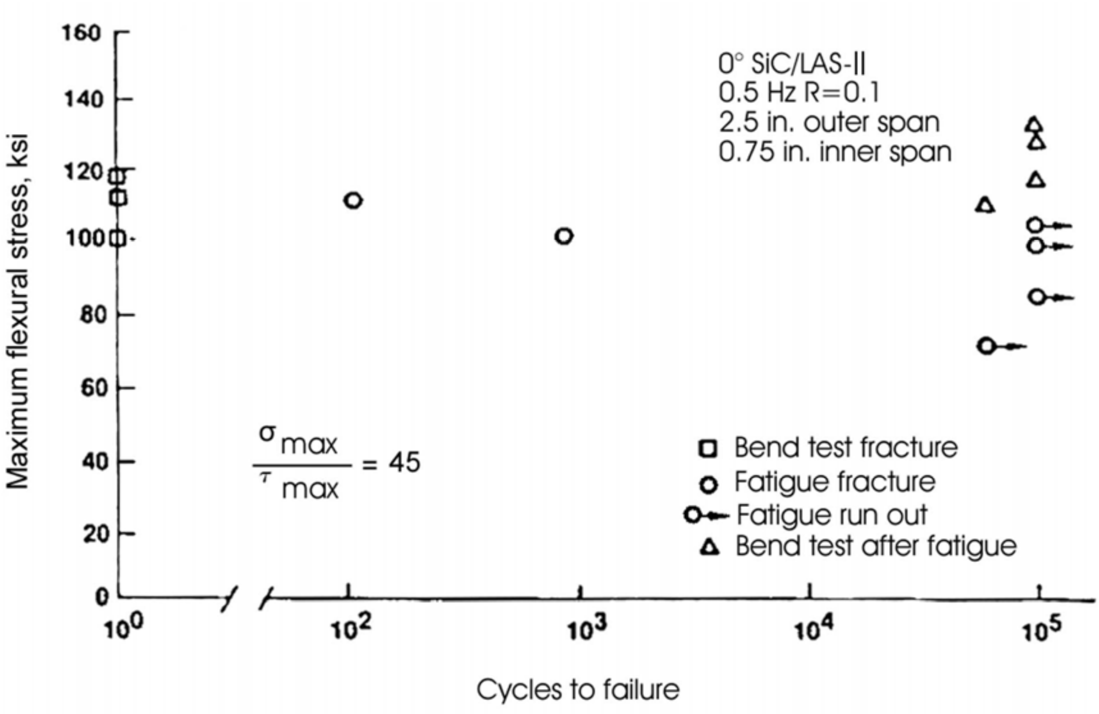


Figure 53.5-12 - SiC reinforced glass-ceramic composite: Room temperature four-point flexural fatigue of 0° SiC/LAS-II

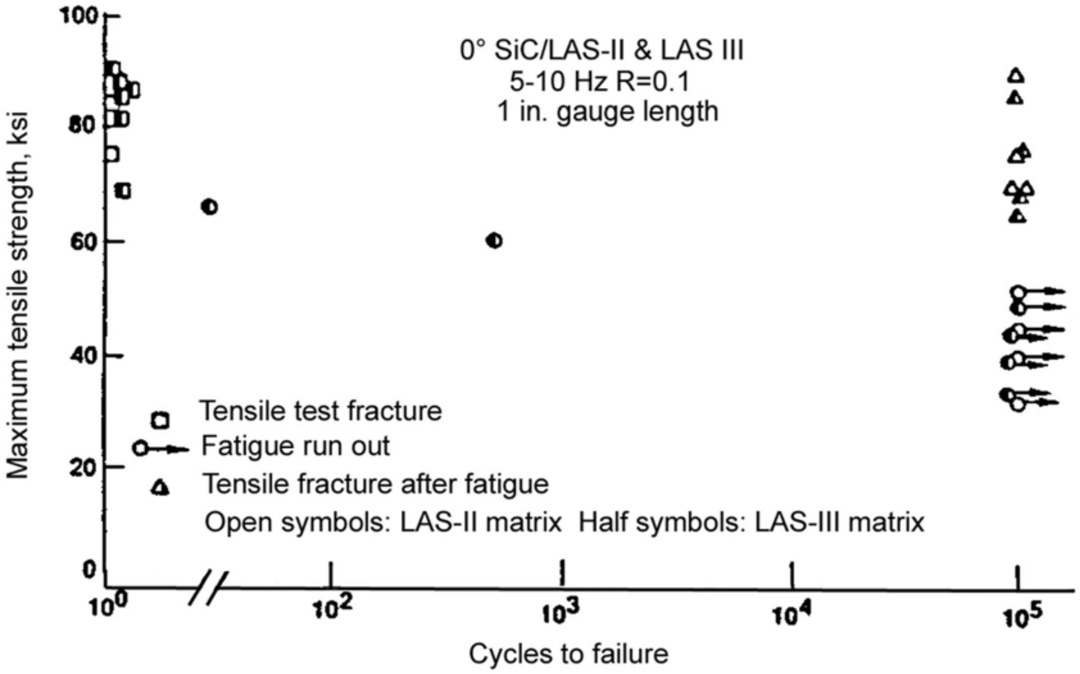


Figure 53.5-13 - SiC reinforced glass-ceramic composite: Room temperature tensile fatigue of 0° SiC/LAS-III

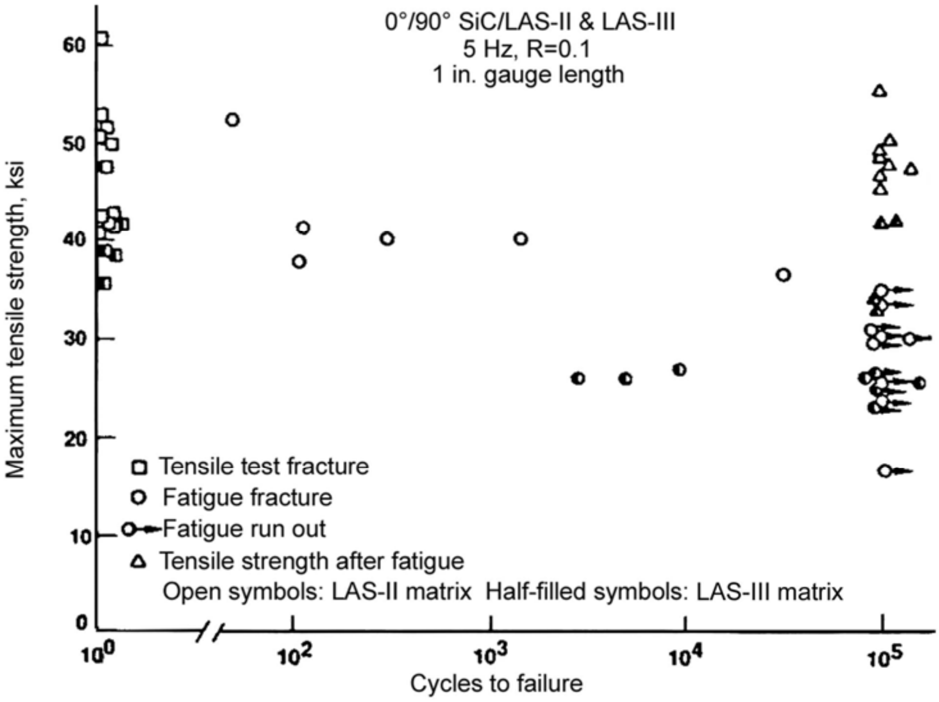


Figure 53.5-14 - SiC reinforced glass-ceramic composite: Room temperature uniaxial tensile fatigue of 0°/90° SiC/LAS-II and 0°/90° SiC/LAS-III

53.5.2.6 Summary of strength data

The conclusion to be drawn from the strength data presented is that the ultimate strengths of these composites at room temperature are respectable at around 800MPa for a unidirectional composite in bending. However, the usable strength for design purposes is lowered by:

- Off-axis plies,
- Tensile and compressive loadings
- High temperatures, up to 1000°C
- Fatigue loading
- The initiation of microcracking.

It is suggested that 200MPa is a realistic design 'strength' figure for 0° unidirectional composite and 100MPa for bi-directional. The term 'strength' is used loosely, but is applicable to tensile, compressive and flexural modes.

53.5.2.7 Fracture toughness

The fracture toughness data on glass-ceramic matrix composites show that LAS-II and LAS-III composites possess attractive properties compared with monolithic glasses, glass-ceramics and ceramics.

The through-thickness fracture toughness of a unidirectional or bi-directional composite are around 30MPa√m, compared with 2 MPa√m for monolithic glass-ceramic matrix. The highest values are for through-thickness and fracture toughness between planes is distinctly lower.

Both notched three-point bend tests and cantilever beam specimens have been used to derive fracture toughness values.

Whilst these values are termed K_{1C} by some sources, they are only for comparative purposes. The knowledge on fracture mechanics of these materials is incomplete.

For 2-D fabric based composites, poor interlaminar and through-thickness strengths pose problems in some applications. Like many composites the option is available to use 3-D fibre preforms (fibre architecture) to improve these strengths. 3-D braided SiC/LAS-III have been successfully prepared, which give more even fracture toughness values in through-thickness orientations, Ref. [53-18].

53.6 Potential applications

53.6.1 Technology status

53.6.1.1 USA

The most highly developed composites are those of UTRC under the trade-name COMPGLAS. These include the LAS systems. These materials are being evaluated for the gas turbine engine and aerospace applications in the USA. However, they are not offered as commercial materials on a world-wide basis.

53.6.1.2 Europe

Developments in borosilicate matrix composites at Aerospatiale (France) and Harwell Laboratory (UK) for engine applications at temperatures of ~600°C are reported, Ref. [53-4], [53-19].

53.6.1.3 Summary of composite development

- Fibre, matrix and interface are all tailored to achieve strong, tough composites.
- Low fibre-matrix interfacial strength implies low off-axis strength.
- Non-linear stress-strain curves and an elastic modulus that decreases with increasing strain should be taken into account in successful designs.
- Flexural tests by themselves are an inadequate means of defining composite stress-strain behaviour or strength.
- Environmental stability and composite structural life prediction are the key issues for successful composite application.
- Non-structural applications, such as tribology and dimensional stability, can provide the first usage of these composites.
- Micro-indentation test techniques are being used to assess the interfacial shear strength between fibre and matrices, Ref. [53-20].

53.6.1.4 Applications resumé

There are two main advantages of glass and glass-ceramic composites over their ceramic matrix counterparts:

- The matrices are thermo-formable, like metals, giving greater freedom on processing and better control of composition.
- The consolidation temperatures of 800°C to 1300°C stay within the stability range of the inorganic, ceramic and carbon fibres.

For intermediate temperatures of 500°C to 1000°C, these composites have weight-saving attractions over metals, e.g. titanium and nickel alloys. For long-term applications, their creep performance has yet to be determined.

In many respects, their ability to achieve specific physical rather than mechanical properties can be a driving force for their use, e.g. low CTE materials (with carbon fibres) can be useful in applications of long-term exposure to space environments, such as LEO, where plastics and metals can show progressive degradation.

These composites can also be used for electronic substrates and carriers.

53.7 References

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54 Carbon-Carbon matrix composites

54.1 Introduction

54.1.1 Applications

The applications for Carbon-Carbon composites can be broadly grouped as those aiming to:

- exploit high-temperature capability, or
- capitalise on dimensional stability characteristics.

54.1.2 High temperature

Based on the experience of using C-C material for short-duration, single-use space applications, their characteristics appropriate for use in reusable, long-life structures were investigated. The work was largely conducted in programmes considering space plane-type vehicles. The applications included thermal protection 'thermal shields' for regions of the vehicle during re-entry, [See also: Chapter 71].

Despite their advanced commercial status, mechanical property data is limited. This is a direct reflection of the influence material processing has on the final material. As such, any data stated are considered as indicative only of what is possible, [See: 54.2].

An important consideration is the oxidation of Carbon-Carbon at temperatures above 500°C. Various protection methods are described, [See: 54.4].

54.1.3 Dimensional stability

The low thermal expansion characteristics of C-C composites make them of interest for applications demanding very high dimensional stability. The knowledge of materials and processing, developed initially for high-temperature applications, has enabled a C-C composite to reach qualified status for some structural parts for space telescopes or scientific instruments, [See: 54.6].

54.2 Material description

54.2.1 Characteristics

54.2.1.1 General

Interest in carbon matrix composites has centred on materials which combine a carbon fibre reinforcement with a carbon matrix. These materials are known as carbon-carbon (C-C) composites. There are many variants, as shown in Figure 54.2.1, arising from the:

- specific fibre used,
- form in which the fibre is used, and
- method of creating the carbon matrix phase.

The selection of materials and processing route used determine the specific mechanical properties of the finished component. A major advantage of multi-directional carbon-carbon composites is the freedom to orientate selected fibre-types and amounts to accommodate the design loads of structural components.

54.2.1.2 Fibre architecture

The architecture of the carbon fibre-reinforcement can take many forms including, [See also: 6.31]:

- random short fibres,
- unidirectional fibres,
- braided structures,
- laminated fabrics,
- orthogonal 3-D weaves, in either Cartesian or cylindrical coordinates,
- multidirectional structures, such as 4-D structures.

54.2.1.3 Properties

General properties of C-C composites are:

- light weight.
- ability to operate at high temperatures owing to their refractory nature.
- good mechanical properties including fracture resistance.
- low thermal expansion.

Mechanical properties are usually satisfactory in the two dimensions containing the reinforcement, but the carbon matrix is weak so the performance in the third direction is very low, [See: 54.3].

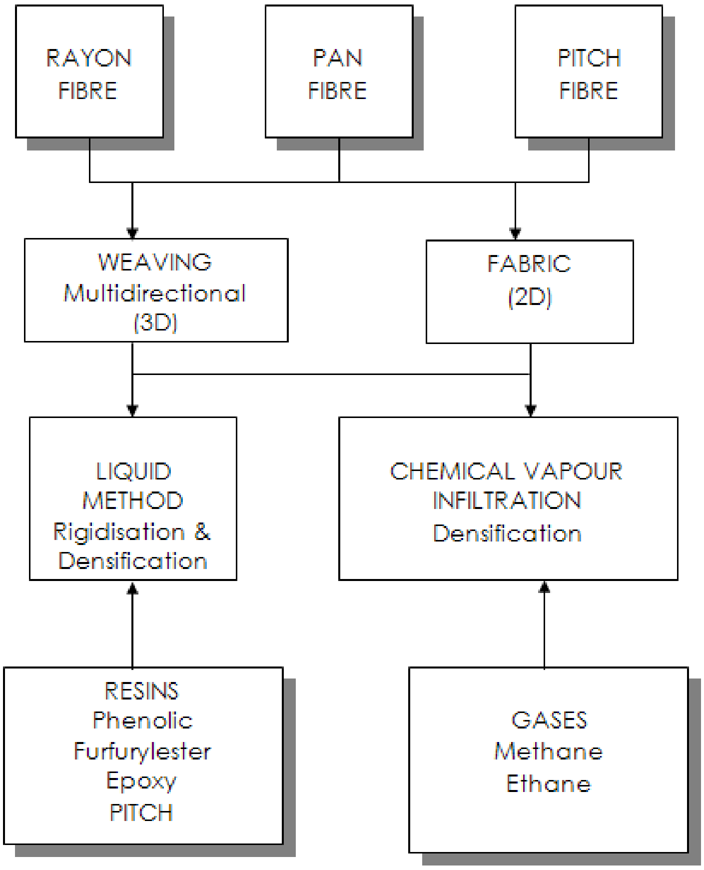


Figure 54.2-1 - Carbon-carbon composites: Schematic diagram of material selection and processing routes

54.2.1.4 Oxidation

The major hindrance is that the oxidation resistance of C-C is poor. Exposure to oxygen-containing atmospheres at temperatures above 500°C results in significant weight loss and property degradation.

To improve oxidation resistance it is necessary to create a barrier to the aggressive environment; usually by coating the composite.

54.2.2 Manufacturing techniques

54.2.2.1 Reinforcement forms

The carbon fibre-reinforcement is generally woven into a preform to produce unidirectional or multidirectional (2-D, 3-D or 4-D) fibre arrangements. Figure 54.2.2 shows the fibre arrangement in SEPCARB® 4-D preform.

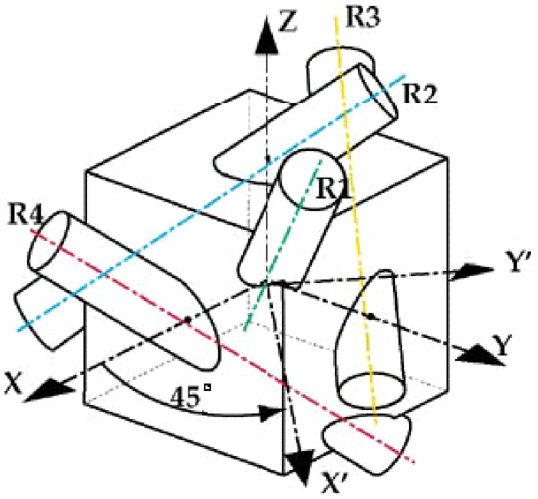
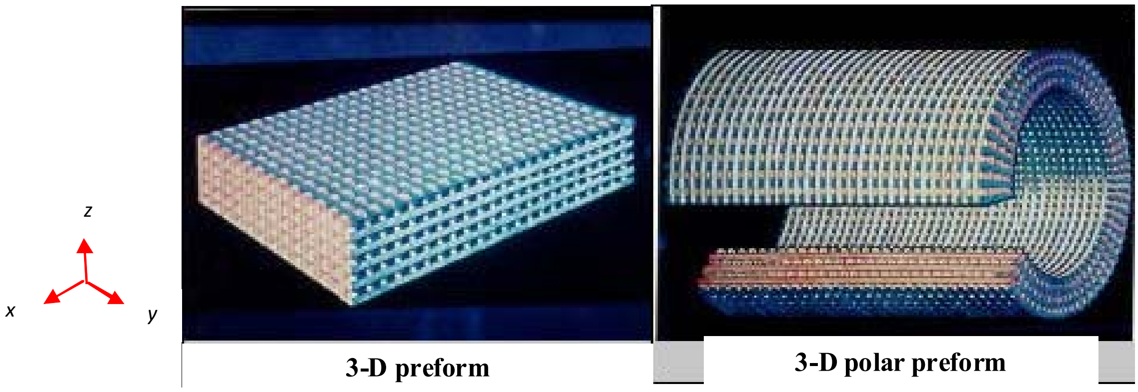


Figure 54.2-2 - Carbon-carbon composites: 4-D fibre architecture in SEPCARB® 4-D

Figure 54.2.3 shows examples of 3-D fibre preforms.



3-D preform

3-D polar preform

Figure 54.2-3 - Carbon-carbon composites: 3-D fibre preforms

The weaving processes used to create multidirectional near net-shape preforms have been the topic of extensive optimisation and automation, Ref. [54-1]. Producing the fibre preform remains a significant cost contributor. The choice of woven preform is linked to the application, e.g. throat nozzles use 3-D and 4-D preforms, some exit cones use 3-D polar weave preforms (cylindrical coordinates) to sustain the severe thermal stresses. Polar weave preforms are used for cylinders and other shapes of revolution, e.g. cylinders and cones, convergent or divergent sections, Ref. [54-23]. 3-D carbon-carbon is also used to manufacture high-temperature fasteners, e.g. screws, nuts and bolts, Ref. [54-22].

Some examples of complex-shaped, multidirectional fibre preforms are shown in Figure 54.2.4.

Figure 54.2-4 - Carbon-carbon composites: Examples of multidirectional fibre preforms

54.2.2.2 Matrix

The matrix phase is introduced into the preform by either:

- Liquid Impregnation: using resins or pitches, which are subsequently carbonised. The use of pitch needs a two-stage process:
  - — partial impregnation or rigidisation of the fibre preform and pyrolysis, then
  - — densification.
- Chemical Vapour Infiltration (CVI): under the controlled temperatures and pressures of a reaction vessel, methane or ethane are converted and deposited as pyrolytic carbon.

The liquid resin route also needs repetition of the impregnation and pyrolysis treatments to achieve densification of the composite. Repetition of the densification stage is undertaken to achieve the desired density and properties.

The CVI method relies on the deposition of the carbon matrix on and between fibres. The processing times can exceed 100 hours.

CVI is normally used for thin-walled parts. Liquid infiltration methods are used for thicker sections. A combination of both techniques has also been used, Ref. [54-2].

54.3 C-C composite: Properties

54.3.1 Mechanical properties

54.3.1.1 General

Although C-C composites are in advanced stages of development and application, compared with the other material options, very little data on mechanical properties have been published openly. This is primarily due to the significant resources put into their development and evaluation and the commercial demands of those companies in capitalising on the expertise gained. There are however some general comments on the mechanical properties of C-C materials which can be presented.

Table 54.3.1 gives mechanical properties which are indicative of those attainable by different C-C composites, but caution is needed in their interpretation, Ref. [54-4], [54-5].

Table 54.3-1 - Carbon-carbon composites: Indicative mechanical properties

Properties at RT		**C-C Composite Type**		
		3-D	**2-D**	**C-C with SiC Coat**
Density	(kg/m^3)	1750 - 1950	1820 - 1950	1700 - 1800
Tensile Strength	(GPa)	200 - 260	127 - 172	100 - 140
Tensile Modulus	(GPa)	90 - 100	68 - 101	63 - 67
Compressive Strength	(MPa)	140	214	88 - 170
Compressive Modulus	(GPa)	68	3.2	61 - 73

54.3.1.2 Multidirectional reinforced composites

The reinforcement fibre architecture influences the composite performance, [See: 54.2]. The mechanical properties are generally satisfactory in the two directions containing the reinforcement, but the carbon matrix is weak so the performance of the other direction is very low. This problem is crucial during manufacturing when high internal stresses provoke delamination of the constituent plies or in applications involving high thermo-mechanical loading, such as re-entry and rocket motors components, Ref. [54-23].

Multidirectional carbon-carbon composites provide the freedom to orientate fibres of various types and amounts to react the design loads of the structural components. They can also be machined and to create small radii. The cost of producing the fibre preforms, even using fully-automated weaving machines, is still significant. This, along with low mechanical performance in non-reinforced direction, are the main disadvantages, Ref. [54-23].

Whilst the nose cone and leading edges of the Space Shuttle Orbitor are formed from 2-D carbon fabric, multidirectional (3-D and 4-D) are used for structures experiencing severe thermal stresses, e.g. throat nozzels, exit cones, [See: 54.2]. Mechanical fasteners, using 3-D reinforcements, show no loss in strength at high temperatures and demonstrates the superiority of C-C compared with metals, Ref. [54-22].

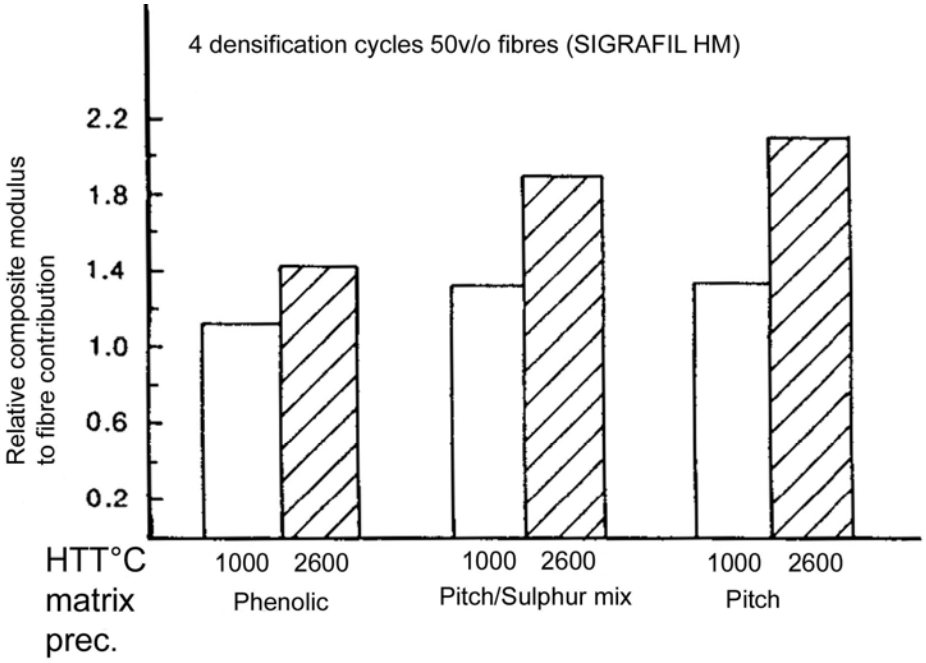
54.3.1.3 Stiffness

The modulus of C-C composites is dictated by the moduli of:

- fibre, and
- matrix.

Usually the stiffness of the matrix in polymeric matrix composites is ignored, but for C-C materials the stiffness contribution is significant.

Figure 54.3.1 shows the stiffness of three C-C materials created from different carbon matrix precursors that have received different heat treatments at 1000°C and 2600°C. The resultant stiffness is determined by calculation of the theoretical modulus without the matrix stiffness contribution, hence values greater than 1.0 are quoted.



Conditions: Materials produced from different matrix precursors, with two different final heat treatment temperatures (HTT).

Figure 54.3-1 - Carbon-carbon composites: Predicted modulus values from conventional theory without a matrix contribution

54.3.1.4 Strength

Theoretically, three parameters control the strength of a composite consisting of brittle fibres in a brittle matrix:

- modulus of fibres.
- strain to fracture ratio of matrix to fibre.
- fibre volume fraction.

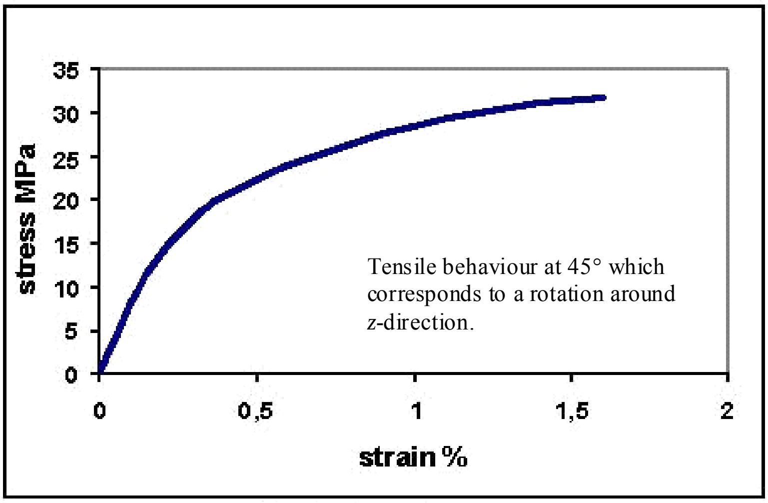
In practice, C-C composites have exceeded theoretically predicted limiting values of strength and strain. This has been attributed to:

- compressive pre-stressing of the matrix, and
- energy-consuming fracture processes in the matrix and at the fibre-matrix interface.

Compressive pre-stressing of the matrix occurs by shrinkage of the matrix phase during processing and is influenced mainly by the carbon residue of the matrix precursor and fibre surface reactivity, Ref. [54-3]. Excessive shrinkage can result in matrix cracking which is deleterious in the extreme to composite properties.

Figure 54.3.2 illustrates the tensile behaviour of 3-D carbon-carbon composite at RT and at high temperatures under an inert atmosphere, Ref. [54-20], [54-21]. The tensile response of 4-D carbon-carbon composite under the same conditions is shown in Figure 54.3.3, Ref. [54-18], [54-19].

A: Room temperature tensile behaviour



B: High-temperature tensile behaviour (inert atmosphere)

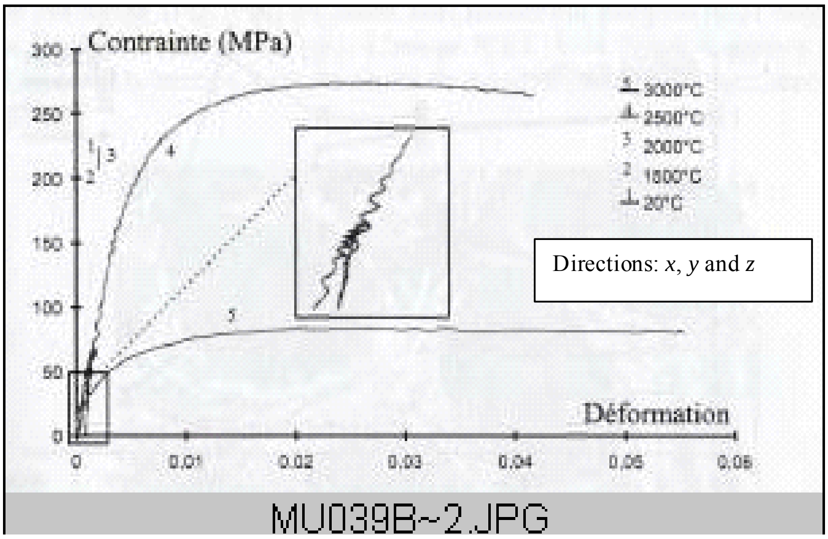
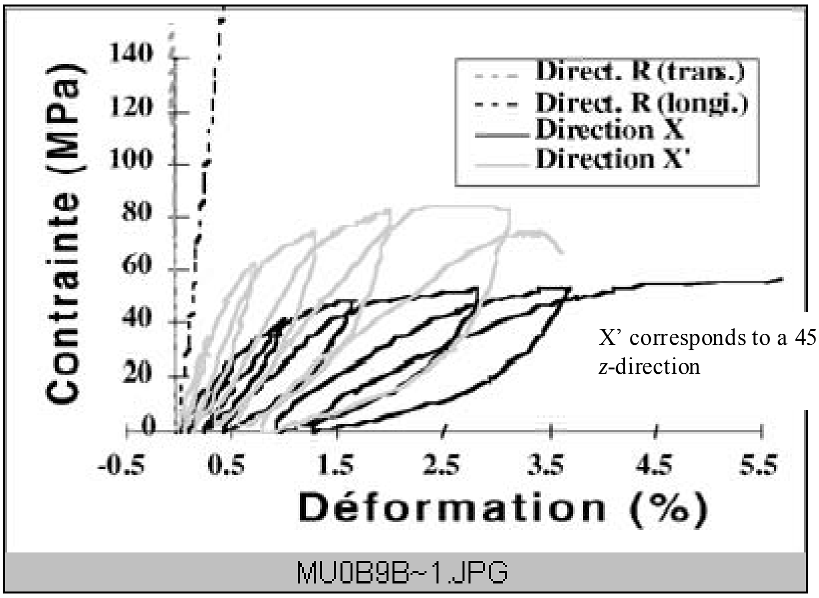


Figure 54.3-2 - Carbon-carbon composites: Tensile response of 3-D composite

A: Room temperature tensile behaviour



X' corresponds to a 45° rotation around *z*-direction

B: High-temperature tensile behaviour (inert atmosphere)

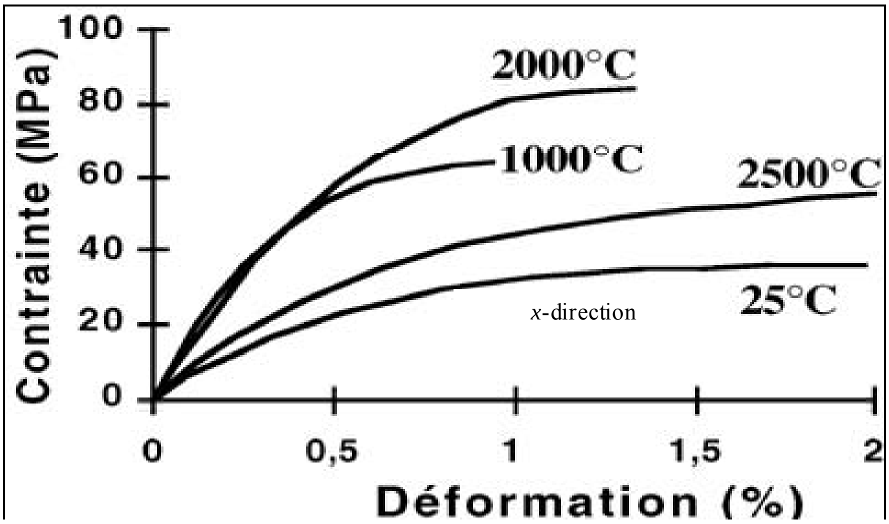


Figure 54.3-3 - Carbon-carbon composites: Tensile response of 4-D composite

54.3.1.5 Fracture

The internal cracks and porosity are responsible for the apparent pseudo-plasticity phenomenon exhibited by C-C composites. Sealing of these imperfections impairs pseudo-plasticity and promotes a brittle fracture mode.

The energy absorption capacity of the composites is linked to the fibre-matrix bonding and crack propagation mechanisms, i.e.:

- Weak bonding enables diversion and blunting of the propagating matrix crack at the fibre-matrix interface, permitting fibre pull-out.
- Strong bonding reduces the possibility of crack deviation and enables the crack to pass through the fibre; limiting both strength and energy absorption capacity.

54.4 Oxidation protection systems

54.4.1 Requirements

To be successful, the coating should retain its mechanical and physical integrity throughout all temperature excursions. This can be in the range of -160°C to +1700°C during one mission of a reusable spacecraft. Consequently the coating should remain adhered to the composite and not crack, which would otherwise enable oxidative ingress.

54.4.2 Coating development

54.4.2.1 General

Significant effort has been placed on the investigation of coatings, as without them the utilisation of C-C materials is severely limited.

The particular coating used depends on the thermal regime encountered, e.g.:

- Silicon Nitride: Si_3N_4 has demonstrated protection up to 1250°C.
- Silicon Carbide: SiC (most commonly reported) which can be enhanced by a SiO_2-based surface layer (TEOS) to provide protection to temperatures of 1700°C, Ref. [54-6].

54.4.2.2 Coating systems

Protection systems can be very complex (multiplex) and a different one specified depending on the life expectancy required in a thermocyclic oxidation environment, Ref. [54-6] to [54-13].

To summarise, the protection constituents can include:

- inhibitors, in the form of particulates added to a resin pyrolysed matrix.
- infiltration of oxidation resistant ceramics into a porous C-C substrate. Infiltration can be achieved by CVI/CVD and include SiC, Si_3N_4, BN, AlN, TiC and B_4C.
- conversion of surface carbon to silicon carbide, to give a diffusion coating.
- an overlay coating, e.g. SiC.
- glassy inter-layers and coatings which act as a sealing medium.

Operation above 1700°C requires more complex coatings composed of, Ref. [54-2]:

- hafnium diboride,
- hafnium oxide, and
- iridium.

54.4.3 Matrix modification

The modification of the carbon matrix by the incorporation of a preferentially oxidising filler material (boron carbide) and organo-metallic materials (which convert to B, Si and Ti during pyrolysis) have shown some increased oxidation protection at temperatures below 1000°C, Ref. [54-7]. This approach differs from the protective coating method in that it provides direct oxidation resistance throughout the composite thickness, whereas coatings rely on surface protection and indirect protection of the composite through-thickness.

The modified matrix route avoids problems of nonuniformity of coatings and potential thermal expansion mismatch which can result in cracking of the coating and a subsequent loss of protection.

The effect of a modified carbon matrix on mechanical performance of the composite is unknown, or whether it has any benefit at temperatures above 1000°C.

54.4.4 Design factors

The design of an oxidation protection system should be closely tailored to the intended application and environment. One of the basic problems is ensuring that complete coverage of the C-C is present at all oxidising temperatures in the intended thermal cycle. This is hindered by the low to negative coefficient of thermal expansion for the C-C compared with the positive expansion of selected coating materials. This usually results in cracking of the primary protective coating on cooling and the need to seal the cracks during subsequent heating cycles.

Each application imposes its temperature spectrum and life expectancy including thermal cycles. Two applications for protected C-C are 'Thermal Protection Systems' for spaceplanes, [See also: Chapter 71], and gas turbine engines for aircraft. These have contrasting expectations, as summarised in Table 54.4.1.

Table 54.4-1 - Carbon-carbon composites: Requirements for oxidation protection systems for two applications

Requirement	**Spaceplane TPS** **Nose cone**	**Gas turbine engine** **Exhaust petals**
Max. temperature (°C)	1700	800 + excursions to 1300
Life expectancy (hours)	30	300 - 2000
Thermal cycles	60	2000+

In general, protection systems increase further the complexity and cost of the component. Coating systems can consist of between five and ten applied layers. In selecting protective materials, the oxidation resistance and coating impermeability to oxygen should be considered. Options include:

- An outer oxide impermeable barrier, e.g. Al_2O_3, HfO_2, ZrO_2, with better permeation resistance than the silica formed on silicon carbide.
- An intermediate layer between the oxide and silicon carbide layer, to bridge the differences in CTE, e.g. aluminium nitride with the alumina outer layer, Ref. [54-14].
- A primary silicon carbide coating deposited in thin layers with a progressive reduction in deposition temperature to fill in the cracks of the previous layer, Ref. [54-15].

54.5 Potential applications

54.5.1 Resumé

54.5.1.1 Single use components

Carbon-Carbon composites have a long history of use in space programmes, particularly for single-cycle, short-duration thermal exposures in a non-reusable application. These include:

- re-entry shields.
- motor components, engines and nozzles.

Looking at the wider use in aerospace applications, C-C composites are appropriate for:

- high-energy braking systems,
- high-temperature seals, and
- dimensionally stable structures.

In all probability, C-C is the natural selection for high-temperature applications (between 1200°C and 2000+°C) of short duration.

54.5.1.2 Reusable components

For reusable components, such as thermal protection systems, the cost of oxidation protection can be prohibitive and preference can be given to ceramic matrix composites. The reliability of oxidation protection systems after repetitive thermal cycling can prove a deciding factor.

During re-entry, extreme temperatures of ~1700°C are experienced by the nose cone and leading edges of a space vehicle. It is to those areas that C-C composites have been applied on Space Shuttle as thermal protection systems, Ref. [54-16]. Other applications include nozzles on Pershing II missiles and other rocket components.

A development programme for a turbine wheel in turbo-jet engines destined for hypersonic aircraft is also advanced, Ref. [54-17].

The most noticeable attributes of C-C composites are thermal stability to 2000°C and beyond, plus good fracture characteristics.

54.5.2 Commercial availability

54.5.2.1 General

One primary benefit of the wide-scale use of C-C composites is that they are significantly advanced in both performance and process characterisation. Those companies active in the application, manufacture and test of C-C composites are:

- Aerospatiale (France): material marketed as NOVELTEX™.
- SEP (France),
- Dunlop (U.K.),

- Sigri (Germany), and
- LTV Aerospace and Defense (USA).

It is the knowledge, expertise and facilities held within these companies that enables a wider-scale exploitation of C-C materials in future projects.

54.5.2.2 Further developments

There are areas which need evaluation to improve confidence in C-C further; such as establishing the inspection procedures and qualification of C-C for more structural usage.

At present the main application areas are in thermal protection barriers. However, the evaluation of rotating engine components can provide information on material performance under dynamic loadings.

Conceptual designs for thermal protection systems within the European reusable vehicle programmes included C-C composites as a candidate for the Hermes nose cone.

[See also Chapter 71 for TPS]

54.6 Dimensionally stable structures

54.6.1 Introduction

Carbon-carbon composites posses near-zero coefficients of thermal expansion and do not suffer from moisture-induced distortion. These characteristics make C-C materials of interest in the manufacture of highly dimensionally-stable structures for space telescopes or scientific instruments.

Components made from the C-C material by the manufacturing processes described have been space-qualified for:

- GOCE gravity field and steady-state ccean circulation explorer programme.
- Pleiades programme.

The composite comprises continuous high-strength carbon fibres, in the form of a fabric, in a carbon matrix. The consolidated composite has a fibre volume fraction of about 60%.

The summary of the main features of the C-C technology includes:

- Very high thermo-elastic stability: CTE of 1.10^{-7}/°C for a quasi-isotropic lay-up configuration.
- Low density with good mechanical properties enabling simple and reliable analyses; as for conventional CFRP materials.
- Moisture insensitivity.
- Not brittle.
- Withstands very high temperature.
- Various architectural possibilities, e.g. thin and large size cylinders, plates and honeycomb sandwiches, which can be adapted into efficient structural concepts.

- Manufacturing facilities available with large size capabilities, e.g. up to 2.5 m.
- Industrial maturity, with further potential growth.

54.6.2 Material characterisation

The material is qualified for different configurations, i.e.:

- 'monolithic', e.g. for cylinders or spider blades.
- structural sandwich panels.

The basic properties are given in Table 54.6.1 for a quasi-isotropic lay-up, at room temperature.

Table 54.6-1 – Carbon-carbon composites: Basic properties

Property	Typical value
Density (kg/m^3)	1600
CTE($\times$ 10^{-6} /K)	–0.1
Tensile strength (MPa)	> 160
Short beam shear strength (MPa)	> 12
Tensile modulus (GPa)	> 60

In the addition to the basic material manufacturing, a number of additional processes were developed for C-C composites in dimensionally-stable structures, i.e.:

- Bonding processes, for both structural bonding and for heater bonding.
- Painting process onto C-C substrate.

Non-destructive inspection procedures, using infrared thermography were also developed and applied to ensure integrity.

54.6.3 Manufacturing process

54.6.3.1 General

The C-C manufacturing process described has been qualified by Alcatel Alenia Space at Snecma Propulsion Solide (Safran group) and Hitco (SGL group) to produce components demanding high stability in space applications.

The overall manufacturing sequence includes the usual steps used for CFRP parts, e.g. lay-up of prepreg and cure, plus high-temperature steps needing special furnaces, e.g. for carbonisation and densification.

Figure 54.6-1 shows the equipment used during some steps of the manufacturing process.

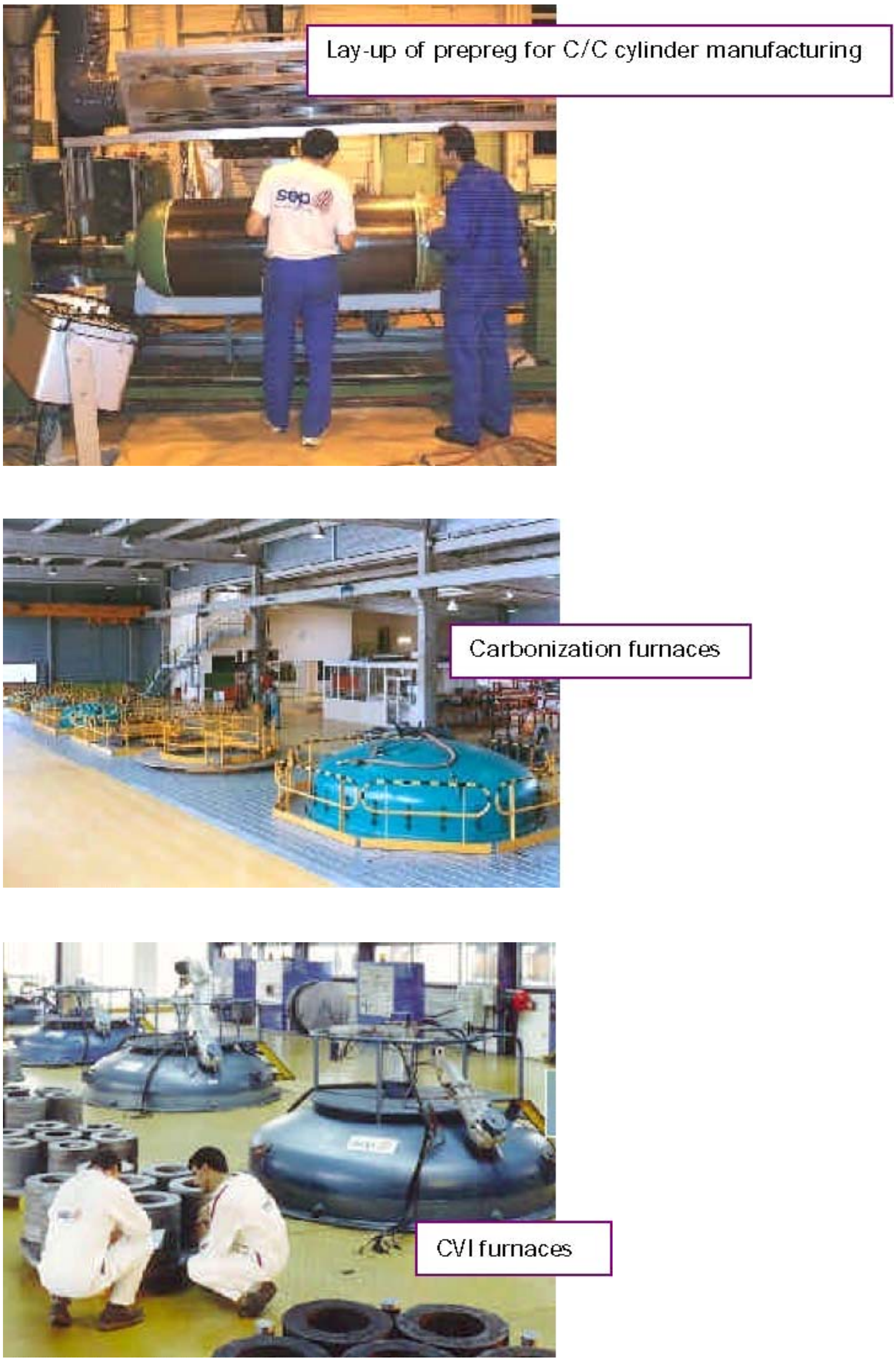


Figure 54.6-1 – Carbon-carbon composites: Manufacturing process equipment

54.6.3.2 Process steps

The manufacturing process has a number of sequential steps:

- Heat setting of the fabric, which is a heat-treatment that is essential in order to stabilise the carbon fabric before it is submitted to very high temperatures later in the processing. The final CTE properties also depend on the temperature of this heat treatment.
- Prepregging, which is the same process used for conventional CFRP materials. The carbon fabric is impregnated with either an epoxy novolac or phenolic resin, i.e. high-char resins. The resin content is chosen with respect to the desired final fibre volume content; taking into account any resin loss by bleeding during the cure.

- Lay-up, which is a ‘state-of the art’ step of the process that has no particular constraints. As with any CFRP part, lay-up angles, stipulated in the design, need to be respected.
- Curing, as with any conventional prepreg CFRP part.
- Carbonisation, which uses high-temperature furnace facilties to convert the organic resin into carbon. The resulting material is relatively fragile, so special care is taken during handling. Since no special processes are undertaken after carbonisation, except weighing, the risk of damaging the part is limited.
- CVI densification, the final process step, is where the porous material is densified using a high temperature chemical vapour infiltration (CVI) process. At the end of this step, the part is no longer fragile because the pyrocarbon has penetrated the microstructure, but this is also present on the surfaces, producing a ‘seal coat’ a few microns thick.

Densified parts can be machined easily with tooling suited to carbon-based materials.

54.6.4 Sandwich structures

54.6.4.1 GOCE programme

C-C sandwich structures have been space-qualified through the GOCE ‘Gravity Field and Steady-State Ocean Circulation Explorer’ programme. GOCE is an ESA programme, which uses a three-axis gravity gradiometer to determine for the first time the stationary gravity field with high accuracy.

C-C technology has been selected for the construction of the highly stable sandwich panels that support the accelerometers and electronics, as well as the thermal control unit of the Electrostatic Gravity Gradiometer of GOCE; as shown in Figure 54.6.2.

Figure 54.6-2 – Carbon-carbon composites: GOCE gradiometer

54.6.4.2 Qualification programme

The qualification programme for the C-C technology included:

- Dimensional verifications, e.g. mass-to-volume, panel flatness and thickness.
- Tensile and compressive tests.
- Bending test.
- Out-of-plane and in-plane pull tests.

- Insert tests.
- Stability measurements.
- Micro-yield test.
- Thermo-optical and thermal tests.

54.6.4.3 Sandwich panels

The C-C sandwich configuration comprises:

- facesheets: 1.5 mm and 3 mm thick, quasi-isotropic.
- honeycomb core: 3/16 – 10 pcf, 20 mm to 80 mm thick.

Small prototypes and full-scale panels were developed and tested during the qualification phase at Alcatel Alenia Space.

Procedures have been implemented at HITCO (SGL group) for the manufacturing of C-C flight parts.

The C-C sandwich structure has been completely qualified to subsystem level, e.g. vibration and stability testing. Two flight structures have been successfully manufactured.

Owing to the high temperature constraints, a special process was developed and qualified to locally strengthen unbonded nodes in the C-C honeycomb.

54.6.5 Cylinder structures

54.6.5.1 Pleiades programme

C-C cylinder structures have been space-qualified through the Pleiades programme.

Pleiades is a CNES (French space agency) Earth observation programme, which is the successor to the Spot series. The optical instrument is currently manufactured under the industrial responsibility of Alcatel Alenia Space.

The structure is made of a C-C cylinder with a carbon/cyanate M2 spider and a Carbon/cyanate reinforcement ring connected by titanium inserts.

Prior to the Pleiades programme, developments of C-C cylinders were conducted at Alcatel Alenia Space, with additional financial support from CNES and the French Ministry of Defense.

54.6.5.2 C-C cylinders

The features of all the manufactured C-C cylinders are:

- Monolithic, i.e not a sandwich structure.
- Thickness 1.6mm to 4.8mm.
- Length: 300mm to 2.5m.
- Diameter: 300mm to 800mm; mandrel available up to 2.5m.

54.6.5.3 Qualification programme

The qualification program for cylinders included:

- Dimensional verifications, e.g. mass-to-volume, circularity.
- Tensile tests.
- Insert tests.
- Stability measurements.
- Micro-yield test.
- Thermo-optical and thermal tests, e.g. conductivity, emissivity.

The qualification program was performed and demonstrated on both small and large test cylinders. Figure 54.6.3 illustrates the range of test cylinder sizes.

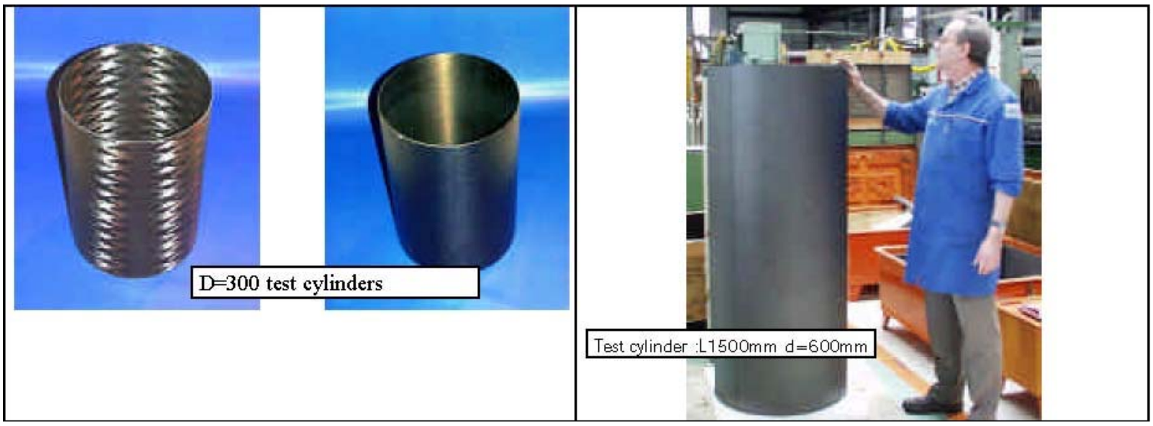


Figure 54.6-3 – Carbon-carbon composites: Test cylinders

54.6.5.4 Flight cylinders

Figure 54.6.4 shows the Pleiades flight cylinder, which is 780mm diameter and 2m long.

Two flight cylinders were successfully manufactured by Snecma Propulsion Solide (Safran group), a partner of Alcatel Alenia Space. As of 2005, these are undergoing instrument integration.

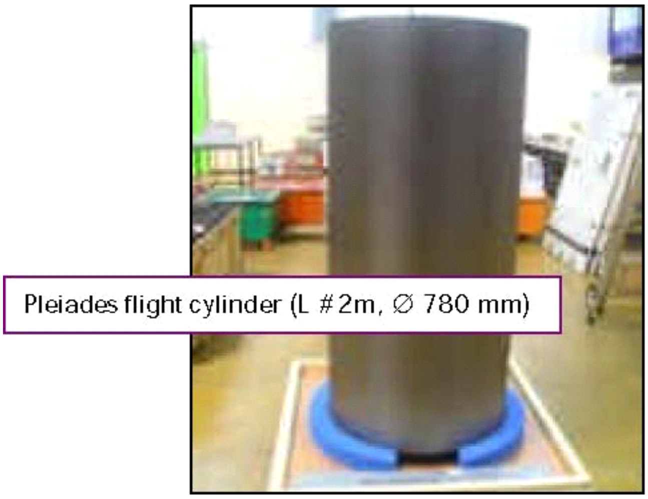


Figure 54.6-4 – Carbon-carbon composites: Pleiades flight cylinder

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55 Material availability

55.1 Introduction

This chapter considers available material forms, with emphasis on differentiating between standard product forms and those in which material and component are created simultaneously; known as 'Net-shape'.

As with all development materials or those with small-volume specialist uses, the amount of data available is limited and very application dependent.

Product support and sources of European expertise in material processing of advanced metal and ceramic-based materials are given.

The factors contributing to the cost of finished components are described, as are indications of the complexity for each material group.

55.2 Material forms

55.2.1 General

Advanced metallic and ceramic materials can be prepared or created in many forms, in an attempt to enhance properties. However, this creates a complex picture for designers and engineers seeking verified design data and manufacturing routes. It is appropriate to differentiate between materials which can be obtained as:

- Standard product forms, and
- Net-shape processes.

55.2.2 Procurement

Procuring new materials can be an evolutionary process, with continual improvements and modifications being introduced. There are few standard product forms equivalent to, for example, CFRP prepregs or wrought metal sections.

55.2.3 Processing

Many of the advanced metal and ceramic composites are fairly difficult materials to process hence the preference for near net-shape or net-shape methods. This indicates specialised process facilities, which are not always widely available.

55.3 Standard product forms

55.3.1 General

It is assumed that basic raw materials have been converted to a form which can be worked to a finished component. In this respect, the material is essentially fully formed but, if necessary, can be:

- mechanically worked,
- machined, or
- heat-treated.

Such materials can be easily characterised by supplier and end user alike.

55.3.2 Wrought metal products

These include:

- Conventional metal alloys (including plate and extrusion product forms), e.g.:
    - Mg,
    - Al,
    - Ti, and
    - Cu.
- ODS and mechanically alloyed (MA) metals: made from consolidated powders, notably:
    - Al, and
    - Cu.
- Particulate reinforced metal matrix composites (MMC), notably aluminium-based..
- Machinable carbon-carbon composite sections: C-C composites are relatively soft materials that can be machined with the correct tooling. 2-D composites can be considered a standard product whereas complex multidirectional reinforcement (3-D, 4-D, 5-D, 6-D, *n*D) are net-shape components.

55.3.3 Standard materials for net-shape processing

There is a range of 'standard' materials and products which are suitable for applying to net-shape processes, including:

- fibres, either for:
    - winding,
    - fabrics, or
    - preforms.
- continuous fibre 'prepregs' or 'foils', notably Ti or Al MMCs.
- ingots of alloys or particulate reinforced MMCs.
- casting compositions.

- powder compositions, for consolidation.

55.4 Net-shape components

As materials become more difficult to process, there is a greater desire to achieve net-shape processing; not least to avoid machining of hard brittle materials. Equally, those ceramic materials which cannot be melted are usually synthesised by vapour deposition or by pyrolysis, whereby the final material and product forms are created simultaneously. In these cases, the final material properties are the responsibility of those conducting the final processing.

The end user has either to characterise the material as- made or rely on a specialist sub-contractor(s) for both processing and characterisation.

Materials for near net-shape or net-shape processes include:

- Metal matrix composites (MMC):
  - Continuous fibre preforms infiltrated with liquid metal, usually aluminium.
  - Consolidated 'foils' and 'prepregs' with continuous fibres or filaments, e.g. Ti/SiC, Al/B, Al/SiC, and Al/C.
  - Forgings and castings of particulate reinforced metals, usually aluminium.
  - Hot isostatically pressed (HIP) powders, including intermetallics.
- Ceramic matrix composites (CMC):
  - Continuous fibre reinforced ceramics, e.g. SiC-SiC and C-SiC prepared by vapour infiltration (CVI) or deposition (CVD).
  - Composites with fibres or whiskers prepared by resin pyrolysis or Sol Gel techniques.
  - Hot pressed ceramic compositions with powders, whiskers or fibres, usually silicon nitride (Si_3N_4) based.
  - Glass and Glass-ceramic matrix composites.
- Carbon-Carbon composites (C-C):
  - Prepared by resin pyrolysis or CVI densification to give either a block or near net-shape component, having multidirectional reinforcement, e.g. 3-D; *n*-D.

55.5 Data and product support

55.5.1 Material supply

New materials prepared in low volumes always present problems in establishing a supply of consistent material. The reasons can include:

- Materials are being optimised and improved.
- Supply is initially from pilot-plant production facilities.
- Insufficient production capacity exists.
- Customer demand is initially insufficient to expand production facilities.
- Single source supply.

- Commercial or strategic restrictions on sales or data dissemination.

55.5.2 Property data

55.5.2.1 General

This ECSS handbook contains indicative data on material capabilities for new metallic and ceramic compositions.

It is impracticable to describe in depth the properties of all materials and grades. An end user or designer should establish a knowledge base on selected materials with specific end applications in mind.

In some cases the technology can prove too expensive to warrant in-house facilities, so specialist contractors provide the necessary expertise.

55.5.2.2 Standard product forms

Where standard products are used, there is a larger pool of knowledge based on the experience of the material suppliers and end users.

55.5.2.3 Net-shape components

Where net-shape components also dictate material properties, greater reliance is placed on the expertise of the material processors.

55.6 Data sources

55.6.1 European expertise

Table 55.6.1 presents a resumé of recognised European expertise on the newer materials.

Table 55.6-1 - Advanced metals and ceramics: Significant European sources of expertise

Material grouping	**Developing technology**	**End user**	**Material/product supplier**
Magnesium compositions	-	-	Magnesium Electron, UK (MMC)
Aluminium compositions	AMS Ltd., UK. (MMC) Raufoss A/S, Norway (ODS)	Aerospatiale, F. (All) MBB, G. (All) British Aerospace, UK (All)	BP MMC Ltd., UK (MMC) Alcan, UK (MMC, Al/Li) Pechiney, F. (Al/Li)
Titanium compositions	BP Ltd., UK. (Ti/SiC)	Rolls Royce, UK SNECMA, F. MTU, G. British Aerospace, UK (SPF/DB) Dornier Luftfahrt, G (SPF/DB)	IMI,UK
Superalloy compositions	-	Rolls Royce, UK. (All) SNECMA, F. (All) MTU, G. (All)	INCO Alloys, UK
Intermetallics (IM) Beryllium(Be)	Max-Plank Institute, G. (IM) ONERA, F. (IM)	-	Brush Wellman (Be) Interatom, G. (Be)
Glass matrix and Glass-ceramic composites	GEC Alsthom, UK Rolls Royce, UK	-	-
Ceramic matrix composites	SEP, F. Dornier, G.	SEP, F.	SEP, F.
Carbon-Carbon composites	MBB, G.	Aerospatiale, F.	Dunlop Aviation, UK Le Carbone, F. Aerospatiale, F.

These are classed as:

- Suppliers of material.
- Collaborators.
- Specialised contractors.
- Major end users.

55.7 Costs

55.7.1 Relative comparisons of materials

55.7.1.1 General

Presenting a full breakdown of the costs of using advanced metallic and ceramic materials is very difficult. Materials in development or produced in low volumes usually have high initial costs indicative of immature commercial products. Some materials represent 'Enabling Technologies', such that projects are totally dependent on them for success, e.g. very high temperature composites. Other materials can be in a competitive position with each other, e.g. for use at 300°C, aluminium MMCs versus SPF/DB titanium alloys versus aluminium ODS alloys versus polyimide matrix composites.

55.7.1.2 Direct material costs

The direct material costs of selected precursor materials and composites are summarised in Table 55.7.1.

55.7.1.3 Production cost control

As the newer materials have significant direct purchase costs, the main means of controlling total production costs are by:

- minimum part counts.
- minimum machining.
- net-shape processing.

The main contributing factors to high costs include:

- expensive fibres or filaments.
- prolonged processing, such as powder attrition (mechanical alloying); chemical vapour infiltration (CVI); repeated resin pyrolysis; complex fibre preforms.
- high temperature tooling.
- machining, particularly diamond machining of hard materials.
- inspection and quality control.

Some of these costs are unavoidable if a solution is required to meet a project need.

Table 55.7-1 - Advanced metals and ceramics: Direct material costs

Precursor material	€ per kg
Fibres	
Carbon	15-300
Silicon carbide fibres	500-750
Silicon carbide monofilaments	400-1500
Alumina fibres	500
Metals	
7XXX series Al alloys (Wrought)	6-8
8090 Al/Li alloy (Wrought)	15-18
Titanium 6Al-4V alloy (Wrought)	30
Aluminide powder	150-1500
Composites **(Flat sheet for test specimens)**	
Silicon carbide fibre reinforced aluminium	>750 <1500
SiC-SiC ceramic matrix composite	>2200 <5000
Carbon-Carbon composite	750-1500
Date: 1992	

55.7.1.4 Finished product cost comparison

Table 55.7.2 is a comparison of the relative cost of finished products in selected materials. They are indicative, but reflect the basic trend.

Table 55.7-2 - Advanced metals and ceramics: Relative costs of components

Materials	Relative cost of finished product †	Complexity scale ‡	Comments
Multidirectional CFRP	Modest	1 to 2	Well understood technology. Costs reducing through automation & lower part counts over aluminium.
Wrought Magnesium Alloys	Low to Modest	1 to 2	Well understood technology. Fewer applications than aluminium.
7XXX series Wrought Aluminium Alloys	Low	1	Well understood technology applied to ambient temperature structures.
8090 Aluminium-Lithium Alloy	Modest to Medium	1 to 3	Technology established for 5 years. Requires more usage to increase confidence.
Aluminium ODS Alloy	Medium	2 to 3	Improves high temperature capabilities of 7XXX series, but lacks applications.
Carbon Fibre Reinforced Aluminium Alloy	Medium to High	2 to 4	Lacks applications. Some fundamental issues still to be resolved, e.g. poor transverse strength & corrosion.
Wrought Titanium Alloy	Medium	1 to 2	Well established technology for intermediate temperature (200° to 600°C) applications.
Silicon Carbide Mono-filament Reinforced Titanium	High	3 to 5	Still under development. Seeking applications principally in gas turbine engines.
Conventional Nickel Superalloy	Medium	2	Well established technology particularly for gas turbine engines.
Consolidated Titanium Aluminide	Medium to High	3 to 5	Still under development. Competing for gas turbine use.
Machined Beryllium	Medium to High	2 to 3	Specialised high modulus material, but has established history. Lack in confidence on low ductility/toxicity has hindered use.
Ceramic Matrix Composite: SiC-SiC by CVI	Very High to Extremely High	6 to 9	Recent development for very high temperature applications. Processing is specialised & capital intensive. Lower processing costs sought.
Hot Pressed Glass-ceramic Matrix Composite: LAS/SiC	Very High	5 to 7	Easier to achieve than CMC's, but are restrained to 1000°C
Carbon-Carbon Composite	High to Very High	4 to 5	Well established technology, although cost and poor oxidation performance can limit application.

Key: † Based on cost-to-weight. However, variations in density are enormous from 1740 kg/m^3 (Magnesium) to 9500 kg/m^3 (Superalloys).

‡ Ranking to reflect:-

· Technical difficulty

· Availability of knowledge & facilities, and

· Material cost

1 = Easily achieved; 10 = Extremely difficult.

56 General design rules

56.1 Introduction

This chapter describes the different mechanical and fracture characteristics of each material group, and considerations for the design of structural components.

Metal and ceramic-based composites are complex, multi-phase materials, in which each phase has a significant influence on both the properties and stability at high temperatures. Defects which affect the required characteristics are discussed.

Composites consisting of hard, brittle phases present problems for machining. The use of net-shape processing aims to minimise the need for machining. However, the factors to be considered along with appropriate techniques are presented when machining is necessary.

56.2 Mechanical response

56.2.1 General

The number of material systems now available or under development is large. Each is being optimised with certain operating environments in mind. This can mean enhancing certain properties at the expense of others. Not all materials can be adequately characterised by their response to mechanical loading, e.g. stress-strain.

56.2.2 Composite development

56.2.2.1 General

The evolution of composite materials based on matrix and reinforcement has increased the complexity not least by introducing anisotropy which renders comparisons with isotropic materials largely superfluous.

56.2.2.2 High temperatures

A general trend is that as higher temperature capabilities are sought from metals and ceramics, the ambient modulus increases but strength and strain to failure gradually diminish. This should be considered by designers, and expectations of material ductility lowered.

56.2.3 Material characteristics

56.2.3.1 Fibre reinforced plastics (CFRP)

- Anisotropic.
- Essentially elastic materials to failure.
- Low strain to failure (<2%), other than for damage tolerant ±45° configurations.
- For laminates:
    - Tensile properties are fibre dominated.
    - Compression and shear properties are significantly influenced by matrix support to fibres.
- Weaknesses, principally low interlaminar and transverse strengths; designs need to avoid delaminations and interlaminar fractures.
- Good fatigue performance in fibre dominated directions, principally in tension.

56.2.3.2 Metals alloys

- Isotropic.
- Essentially elastic-plastic materials.
- Designs based on proof stresses, e.g. 0.2% PS.
- UTS and elongation to failure (ductility) are in plastic deformation zone.
- Good ductility provides confidence for damage tolerance.
- Conform to fracture mechanics predictions, e.g. fracture toughness.
- Heat treatment and mechanical worked condition important.

56.2.3.3 Particulate reinforced metals

- Near-isotropic.
- Elastic-plastic materials, with shortened elastic region.
- Design modulus difficult to establish due to small elastic region, but higher than unreinforced metal.
- Elongation to failure usually in 2% to 8% range.
- Small particles (1μm to 3μm) preferable to larger particles (above 15μm) in retaining 'metallic' characteristics of ductility and fracture toughness.
- Heat treatment and mechanically worked condition important.
- Tensile strengths equal to or marginally better than unreinforced metal.
- Hardness and creep resistance improved.
- CTE lowered.

56.2.3.4 Continuous fibre reinforced metals

- Anisotropic.

- Essentially elastic materials to failure and fibre dominated.
- Higher modulus than unreinforced metal alloys in fibre directions.
- Longitudinal tensile strength dictated by 'in-situ' fibre strength.
- Transverse and interlaminar strengths should be better than CFRP, but often limited. Controlled by fibre-matrix interface and transverse fibre strength, it can contribute to 'poor performance', i.e. low utilisation of matrix capability due to strain incompatibilities and embrittlement.
- Reduced thermal expansion.
- High internal stresses, due to CTE mismatch between matrix and fibre.
- Better creep resistance than matrix alloy.

56.2.3.5 Advanced metallic systems

(Includes ODS, MA, RSP alloys and intermetallics).

- Isotropic.
- Refined microstructures usually from powder processing which give improvements in modulus, creep resistance, hardness and thermal stability.

56.2.3.6 Monolithic ceramics

- Isotropic.
- High modulus and thermal stability.
- Good strengths (best in compression).
- Low strain to failure, <1%.
- Very defect sensitive, prone to catastrophic failure.

56.2.3.7 Ceramic matrix composites

(Includes GMC, GCMC & CMC with continuous fibres).

- Complex anisotropic.
- Microstructure influenced by matrix, fibres, matrix-to-fibre interface, voidage and population of microcracks.
- Principally thermo-structural materials.
- Elastic materials, but with two strain components:
  - matrix, $\varepsilon = 0.1\%$ to 0.3%, and
  - fibres, $\varepsilon = \sim 1\%$.
- Ultimate tensile strengths and strain to failure determined by 'in-situ' fibre strength.
- Modest strength, but benign fracture characteristics, compared with those of monolithic ceramics.

56.2.3.8 Carbon-carbon composites

- Complex anisotropic.
- Similar characteristics to CMCs, but lower modulus and tougher.
- Tensile strength gradually increases in temperature range 1000°C to 2000°C, which is a rare feature of any material.

56.3 Stress-strain response

56.3.1 Isotropic and anisotropic materials

56.3.1.1 General

There is always a desire to compare materials even if their microstructures are radically different. The greatest complications arise in comparing isotropic and anisotropic materials. All materials have their attributes and disadvantages.

Figure 56.3.1 and Figure 56.3.2 provide representative stress-strain profiles for advanced metallic and ceramic systems. These curves do not reflect the lower density of the composites over their heavier metal alloy counterparts. The strain axis in Figure 56.03.2 is modified to reflect the lower strain capability of ceramic systems.

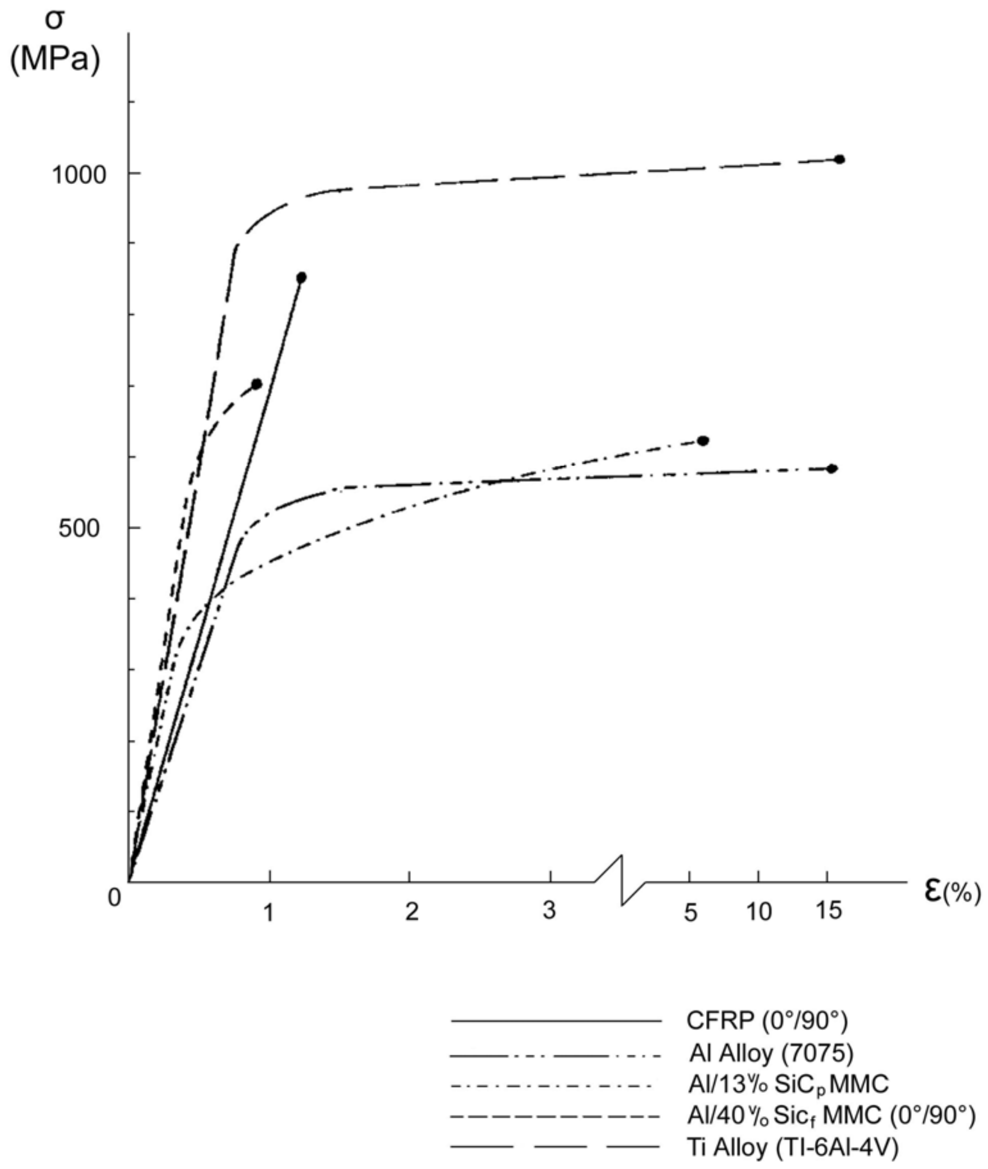

Figure 56.3-1 - Metals and MMCs: Stress-strain response compared with CFRP

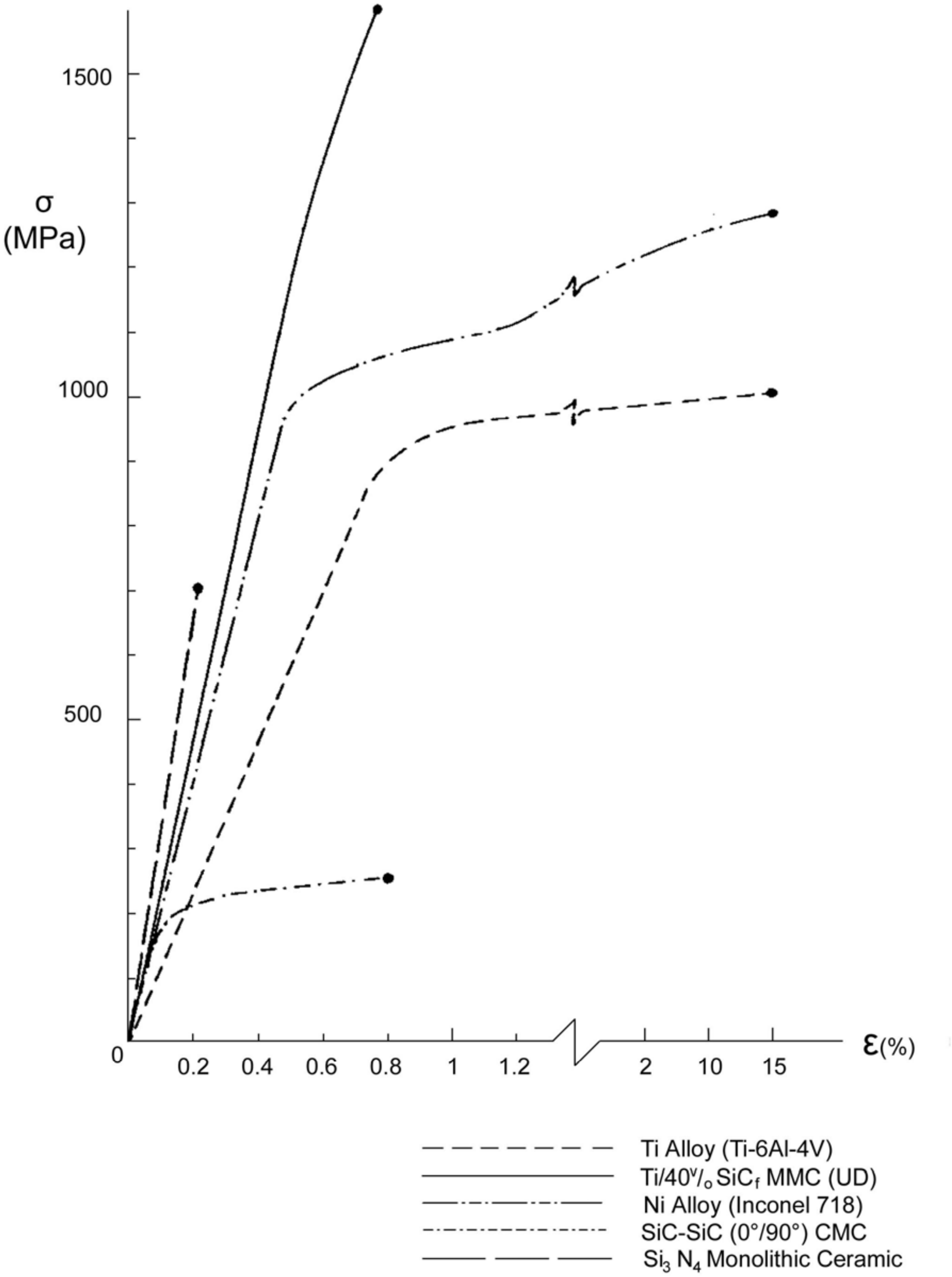

Figure 56.3-2 - Metals and ceramic-based materials: Stress-strain response

56.3.1.2 Strain to failure

As a broad statement, all anisotropic materials (composite) possess lower strain to failure (elongation) than isotropic metals (ceramics excluded). This can be perceived as a weakness or in some cases unacceptable.

Experience has, however, shown that mass-efficient structures can be produced in low strain to failure (1% to 1.5%) composites.

56.3.1.3 High temperatures

For higher-temperature applications, increasing emphasis is placed on composites for some structures seeking mass efficiency or extended life expectancy.

56.4 Fracture characteristics

56.4.1 General

Isotropic alloys of magnesium, aluminium, titanium, nickel and copper behave broadly in accordance with conventional fracture mechanics.

As materials become progressively more anisotropic, their fracture behaviour becomes less predictable by theoretical models. Comparisons are provided for guidance.

56.4.2 Near-isotropic materials with modest ductility

This group covers materials with ~2% to 6% ductility and includes:

- low volume fraction (< 20 vol.%) particulate MMCs,
- pressed powder derivatives, e.g. ODS, MA, RSP alloys, and
- intermetallics, e.g. aluminides.

They can be treated as similar to isotropic alloys in the basic modes of fracture.

56.4.3 Anisotropic, fibre reinforced MMCs

56.4.3.1 General

These materials cannot be compared with isotropic alloys. Their behaviour is more closely linked to that of fibre-reinforced plastics.

56.4.3.2 Effect of matrix

The difference between MMCs and FRPs centres on the matrices, which for metals have inherently higher moduli and strengths than plastics, e.g. epoxy.

Typically for MMCs, the matrix modulus is a factor of 20 to 40 times higher and the matrix strength some 6 to 20 times greater compared with FRPs. The metal matrix can also deform plastically, whereas epoxies rarely exceed 1.5% to 2% failure strain.

56.4.3.3 Tension

For tensile characteristics, a fracture model similar to that of CFRP can be used. However, overall strength is dictated by the 'in-situ' fibre strength. There is no loss in strength through fibre degradation in CFRP, which is not necessarily true for MMCs.

56.4.3.4 Compression and shear

For compressive and shear performance of MMCs, the interface between fibre and matrix is significant in determining permissible strains.

Transverse strengths of MMCs are considerably lower than those for the metal (matrix) alone. This is because the fibre in the transverse direction and interface cannot sustain the load.

56.4.4 Anisotropic, fibre reinforced CMCs

56.4.4.1 General

The ceramic matrix composites, such as SiC-SiC, cannot be compared with monolithic ceramics. CMCs modify the microstructure of monolithic ceramics to improve the tolerance to mechanical loading and thermal shock.

Standard fracture mechanic principles are inappropriate, as the materials are not sensitive to a single, small crack propagating to a critical size.

56.4.4.2 Effect of matrix

By incorporating high modulus fibres with strain to failures of 1% to 1.5%, this level of strain capacity is then conferred to the composite, even though that of the matrix alone is only about 0.2%. This gives a far from ideal engineering material, where elasticity is exhibited to 0.2% and thereafter microscopic crack damage propagates and multiplies whilst the fibres hold the composite together.

56.4.4.3 Strength

The ultimate composite strength is determined by the 'in-situ' fibre strength. This relies on the fibre and matrix being decoupled by an interface material such that the matrix cracks are stopped and deflected, whilst providing opportunities for fibre pull-out. Such a composite possesses excellent thermal shock resistance; as is also seen with carbon-carbon composites. However, overall strength is modest compared with other engineering materials. Hence, their use for thermo-structural applications, where thermal and heat management requirements prevail.

Compared with nickel-based superalloys, CMC strengths are low, however their density is approximately 35% less than these alloys, providing opportunities for using greater sectional thicknesses without incurring a weight (mass) penalty.

56.4.4.4 Permissible stress

When designing with CMCs, the maximum permissible design stress has to be less than the 'yield stress', i.e. onset of significant microcracking.

The remaining strain capacity is then the margin of damage tolerance of the composite. This could be equated with the 'ductility' shown by metals.

56.5 Residual stresses

56.5.1 Isotropic materials

For metals, residual stresses can be reduced by heat treatment processes. Also, the range of temperatures seen by the application is usually well within the 'stable' range of the material and few microstructural changes occur over the working life of the structure.

56.5.2 Anisotropic materials

56.5.2.1 General

Residual stresses are more pronounced in anisotropic materials or when joining dissimilar materials.

56.5.2.2 Effect of temperatures

If the intended range of application temperatures is wide, then residual stresses can also determine the integrity of both the material and the structure. Designs should evaluate the effects of residual stresses.

Where materials are used at high temperatures or for a short duration (life), there is a tendency to operate a material close to its limits. Often a slow degradation occurs which gradually changes the characteristics of the material, e.g. microcracking, oxidation, creep, diffusion (chemical) reactions.

56.5.3 Influence on microstructure

Residual stresses can be tensile or compressive and occur when adjacent material phases, e.g. fibre and matrix, have different moduli (stiffness) and CTE. These can be sustained in material systems with ductility or significant strain capacity. More susceptible are high modulus, low strain phases which can fracture to relieve stress.

Residual stresses are important with respect to:

- Fibre coatings: If a protective coating is applied to a fibre at high temperatures, then on cooling to ambient the coating becomes stressed. As most fibres have low axial expansivity and are high modulus materials, the coating experiences tensile stresses.
- Brittle matrices: When preparing ceramic matrix composites, the matrix is stressed for the same reasons as for 'fibre coatings'. A significant population of matrix microcracks can result from stress-relieving mechanisms. Whilst this is tolerated, the cracks provide an entry point for oxidation. Minimising the initial microcracking by low process temperatures has advantages.
- Protective coatings: Coatings applied to components should contain low residual stresses to avoid spalling. Residual stresses determine the maximum permissible coating thickness.
- Reduction in transverse properties: In either MMCs or CMCs, residual stresses are influenced by process temperatures used to form the composite. If a matrix is stressed then its capacity to sustain further applied load is limited. This is a contributing factor to the modest transverse (matrix dominated) strengths of high-temperature composites.

As with CFRP, the fibre orientations in adjacent lamina can determine the viability of a composite construction.

56.5.4 Influence on structures

56.5.4.1 Temperature

Changes in application temperatures can have significant implications if residual stresses exist, some examples include:

- Distortion: This can occur in unbalanced constructions, e.g. thin sections with a single surface protective coating or joints between dissimilar materials. Out-of-plane distortion, such as bending or twisting, is a stress-relief mechanism.
- Reduced sectional strength: A material can have an acceptable strength at ambient temperature, but cooling to cryogenic levels can compound residual stresses to unacceptable levels.
- Thermal gradients which can producing through-thickness variations or compound residual stresses.

56.6 Defects

56.6.1 General

With a wide range of materials available it is difficult to state the significance of defects and flaws on the integrity of the material.

56.6.2 Defect sources

Defects can arise due to:

- manufacturing route used.
- impact damage.
- mechanical or thermal fatigue
- corrosion or other environmental degradation.

56.6.3 Isotropic materials

56.6.3.1 General

Broadly, a single crack or flaw ultimately determines the fracture of isotropic or near-isotropic materials.

56.6.3.2 Alloys

Fracture mechanics can be used for metal alloys to determine the significance of a crack at any stage within structural life.

56.6.3.3 Particulate MMCs

These materials can be treated like alloys, although full densification does not guarantee material integrity when load is applied.

Before considering the use of particulate reinforced composites, evidence is sought that bonding exists between particles and matrix. Without an interface for load transfer, the particle can be considered as to be an inclusion, with the matrix required to sustain the load.

In the event of poor bonding or debonding, the interface between the particle and matrix becomes a source for crack initiation and propagation.

56.6.4 Anisotropic materials

56.6.4.1 General

For anisotropic composites, the final fracture is largely a result of many cracks accumulating to reach a critical population density.

Within laminar composites, there are planes with different fracture characteristics:

- Interlaminar planes (2-D composite) are usually the weakest (matrix dominated), and
- Through-lamina planes show greater resistance to crack propagation (fibre assisted).

The use of 3-D or multi-directional reinforcement assists by increasing interlaminar strength but lowering strengths in the other major axial planes through a dilution effect.

56.6.4.2 Continuous fibre MMCs

The phases present are fibres, matrix and interface. Like CFRP, voidage levels should be low, <2 vol.%. Anything greater than this can be viewed as unacceptable and the manufacturing route at fault.

Excessive fibre-matrix interaction, with fibre degradation, is also a concern. The 'in-situ' strength of fibres is sometimes less than predicted and a judgement is then made as to whether satisfactory levels have been attained. Prolonged contact with molten metal (matrix) or lack of a protective coating are usually the cause of fibre degradation.

Evidence of fibre breakage as a result of composite manufacture, often from press-forming techniques, is again cause for concern. Large diameter monofilaments can prove susceptible to breakage if over-formed. Small diameter fibres are more tolerant of mechanical handling and forming to radii.

With continuous fibres, there is the possibility of fibre contact without matrix wetting between the fibres. These are sometimes called 'neckless defects'. High levels indicate a poor manufacturing technique, e.g. lack of pressure or time for melt infiltration. Occasional instances should be tolerable.

The presence of reinforcement phases can modify the solidification and the microstructure of the metals alloys used as matrices. It cannot be presumed that characteristics seen in unreinforced alloys are automatically conferred to the matrix; especially as alloys can be controlled with heat treatment and mechanical working.

56.6.4.3 Continuous fibre CMCs

These are complex materials consisting of fibre, matrix, interface, voids and microcracks.

As with MMCs, 'in-situ' fibre strengths are generally lower than anticipated by a simple Law of Mixtures. Greater opportunities exist for thermal degradation of fibres and corrosive attack, even assuming a fibre coating (interface) is used.

The matrix is the more complex phase due to its inhomogeneity. Most ceramic matrices are made by low-pressure infiltration techniques, although hot pressing has some attractions. Low pressure synthesis relies on a gradual build up of matrix, possibly with pyrolysis stages, and this gives rise to discontinuities such as entrapped voids and local cracking. Voidage up to 10% can be tolerated, and is unavoidable in some processes.

In view of their use as thermostructural materials, modest strengths should be accepted. It can be argued that some voidage makes a constructive contribution to the benign fracture characteristics. Excessive voidage hinders the integrity of the composite by reducing interlaminar integrity. Voidage in excess of 10% is generally unacceptable, unless for thermal insulation purposes rather than for structural engineering.

The significance of microcracks is a more difficult issue to resolve. It is recommended that an acceptable composite be established which fulfils the requirements. That composite is then characterised by metallography and NDT to determine its state of integrity. NDT techniques such as X-ray and β-backscattering are used for imaging the bulk of the material. The validity of NDT techniques which can detect individual microscopic features is less appropriate in view of the large population of micro-features.

56.7 Machining

56.7.1 General

With the possibility of using materials which are hard and brittle or contain reinforcing phases, their machining characteristics can be summarised as advisory statements.

56.7.2 Isotropic metal alloys

Conventional machining techniques are used, with accepted practices for each alloy group. Whilst aluminium is readily machinable, there is an increasing reluctance to remove large amounts of metal for titanium and superalloys. A 90% metal removal is not uncommon for aluminium, but as material costs increase there is reluctance to create unnecessary scrap. Segregation of scrap is also necessary for some alloys, especially those containing lithium.

56.7.3 Particulate MMC

Machining is possible, but at a cost. These materials tend to rely on silicon carbide or alumina particles for the reinforcing phases. These are hard and extremely abrasive. Conventional high-speed steel and carbide tooling wear out very fast. Diamond tipped or coated tooling provides the only realistic option for prolonged tool-life and an acceptable surface finish.

56.7.4 Continuous fibre MMC

Other than trimming, these materials are normally consolidated via net-shape process routes; for the same reasons as particulate MMCs. The fibres or filaments are not amenable to clean cutting, other than perpendicularly through the fibre.

56.7.5 Carbon-Carbon composites

These are machinable, as the matrix is relatively soft. Carbide tooling is appropriate for the harder carbon fibres. This is true provided that no glassy or ceramic oxidation-inhibiting phases are present.

56.7.6 Ceramic matrix composites

All the phases present are very hard and abrasive. Diamond tipped tooling is the only mechanical machining option available. That said, all machining is kept to an absolute minimum and ideally restricted to slitting or trimming. This places a firm emphasis on net-shape process techniques.

56.7.7 Techniques

In addition to those highlighted for each material, MMC and CMC components can be laser machined, although considerable expertise is required.

57 Environmental aspects of design

57.1 Introduction

This chapter describes the environmental factors associated with space which have a direct influence on material selection. Such factors form part of the material development process, where an application dictates the use of a particular material type.

Where the materials available cannot meet the requirements alone, protection systems are used. These can be in the form of a coating or a more substantial structure, such as a shield. In both cases, the role and life of the system needs evaluation with respect to the whole structure.

57.2 Space parameters

57.2.1 Material selection

Material selection is biased towards the specific needs of space programmes. Some of the issues associated with the acceptance of fibre-reinforced plastics are of less concern if metals and ceramics are considered.

Equally, metals and ceramics are applied within environments where it is inconceivable to use plastics, particularly at high temperatures.

Table 57.2.1 summarises the materials environmental response.

Table 57.2-1 - Advanced metal- and ceramic-based materials: Relevance of space parameters to material selection

Parameter	Material Group		
	Plastics (CFRP)	**Metallics**	**Ceramics**
Outgassing/Offgassing	✓	×	×
UV or Radiation Stability	✓	×	×
Atomic Oxygen (LEO)	✓	Bulk material stable Thin films may degrade	×
Toxicity	✓	×	×
Flammability	✓	×	×
Moisture Absorption	✓	×	×
Dimensional Stability	✓ Low CTE but some instability	✓ Controlled CTE possible	×
Aqueous Corrosion	NA	e.g. SCC	×
Embrittlement at Cryogenic Temperatures	✓	✓	×
Thermal Cycling	✓ Will accept -170°C to +200°C	✓ Will go close to 1000°C as maximum	✓ Will go to high temperatures
Thermal conductivity	Low, Anisotropic	✓ Good to High	✓ Low to Medium
Thermal expansion	✓ Low axial CTE. High transverse CTE	✓ Wide variations possible	✓ Modest CTE, temperature range important
Oxidation Resistance	NA other than LEO	✓ Engines, (Ni).	✓ Engines & TPS
Hydrogen Embrittlement	✓ For fuel tanks	✓ For propulsion systems	✓ For engines
Emissivity	NA	✓	✓
Flux Capacity	NA	✓	✓
Hot Gas Corrosion	NA	✓	✓

Key ✓ : Issue for material selection.
× : Unimportant, due to good material stability.
NA : Not appropriate.

57.3 Application specifics

57.3.1 Material selection

From the specific requirements of space programmes, it is possible to identify key issues which influence material selection. These are instances where compromises should be made in materials development to ensure that a particular parameter is addressed to reach an acceptable performance level.

Such issues include:

- Thermal expansion: controlled and constant, despite persistent thermal cycling.
- Hydrogen effects: avoidance of hydrogen embrittlement in the handling of hydrogen fuel, throughout the range of temperatures.
- Oxidation and hot-gas corrosion: sufficient resistance to survive 30 missions for a reusable thermal protection system (TPS).
- Thermal conductivity: very high.
- Creep: resistance for short, single-cycle life expectancy at 550°C.

57.4 Protection systems

57.4.1 Requirements

Protection systems are used in environments which can severely damage a material or structure were it directly exposed. The more obvious occurrences are linked to high temperatures or high energy situations.

With the advent of reusable structures, other issues that affect the integrity of materials or structures include:

- Atomic oxygen attack in Low Earth Orbit (LEO),
- Micrometeorites and high velocity debris impact,
- Oxidation by heated air or combustion gases,
- Hot exhaust gas corrosion,
- Aqueous corrosion, salts and acids,
- Biofungal attack,
- Lightening strike,
- Thermal flux.

Some of these phenomena were investigated in the ESA-funded ‘WEPROT’ study, Ref. [57-1].

57.4.2 Types of protection systems

57.4.2.1 General

Protection systems are usually thin coatings (less than 1mm), but they can be more substantial in terms of shields or thermal protection panels. Coatings are used on both metallic and ceramic-based materials.

57.4.2.2 Function

Traditionally, a protection system is sacrificial in shielding the underlying substrate or structure and is not expected to contribute to overall strength, e.g. thermal barrier coatings. Thermo-structural components perform a combined role, but some materials need an additional surface coating, e.g. oxidation protection systems for carbon fibre-reinforced composites, such as carbon-carbon and C/SiC CMCs.

57.4.2.3 Integrity

The integrity of the protection system should be such that it continues to function throughout the life of the application.

Coatings that crack or spall have limited use if this occurs early in the life of the component. In some cases, protective coatings are far from ideal, but are the only solution.

Reproducible and predictable performance are preferable, even if regular repairs or component replacements are necessary.

57.4.3 Evaluation of protection systems

57.4.3.1 WEPROT study

Within the ESA-funded study ‘WEPROT’, a survey was conducted of the major terrestrial and orbital environments for thermal protection systems on RV and RLV, Ref. [57-1].

The study compared the performance of candidate metallic-based systems (γ-titanium aluminide and PM1000 ODS) with ceramic-based (oxide-based and C/SiC CMCs) against terrestrial and orbital environments identified as appropriate for reusable vehicles.

57.4.3.2 Ceramic-based TPS

For C/SiC TPS, the environmental phenomena which cause damage to the surface coating or the structural material, so reducing reusability, can be summarised as, Ref. [57-1]:

- A low speed impact, e.g. tool drop during assembly or maintenance, of about 0.5 Joule can cause damage to the oxidation protection system (OPS) that can reduce the life performance due to oxidation of carbon fibres during re-entry. Repair of the damaged area can probably restore reusability
- Humidity affecting the insulation below a C/SiC panel. Use of suitable coatings or sprays can avoid water penetration; but has not been investigated further.
- Rain erosion is a key issue for the economical operation of an RLV. The test activities aim to identify the effect that repair of the OPS has on service life.

- Hail impingement damages the OPS and probably the underlying structure when it occurs during launch or descent and landing. Replacement of the TPS is needed if the structure is hail-damaged. During landing, catastrophic failure caused by hail is unlikely; but has not been investigated further.
- Lightning strike during descent or landing causes damage to the TPS. Precautions in the form of proper design of attachments can avoid serious damage.
- Hypervelocity impact by micrometeoroids or debris is a key issue for the life of the TPS. Published literature indicated that orbital environmental phenomena affecting the life were more serious than expected at the beginning of the TPS development for RLV. A 'weather proofing' investigation, including hypervelocity tests, was necessary, Ref. [57-5].

57.4.3.3 Metallic-based TPS

TPS made from γ-TiAl was identified as the most advanced metallic-based system because of its strength-to-weight ratio for sandwich panels, along with surface stability against oxidation or degradation after thermal treatments. The main findings can be summarised as, Ref. [57-1]:

- Low speed impact probably causes dents in the face sheet but no cracking
- Although humidity is not a problem for a metallic sandwich panel, the insulation system beneath has to be protected by a waterproof coating.
- Rain erosion at typical landing speeds probably causes serious damage because medium-energy impact causes dents with cracking. Rain erosion tests, with subsequent plasma and thermo-mechanical testing, are intended to show the occurrence and extent of damage, Ref. [57-3].
- Although the lightning strike behaviour of γ-TiAl is unknown, catastrophic failure of ODS and Ti-alloys did not occur. It is expected to perform in a similar manner to hypervelocity impacts, i.e. possible holes without cracks. This phenomenon was not considered further during test programme.
- Hypervelocity impact by micrometeorites or debris causes holes without cracking, this was confirmed by initial hypervelocity impacts tests on γ-TiAl. The differences in damage caused by debris and micrometeorites is for further investigation.

An assessment of damage tolerance against tool drop, rain erosion and repeated thermal cycling formed part of the WEPROT test campaign, Ref. [57-2], [57-3], [57-5].

57.5 References

57.5.1 General

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58 Joint selection factors

58.1 Introduction

This chapter describes the factors to be considered for the design and manufacture of joints between metals and ceramic materials. As most joints experience high temperatures, the effect of material selection and manufacturing method on residual stresses is considered.

The benefits and problems associated with using an interlayer in a fused joint is described, along with those offered by mechanical joints or graded structures.

58.2 Basic considerations

58.2.1 Material characteristics

When dissimilar materials, such as metals and ceramics, are joined, there are specific physical characteristics of the materials which are important. Their importance is closely linked with the thermal history of the joint, i.e.:

- creating the joint, and
- the operating conditions that are applied to the joint.

Wherever possible, the physical and mechanical properties of dissimilar materials should be matched as closely as possible. Stiffness and coefficient of thermal expansion are the most significant properties.

With some material pairings, there is considerable disparity in properties and a viable joint can need an interface material to bridge the difference.

To provide an insight into the variations in properties of prospective constituents of joints, Table 58.2.1 provides indicative data on the range of materials that can require joining.

Table 58.2-1 - Dissimilar materials for joints

Material	**Properties**						**Comments**
	CTE, α (x 10^{-6}°C^{-1})	Stiffness, *E* (GPa)	Strength, UTS (MPa)	Max. Temp. (°C)	Melting Temp. (°C)	Conductivity @ RT, (Wm^{-1} °C^{-1})	
Metallic alloys							
Aluminium: 7075	23.0	70	400	110-150	600	150	Standard aerospace alloy.
Titanium: Ti-6AI-4V	11.0	120	890	450	1725	6.0	Most common Ti-alloy.
Steel: SS 316	14.0	196	650-865 (YS: 310-750)	700	1500	150	Common stainless steel.
Nickel: lnconel 718	13.0	200	1276 (0.2%PS: 1056)	800	1455	11.2	Well established Ni-alloy.
Aluminide: Ni$_3$AI	12.5	226	1310	900	1390	-	New material.
MMC							
Aluminium: DWG-A1/P100(UD)	~0 to -I	379-414	552-834	~200	600	-	Anisotropic, Fibre-reinforced, high modulus, unidirectional.
Aluminium: 2124/18vol.% SiCp	<23.0	100	610 (0.2%PS: 490)	~200	600	-	Particulate reinforced.
Titanium/SiCf: Ti-6AI-4V/SCS-6(UD)	<11.0	225	1040 (L)	~500	1725	-	Monofilament reinforced.
Nickel/W Fibre (TFRS)	-	TD	TD	~900	1455	-	Monofilament reinforced.
Monolithic ceramic							
Silicon Nitride	2.1 to 3.5	310	Flex: 400-845	1400	1900	10-30	Powder based.
Sialon	3.2	280-331	Flex: 845	-	-	21.3	Powder based.
Silicon Carbide	4.2 to 5.4	345-470	Flex: 300-540	1600	-	125-200	Powder based.
Alumina	7.7 to 8.1	300-372	Flex: 240-400	1700	2050	39(25)	Powder based.
Zirconia (ZrO_2)	6.5	186	Flex: 405	-	2960	1-2	Powder based.
CMC							
C-SiC	~1 to 2	~200-250	~400	~1600	N/A	-	Anisotropic. 2-D carbon fibre-reinforced.
SiC-SiC: 2-D fabric	~5	210	230	~1600	N/A	25(L) 6(TT)	Anisotropic. 2-D SiC fibre-reinforced.
C-C: 2-D fabric	~0 to 1	90-100	127-172	~2000	N/A		Anisotropic. 2-D C-C composite.

Base material or interlayer (Pure)							
Aluminium	25.3	69	69 (0.2%PS: 25)	AD	660	238	-
Silver	20.6	71	140	AD	960	418	-
Copper	18.3	117-132	220 (0.2%PS: 50)	AD	1083	397	-
Nickel	15.2	210	323 (0.2%PS: 63)	AD	1452	79	-
Molybdenum	5.1 to 5.7	303	435	~900	2615	135	Refractory metal
Niobium	7.2 to 8.1	98	240	~1000	2467	52	Refractory metal
Tungsten	4.5	411	550	~1200	3387	130	Refractory metal
Titanium	7.6	108	369 (0.2%PS: 246)	AD	1675	16	-

Key: YS: Yield stress. PS: Proof stress. Flex: Flexural. N/A: Not applicable. TD: Temperature dependent. AD: Application dependent.

58.2.2 Joint strength

58.2.2.1 General

Designing and implementing joints always requires an element of compromise, notably with respect to the strength attainable.

- A suitable joint is one having sufficient strength for the intended application with retained integrity over a desired time period.
- A joint cannot be stronger than the weakest material being joined and failure at ultimate load occurs somewhere in the system.
- By necessity and for confidence, that failure is consistent and reproducible.

58.2.2.2 Residual stress

In fused joints between dissimilar materials, either metals or ceramics, the major limiting factor to joint strength is residual stress in one of the materials. This stress increases with temperature changes away from that at which the joint is first formed, especially on cooling.

In some non-optimised joints, the residual stress can exceed the basic strength of one of the materials and fracture occurs without external loading. Whereas other non-optimised joints might withstand cooling, but only very small sustained loads are needed to compound the residual stresses and cause joint failure.

58.2.2.3 Failure

In ceramic to metal joints, failure is most prevalent in the ceramic because of its brittleness, low strain to failure, higher stiffness and modest strength characteristics, [See: Table 58.2.1].

In practice, joints between radically dissimilar materials require considerable ingenuity to obtain reasonable joint strengths.

58.2.2.4 Effect of fusion temperature

It is common to use fusion temperatures in the range 800°C to 1000°C between ceramics and metals. The actual amount of expansion at these temperatures is quite considerable, e.g. 0.27% for silicon nitride and 1.3% for steel.

At the fusion temperature, residual stresses are assumed to be zero. On cooling, the degree of contraction of these materials differs and constraints are imposed by the differences in physical properties.

For example:

	E	α
Si_3N_4	310	3.0
Steel	196	14.0

The Si_3N_4 is at a disadvantage because it contracts by a small amount and cannot stretch because of its high modulus. It has limited strength with no capacity for ductile-plastic behaviour. On cooling to ambient, it is therefore highly stressed at the direct point of connection to the steel before any external load is applied.

It has been calculated that for a supposed direct silicon nitride-to-steel joint fused at 1200°C, the residual tensile stresses in the Si_3N_4 approach 1000MPa, Ref. [58-1]. Such a stress is beyond the ability of Si_3N_4 to sustain without fracture. Indeed, the fusion temperature has to be lowered dramatically before Si_3N_4 can sustain any significant external tensile loading.

58.2.2.5 Reproducibility

Given the effect of the fusion temperature, significantly different strengths are reported for what appear to be joints between identical materials (substrates).

Joint strength is highly dependent on the precise conditions used in forming the joint. In an optimised joint, the residual stresses can be reduced by several hundred MPa over non-optimised variants. This differentiates between an acceptable and unacceptable joint purely from consideration of basic strength, let alone durability.

58.2.3 Joint design factors

The close matching of stiffness and CTE of dissimilar materials has been highlighted. With dissimilar materials some element of mismatch is inevitable, so a fused joint is designed and made to minimise the consequence of these mismatches.

In undertaking this, careful consideration is given to:

- The presence, or not, of an interlayer material.
- The temperature and pressure of joint consolidation.
- Chemical compatibility of the two substrates.
- Load introduction into the joint.
- Operating environment, including:
    - maximum temperature, and
    - fatigue.

58.3 Interlayers

58.3.1 Function and effect on fused joints

58.3.1.1 General

Introducing a third material can affect a joint in several ways. The thickness of the interlayer is important. The principal effects include:

- Residual stresses: Probably reduced within the joint, and are alleviated further by the use of a thick interlayer.
- Joint consolidation temperature: Determined by the melt characteristics of the interlayer, or its ability to form a diffusion bond with the substrates.

- Joint strength: Usually determined by the weakest substrate to interlayer bond, or cohesive strength of the interlayer.
- Interlayer material: Selection determines the ultimate service or operating temperature of the joint. Depending on the dissimilar materials to be joined, the materials tried include:
    - Aluminium
    - Copper
    - Niobium
    - Molybdenum
    - Titanium
    - Nickel
    - Iron
    - Silver

58.3.1.2 Interlayer materials

Some interlayer materials have low melting points, which eases problems when fusing joints. Others have much higher melting points which is also reflected in the temperature capability of the joint.

The complicating factors are the solid-state reactions (diffusion) which occur between interlayer and substrate. These can occur at varying temperatures, with or without pressure assistance (0MPa to 100MPa).

58.4 Joint consolidation

58.4.1 Temperature and pressure

58.4.1.1 General

These two parameters have a synergistic effect. A low consolidation temperature is desirable to minimise residual stresses on cooling. This can be aided by applying high pressures. However, the use of high pressures, e.g. within a hot isostatic pressing (HIP) chamber, poses limitations on size, shape and complexity of components and is normally avoided.

Low pressure brazing has always been attractive for fabricating components, such as gas turbine nozzle guide vanes, because of its relative simplicity.

The majority of work on fusion joining of dissimilar materials has been with simple butt joints of small cross-sectional area. This enables virtually any fabrication process to be used, avoiding the issue of complex assembly.

To date, the pressure regimes used have been:

Low pressure:	0 to 0.6MPa (to 87 psi)
Medium pressure:	0.6MPa to 15MPa (to 2175 psi)
High pressure:	60MPa to 207MPa (to 30000 psi)

Consolidation temperatures with interlayers range between 450°C for aluminium and 1400°C for the refractory metals Nb and Mo.

58.4.1.2 Metal substrates

Without the interlayer, joining is by either:

- Diffusion bonding, or
- Melting of one of the substrates. It is only feasible if one of the substrates is metal, with fusion occurring at 0.5 to 0.98 of the metal melting temperature (T_m).

58.4.1.3 Ceramic substrates

For connections between ceramics, either similar or dissimilar, melting of either substrate is neither practical nor possible in most cases. Therefore, a metallic interlayer is used unless fusion can be achieved by:

- High temperature inorganic refractory cement
- Pyrolysis of polymer adhesive, e.g. polycarbosilane, to a ceramic, such as SiC.
- Infiltration and densification of the bondline at a high temperature by CVD/CVI to give SiC.

58.5 Material compatibility

58.5.1 Chemical and physical

58.5.1.1 General

Compatibility between dissimilar materials is difficult to define when materials are expected to function at high temperatures.

58.5.1.2 Requirements

After the initial fusion, it is desirable to have a stable chemical and microstructural composition within the joint zone. This enables consistent and durable joint performance to be obtained.

It is undesirable to have continuing chemical activity and diffusion occurring during the operational life of the joint, as the performance can be unpredictable.

58.5.1.3 Potential problems

When a fused joint, with or without a thin interlayer, is created, those occurrences which can be detrimental include:

- Localised microcracking and flawing of a brittle substrate.
- Presence of excessive quantities of brittle phases within the fusion or diffusion zone.
- Inappropriate alloy elements present in metallic substrate or interlayer.

In some cases heat treatments can be used to reduce thermal stressing within a joint.

Chemical and physical incompatibilities are of less concern in mechanically interlocking parts, [See: Chapter 61].

58.5.1.4 Use of alloy interlayers

The majority of interlayer materials studied have been pure metal foils and not alloys. If alloys are used, then a more complex joint microstructure can be anticipated. This is true of braze materials, although useful information is presently available from experiences in brazing nickel and titanium alloys.

58.6 Load introduction

58.6.1 Basic principles

58.6.1.1 General

The basic principles for load introduction are similar to those for adhesively bonded or fastened joints, although special care is taken if one of the adherends is a brittle ceramic.

58.6.1.2 Fused joints

- Direct tensile, cleavage and peel loadings are avoided because joint strengths are lowest in these modes.
- Compressive and shear loadings are preferable. The former when a ceramic is present.

58.6.1.3 Graded structures

These are tolerant of most localised loading modes as a gradual transition in composition between the two materials is achieved. If one of the materials is a ceramic then compressive loading is preferable, but not essential. Mechanical interlocks, pinning and fastening

This class of joints enables disassembly and the inclusion of seals. They also avoid the additional thermal transient necessary in fusion fabrication. This eliminates thermal distortion on cooling. However, additional problems arise when assembly is undertaken at ambient temperature and subsequent heated in service.

Positional tolerances take into account thermal expansion and the need to sustain load. Subjects requiring attention include:

- Localised bearing and crushing strength
- Notch sensitivity at changes in section and at immediate load transfer points
- Slackening or over-tightening of joints by differential expansion.

[See: Chapter 61]

58.7 Operational environment

58.7.1 Environmental factors

58.7.1.1 General

For joints involving metals and ceramics applied in high temperature situations, there are a number of environmental conditions which can invoke instability leading to reduced joint integrity. These include:

- Hot corrosion by reactive gases, e.g. O_2 and H_2O.
- Thermal shock, introducing differential stresses across the joint.
- Thermal cycling induces a microcrack population that propagates with repetitive cycling.
- Mechanical loading, compounded.
- Acoustic fatigue.

58.7.1.2 Joint design

With all of the environmental conditions, fracture damage is more likely to occur in the most brittle materials present, i.e. the ceramic in a metal-ceramic connection.

The important aspects to determine are the:

- actual loads to be transmitted by the joint.
- life expectancy (durability) of the joint.
- joint strength, with a sufficient margin to avoid a catastrophic failure in service.

58.8 References

58.8.1 General

[58-1] A. Frisch et al
'Diffusion Bonding of Si3N4 to ODS Superalloy MA6000 by Hot Isostatic Pressing'
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Paper 11, Volume 2, p52-60

59 Joints between dissimilar materials

59.1 Introduction

This chapter summarises the requirements for joints between advanced metal and ceramic-based materials. The effect of operating environment and the options available for manufacturing the joint are also given.

59.2 Requirements

59.2.1 Temperature range

With the advent of spaceplanes and advanced launchers, there are significant thermal management problems to be resolved within structural configurations.

Structures spanning the temperature range from +1600°C down to below -250°C (20K) can be grouped as:

- Hot
- Warm, or
- Cold.

The extreme high temperatures are at the external surfaces of spaceplanes on re-entry or in and around power plants. The lower and ambient temperatures are in the main structural airframe and in liquid fuel containment.

59.2.2 Structures

59.2.2.1 General

Joints between components of dissimilar materials within a structure largely reflect the points at which different operating environments meet.

59.2.2.2 Materials

Connections are likely to be made between:

- metallic and metallic,
- metallic and ceramic, and
- ceramic and ceramic.

Metallic includes both alloy and metal matrix composite (MMC). Ceramic covers monolithics, composites (CMC), and carbon-carbon (C-C).

Representative materials are summarised in Table 59.2.1.

Table 59.2-1 - Joints between dissimilar materials: Representative list of materials

Metallic	Ceramic
Alloys: Nickel (Superalloys) Steel Copper	**Monolithic:** Si_3N_4 Sialon Al_2O_3 SiC
MMCs: Ti-based Ni-based Cu-based	**CMCs:** SiC-SiC C-C Glass-ceramic

59.2.3 Loading

Joints between dissimilar materials are likely to be structural and to some extent load-bearing. The integrity of such joints in some cases can be critical to the integrity of the space structure.

The joints need to withstand:

- direct mechanical loading.
- stresses caused by:
  - thermal gradients.
  - thermal cycling.
- fatigue:
  - mechanical.
  - thermal.

Longevity is of high importance in reusable structures, such as spaceplanes.

59.2.4 Joining methods

59.2.4.1 General

The principal options for joining are:

- fusion bonding in all its forms, [See: Chapter 60].
- mechanical interconnections, including fastening,

[See: Chapter 61]

59.2.4.2 Fusion bonding

Fusion bonding practices include:

- Diffusion bonding,
- Brazing,
- Reaction bonding,
- Fusion welding,
- Resin pyrolysis.

59.2.5 Joint components

Within joints there can also be:

- cements,
- seals, [See: Chapter 75].
- interlayers, [See: 58.3].
- gaskets.

60 Fusion joining

60.1 Introduction

Joints can be achieved in a number of ways, but are principally made by either a liquid-phase or solid-phase transformation. Broadly, liquid transformations are made at higher temperatures than comparable solid-phase bonding. This is significant as there is usually a preference for lower-temperature processing. However, this is offset by the fact that solid-phase transformations usually require higher consolidation pressures than liquid-phase bonding to achieve a sound integral bond.

Fusion bonding methods are described as is development work aimed at evaluating joint performance, Ref. [All].

60.2 Joining techniques

60.2.1 General

Table 60.2.1 compares the relative merits of the different techniques described.

Table 60.2-1 - Comparison of jointing and consolidation techniques

Jointing/ consolidation technique	Advantages	Disadvantages
Fusion welding	Good for glass to metal	Limited practical combinations
	Good for localised connections	Inappropriate for large-area joints
	Appropriate to similar materials	Cannot accommodate significant CTE differences
Liquid phase bonding - Brazing	Low pressure technique	Requires wettability
	Allows use of brazes and frits to achieve workable joints	Requires understanding of chemical capabilities
		Cannot accommodate significant CTE differences
Diffusion bonding - with or without interlayer	Offers means of reducing jointing temperature	Requires consolidation pressure
	Interlayer gives better accommodation of CTE differences	Requires understanding of diffusion mechanisms
Graded structures	Offers means of accommodating significant differences in material CTE and other properties, e.g. modulus and conductivity	A sophisticated process technique is to be used to create a true transition zone
	Appropriate for joining dissimilar materials	

60.2.2 Liquid-phase processing

60.2.2.1 Melt refining

A transition zone is created between the two materials by localised compositional refining of the molten phase. The materials are usually metals, e.g. steels, and the change occurs in the alloying constituents, Ref. [All].

This includes ‘zone refining’ and ‘vacuum arc refining’.

60.2.2.2 Fusion welding

One or more component materials are melted and fused with the others. In metal-to-ceramic combinations, the metal is usually melted. This process is suited to small localised joints where a controllable heat source can be used.

60.2.2.3 Liquid-phase bonding

Both the materials to be joined remain solid. The connection is made by a third constituent which is introduced at the faying surfaces and melted, so fusing both materials together as it solidifies. This third constituent is a lower melting point material and hence the joints thermal capability is determined by its characteristics.

This includes brazing.

60.2.3 Solid-phase processing

60.2.3.1 High-pressure (HIP) bonding

Both materials to be joined remain solid, but sufficient temperature and pressure are applied to cause bonding by interdiffusion. This can be carried out with or without a thin interlayer of a third material. Diffusion bonding occurs at a temperature close to, but below, the melting point of the least thermally stable material present.

60.3 Joint configuration and performance

60.3.1 Technology status

60.3.1.1 General

Table 60.3.1 presents a review of published papers on the fusion bonding of dissimilar materials. Most of the work consists of joining trials, with or without interlayers, Ref. [All]. There is rarely any explanation as to why the materials are joined, i.e. the applications are not given, or any justification for the selection of the various interlayers.

Table 60.3-1 - Fused joints: Technology review of joints

Material A	Material B	Interlayer material	Consolidation technique	Process conditions	Comments [Reference]
2.25%Cr Mo-steel	316 stainless steel	None	Vacuum arc remelting	Welding of dissimilar electrodes	Graded structure for steam systems in power stations, Ref. [60-1], [60-2]
Steel	Alumina (AI_2O_3)	Nb, Mo, Ti, (1 to 2mm)	HIP	1000-1300°C at 100 MPa	Optimisation of interlayer thickness, single and multiple, Ref. [60-3]
Type 405 stainless steel	Silicon nitride Si_3N_4	Ni,Fe,Ti,Nb (pure) + W	HIP	1200-1400°C at 100 MPa	Study to identify efficiencies of interlayers, Ref. [60-4]
INVAR (Fe-32Ni-5Co)	Si_3N_4	Al (pure) (0.5mm)	Hot pressed	700-950°C at 0-0.15 MPa	Bond strength optimisation, Ref. [60-5]
AI_2O_3	AI_2O_3 & Ti, Pt, Fe, SS316, Cu	AI, Ag, Cu, & Ni foils	Hot pressed	>450°C for Al >600°C for Ag & Cu >900°C for Ni	Evaluation of bond strengths, Ref. [60-6]
ODS nickel super-alloy MA 6000	Si_3N_4	NiCo 36 (Fe-36%Ni) W-Ni-Cu alloy Ni & Ti (pure)	HIP	1100°C-1300°C, 100 MPa	Optimisation of interlayers, both single & double, Ref. [60-7]
W-6Co alloy	AI_2O_3 (2% TiC)	Nb plus Ni-based filler	HP bonding LP brazing	1200°C, 60MPa 1255°C, 0.2-0.6MPa	Comparison of techniques. LP brazing preferred, Ref. [60-8]
Ni	AI_2O_3	None	HIP	1400°C, 207MPa	Demonstration of seven zone graded compositions, Ref. [60-9]
Steel	AI_2O_3			1400°C, 207MPa	
Al	SiC			600°C, 207MPa	
Ti	TiN, TiC	None	PVD	-	Functionally gradient materials (FGM) from Japan organised by Science & Technology Agency, Ref. [60-10]
Cr	CrN, Cr_3C_2	-	PVD	-	
C	SiC, TiC	None	CVD	-	
Ti	TiC	None	PVD-CVD	-	
C	SiC	-	PVD-CVD	-	
Superalloy	ZrO_2	None	Powder metallurgy,	-	
Superalloy	ZrO_2	None	Wet or dry sprayed, 1 or 2 gun	-	
Cu	TiB_2, TiC	-	-	-	
Ni	TiB_2, TiC	-		-	

Material A	Material B	Interlayer material	Consolidation technique	Process conditions	Comments [Reference]
Stainless steel SS	Al_2O_3	Cu	Reaction bonding	950°C at 3MPa	Demonstration of strong joints, Ref. [60-11]
	ZrO_2 (PSZ)	Cu		950°C at 3MPa	
AI_2O_3	Mo.Nb,W, Kovar	None	Fusion Welding	Material B melted	Largely impractical, Ref. [60-12]
AI_2O_3	Cu	None	Diffusion bonding	980°C at 8.5MPa	Temperatures between 0.5 to 0.98 Tm Pressures between 1 & 100MPa
AI_2O_3	Al	None		600°C at 8.5MPa	
AI_2O_3	Ta	None		1400°C at 10MPa	
AI_2O_3	Fe	None		1375°C at 1 MPa	
AI_2O_3	Nb	None		1575°C at 15MPa	
Cu	AI_2O_3	Ti	Liquid phase bonding	Direct wetting sought	Effectively brazing. Direct melting within joint
AI_2O_3	Ti alloy, Steel	Al	Solid phase bonding	Activity within thin interlayer	Hot pressing required
Si_3N_4	Si3N4	lμm Ti + braze Ag-Cu or Au-Ni or Au-Ni-Pd	Brazing	Brazing temperatures: Ag-Cu: 790°C Au-Ni: 970°C Au-Ni-Pd: 1130°C	1μm Ti to improve wetting by braze. High strength joints obtained, Ref. [60-18], [60-21]
AI_2O_3 or Si_3N_4	Titanium alloy (TA6V) or Nb	Cu-40Ag-5Ti braze	Active brazing	Under vacuum, 0.1MPa, applied pressure at 850 to 890°C for 2 to 10 minutes	Studies on reactions between braze & substrate, Ref. [60-20]
SiC fibre/AI_2O_3 matrix	Stainless steel 304L	Ag/Cu/Ti braze	Active brazing	Under vacuum, 1000°C for 20 minutes	Initial trials, Ref. [60-24]

60.3.1.2 Objectives

The principal objectives of the work are to obtain strong bonds when tested at room temperature and provide a better insight into joining mechanisms. Various theories and models for joint response are also presented, Ref. [All].

60.3.2 Joint strength

60.3.2.1 General

Table 60.3.2 provides a selection of reported bond strengths for fusion joints, Ref. [All]. The tests are for direct tensile loading normal to the bonded interface, conducted at room temperature. This represents a fairly exacting stress condition with residual stresses at their maximum, coupled with undesirable tensile loading of brittle materials.

Consequently the reported figures are widely scattered, varying from 5MPa to 175MPa. A strength of 450MPa was achieved when like materials were joined, i.e. Si_3N_4 to Si_3N_4 with a Cu interlayer. A strength of 5MPa is very poor, whereas 175MPa provides a useful strength. The quoted strengths provide a broad insight into that possible.

Table 60.3-2 - Fusion joints: Published bond strengths for various joints

Material A	Material B	Interlayer(s)	Technique	Bond strength, at RT. [Reference]
Steel	Al_2O_3	Mo + Nb	HIP (DB)	Mean 63 MPa, Ref. [60-3]
405 S Steel	Si_3N_4	Nickel braze + W + Fe	HIP (DB)	Mean 65 MPa, Ref. [60-4]
405 S Steel	Si_3N_4	Nickel braze + W + Fe	LP (DB)	Mean 51 MPa, Ref. [60-4]
Si_3N_4	Si_3N_4	Al	HP (DB)	Max ~450 MPa, Ref. [60-5]
Si_3N_4	Si_3N_4	Ag-Cu	Brazing	Max ~328±38 MPa, Ref. [60-18]
INVAR	Si_3N_4	Al	HP (DB)	Max ~175 MPa, Ref. [60-5]
Al_2O_3	Al_2O_3	Al	HP (DB)	Max ~70 MPa, Ref. [60-6]
Al_2O_3	Al_2O_3	Ag	HP (DB)	Max ~40 MPa, Ref. [60-6]
Al_2O_3	Al_2O_3	Cu	HP (DB)	Max ~50 MPa, Ref. [60-6]
Al_2O_3	Al_2O_3	Ni	HP (DB)	Max ~45 MPa, Ref. [60-6]
Al_2O_3	Ti	Al	HP (DB)	Max ~50 MPa, Ref. [60-6]
Al_2O_3	Fe	Al	HP (DB)	Max ~20 MPa, Ref. [60-6]
Al_2O_3	SS 316	Al	HP (DB)	Max ~10 MPa †, Ref. [60-6]
Al_2O_3	Cu	Al	HP (DB)	Max ~5 MPa, Ref. [60-6]
Al_2O_3	Al_2O_3	Cu	LP (RB)	Max ~124 MPa, Ref. [60-11]
Al_2O_3	S Steel	Cu	LP (RB)	Max ~167 MPa, Ref. [60-11]
PSZ (Zr_2O_3)	S Steel	Cu	LP (RB)	Max ~70 MPa, Ref. [60-11]

Key
† : 70 MPa achieved by annealing
HIP - Hot isostatic pressing
DB - Diffusion bonding
RB - Reaction bonded
LP - Low pressure
HP - High pressure

The strengths are very much dependent on the:

- materials selected,
- specimen configuration, and
- precise joining technique used.

60.3.2.2 Effect of temperature

Joint strengths vary with temperature. It can be expected that lower strengths are seen at ambient or close to the fusion temperature, whilst a maximum strength occurs somewhere in between.

60.3.2.3 Factors affecting joint strength

Greater bond strengths are seen in those joints which:

- minimise residual stresses by use of material gradation, and
- low fusion temperatures.

Where these rules are not followed, low strengths or even fracture on cooling are possible.

The use of heat treatment can significantly increase ambient strengths, particularly where a very low strength is otherwise indicated.

60.4 References

60.4.1 General

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61 Mechanical connections

61.1 Introduction

61.1.1 Requirements

61.1.1.1 General

Joints enable a number of components to be assembled into an integrated structure and load to be transferred between the components parts.

61.1.1.2 Similar materials

Joining similar materials is the easiest situation, achievable by:

- mechanical fastening,
- bonding, or
- welding (metals and some plastics).

61.1.1.3 Dissimilar materials

With dissimilar materials there is greater uncertainty on the compatibility of two connecting surfaces, particularly if thermal excursions are envisaged. If reliability and consistency of joint performance is paramount, then greater reliance is placed on mechanical connections than those solely using fusion or bonding techniques.

61.1.1.4 In-service

Mechanical connections have the added ability to be disassembled and re-assembled. This is particularly useful in power units containing rotating components such as fan blades and pumps. Equally, at regular intervals, individual components can be:

- Monitored,
- Removed,
- Cleaned,
- Inspected, and
- Repaired or replaced.

61.2 Versatile joints

61.2.1 Applications

61.2.1.1 General

A distinction is made between the demands of:

- Static, cold structures: such as airframes, thin skins and sandwich structures in CFRP and aluminium, and
- Dynamic, hot structures: such as engines and thermal-resistant structures using titanium, superalloys, high-temperature composites or combinations thereof.

61.2.1.2 Static cold structures

Predominant methods are:

- Mechanical fastening, [See: Chapter 22]:
    - threaded fasteners.
    - inserts for sandwich panels, [See: Chapter 23].
- Adhesive bonding, [See: Chapter 21].

[See: ECSS-E-HB-32-21 – Adhesive bonding handbook, ECSS-E-HB-32-22 – Insert design handbook, ECSS-E-HB-32-23 – Threaded fasteners handbook, ECSS-Q-ST-70-46 – Requirements for manufacturing and procurement of threaded fasteners]

61.2.1.3 Dynamic hot structures

With the likelihood of thermal excursions, allowance is made for different thermal expansions and the need for relative movement.

Mechanical connections, welding and brazing are common. Whilst fasteners can be used, e.g. bolts, their reliability under hot, cyclic and corrosive conditions should be ascertained.

The use of fastener systems in joint configurations between dissimilar materials is often the only option for applications such as thermal structures and TPS on reusable vehicles. Rivets are avoided.

61.2.2 Mechanical techniques

Mechanical joint methods include:

- Retention rings.
- Tapers.
- Interlocks.
- Collars.
- Pins.
- Clips.
- Compression joints.

- Threaded fasteners systems, e.g. screws/bolts, nuts, washers and bushes, made from:
    - specialist high-temperature metals.
    - ceramic-based composites.
    - monolithic ceramics.

In selecting an appropriate joint configuration, important factors include the:

- Intended life span,
- Re-use of structures and components,
- Service intervals,
- Access for inspection and replacement.

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