

MATERIALS EVOLUTION IN HOT PARTS OF AERO-TURBO-ENGINES

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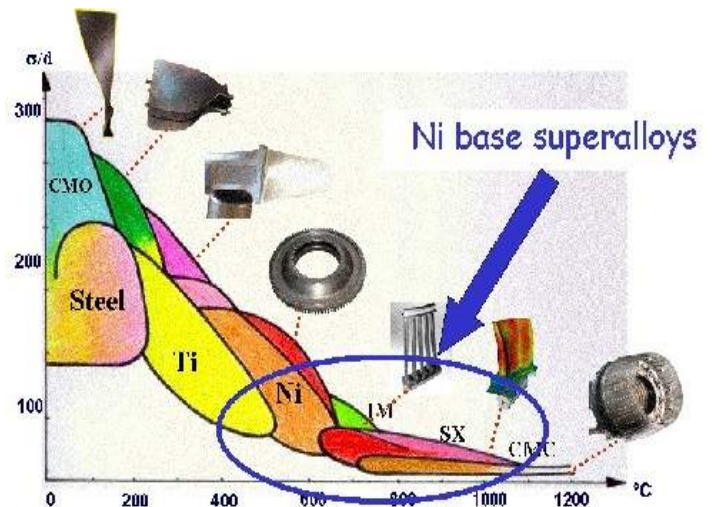
Abstract

For 30 years, aero-turbo-engines manufacturers have developed, in collaboration with university and industry partners mechanical and thermal resistant Ni base superalloys. Cast alloys grades have been optimized from equiaxed multi-grained to DS microstructures and nowadays single crystals enabling to get tailored properties at high temperatures. After the 80's-90's first and second generations Ni base superalloys development, Research activities have mainly concerned reliability improvement and cost savings. New Ni base grades for higher performances have been still studied but their improvement capabilities appear now more and more limited. Moreover the implementation of rare and costly chemical metallic elements lead to economical and strategic issues. Innovative technologies are currently in progress to increase the temperature in operating metallic parts such as ceramic thermal barrier coatings on blades and vanes. For Future, light resistant materials for high temperatures are sought beyond Ni base alloys. Ceramics matrix composites, new ceramic systems (eutectic solidified oxides, silicon nitrides) and refractory intermetallics are investigated as potential solutions for the 2020 aero turboengines.

1 – Introduction

Aero-turbo-engines are complex machines where mechanical and thermal loading strongly interact at very high loading levels for long operating times which have imposed the development of specific high technology materials. Therefore the search for endless improved performances has always been a major issue, first from a technical point of view for which the increase of thrust over weight ratio is a relevant parameter. Then the

economical aspect and long operating times have been focused on optimising acquisition and life cycle costs. So in -service lives and levels of fuel economy increases became key-points and today the environmental consideration lead more and more to the stringent objectives for short term of higher decrease in NO_x and CO_2 emissions as noise reduction. In all cases these challenges could be taken up through higher overall pressure ratios, compressor discharges and turbines entry temperatures. Consequently these requirements imply more and more severe thermo-mechanical loadings in critical parts such as turbine discs and blades. So the availability of highly resistant materials is a key point for success. Basically, Ni base superalloys revealed to be the best metallic materials for high temperature (above 600°C) applications in critical parts. Therefore they have been continuously developed since the 50's and represent now more than 50% in weight of an aero-turbo-engine. The perspectives for Future are oriented towards low density refractory materials (intermetallics, ceramics) and/or composites with carbon or ceramic fibres and ceramic matrix (figure 1).

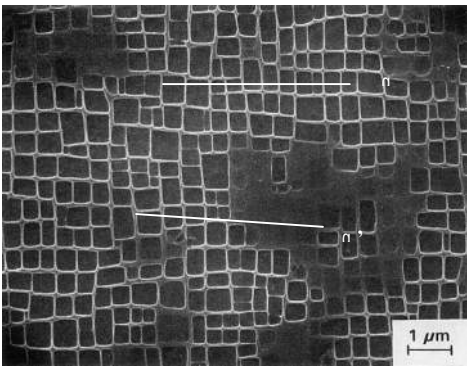


‘Fig.1. Specific resistance versus temperature’

2- Nickel Base superalloys

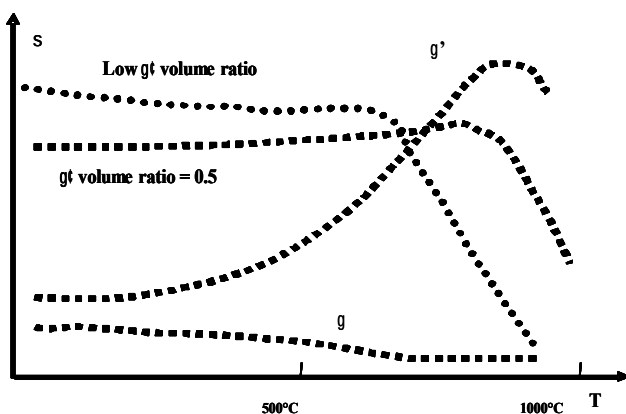
2.1 Presentation of Ni Base superalloys

Ni base superalloys [1] are quite affordable materials on an industrial point of view since they are prone to be cast, forged, heat treated, machined, welded, coated... They exhibit elevated mechanical resistances at high temperature (above 600°C) significantly higher than those of other metallic alloys (Al, Steels, Ti) due to their intrinsic hardening mechanisms: among an austenitic Ni base matrix γ (FCC structure, which means ductility), coherent precipitates γ' ($\text{Ni}_3\text{Al-Ti}$), with ordered FCC structure contribute to strengthen the alloy (see figure 2).



‘Fig.2. γ (white) / γ' (black) structure in the Ni superalloy AM1 single crystal’

The γ' precipitates exhibit the peculiar behaviour of an increasing resistance with temperature up to about 800°C and accordingly, the alloys resistances increase too, depending upon the γ' precipitates content (figure.3).



‘Fig. 3. γ , γ' and Ni base superalloys resistances versus temperature’

2 families of Ni base superalloys have been developed :

- High resistant alloys up to 700°C with fast decreasing mechanical strength at elevated temperature, containing less than 50% γ' . They

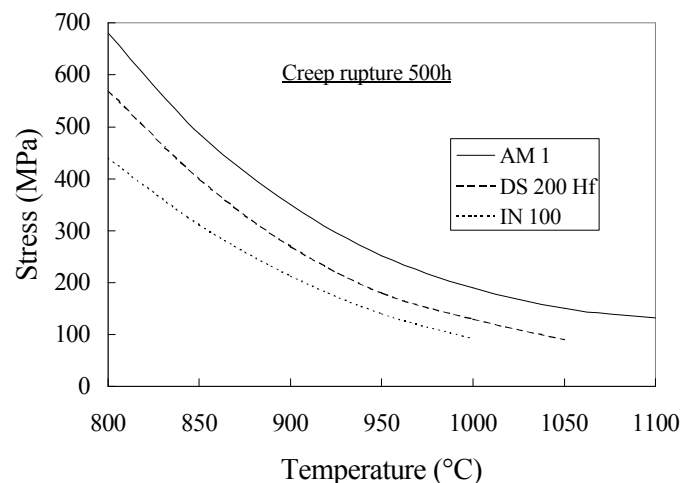
are prone forging and consequently their resistance can be improved by strain hardening. They are mainly used in discs.

- High temperature alloys up to 1100°C with a medium resistance up to 700°C mechanical. These alloys cannot be forged and are implemented only by investment casting in turbine blades and vanes for example.

The most performing alloys in this last family will be shortly presented hereafter.

2.3 Turbine blade superalloys for high temperature

The increasing temperatures in turbine blades and vanes has required beyond the equiaxial casting (EQ) the implementation of Directional Solidification (DS) and eventually the removal of grain boundaries with single crystals (SX) casting process development. Optimized chemical compositions have been determined, allowing an increase of the burning temperature by about 50°C and consequently an improvement in creep resistance by 40 to 50°C as compared to the best columnar grained structure alloys (figure 4). The AM1 (Table 1) selected by Snecma [2] proved to be equivalent to the best first generation single crystal superalloys [3]. This alloy is used for manufacturing military and commercial engines turbine blades and vanes. After a solutioning and homogenizing treatments followed by temper hardenings, its microstructure consists in regular 0,4 to 0,5 μm γ' cubic precipitates with edges along the $\langle 001 \rangle$ axis (figure 2) allowing an excellent static resistance (tension and creep) up to 1100°C.



‘Fig.4. Creep resistance of cast superalloys’

Future engine performances requirements imply the use of single crystal alloys with enhanced specifications at high temperature. For this purpose, new generation grades have been developed between 1980 and 2000: 2nd generation with limited amount (up to 3%wt) of Re, 3rd with higher Re (up to 6%wt) and eventually 4th with both Re and Ru contents (up to 4%wt) as shown on Table 1 [4].

%wt	Cr	Co	Mo	W	Ta	Re	Ru	Nb	Al	Ti	Zr	Hf	Pt/Rh/Ir/Pd	Ni	Density
1st gen.															
PWA1480	10	6		4	12				5	1.5				Bal	8,7
RenéN4	12,8	9	1,9	3,8	4			0,5	3,7	4,2				Bal	8,55
SRR99	8	5	0	10	3				5,5	2,2				Bal	8,56
AM1	8	6	2	6	9				5,2	1,2				Bal	8,59
AM3	8	6	2	5	4				6	2				Bal	8,25
CMSX-2	8	5	0,6	8	6				5,6	1				Bal	8,56
CMSX-6	10	5	3	0	2				4,8	4,7		0,1		Bal	7,98
MC2	8	5	2	8	6				5	1,5				Bal	8,63
2nd gen.															
CMSX-4	6,5	9	0,6	6	6,5	3			5,6	1		0,1		Bal	8,7
PWA1484	6	10	2	6	9	3			5,6	0		0,1		Bal	8,95
SC180	5	10	2	5	8,5	3			5,2	1		0,1		Bal	8,94
LEK 94	5,8-6,4	7,2-7,8	1,7-2,3	3-4	7	2-2,6	2,3-2,6		6,2-6,8	0,9-1,1		0,05-0,15		Bal	8,53
RenéN5	7	7,5	1,5	5	6,5	3			6,2	0		0,15		Bal	8,63
3rd gen.															
CMSX-10	2	2	0,4	5	8	6		0,1	5,7	0,2		0,03		Bal	9,05
RenéN6	4,2	12,5	1,4	6	7,2	5,4			5,75	0		0,15		Bal	9,98
RR2100	2,5	12	0	9	5,5	6,4			6	0		0		Bal	
TMS75	3	12	2	6	6	5			6	0		0,1		Bal	8,89
4th gen.															
MCNG	4	0	1	5	5	4	4		5,2	1,1		0		Bal	8,75
EPH102	2	16,5	2	6	8,25	5,95	3		5,55	0		0,15		Bal	9,2
RR2101	2,5	12	0	9	5,5	6,4	2		6	0		0		Bal	
TMS173	2,8	5,6	2,8	5,6	5,6	6,9	5		5,6	0		0,1		Bal	
TMS138	2,9	5,8	2,9	5,8	5,5	4,9			5,8	0		0,1	3 Ir	Bal	8,95
5th gen.															
TMS162	2,9	5,8	3,9	5,8	5,6	4,9	6		5,8	0		0,1		Bal	9,04
TMS196	4,6	5,6	2,4	5	5,6	6,4	5		5,8			0,1		Bal	9,01
6th gen.															
TMS ?														Bal	
GE alloy	1,25-10	4,25-17	1 to 4	3-7,5	5,8-10,7	3 to 8	0,4-6,5	0,5-2	5-6,6	0-2	0,05-0,5	0,1-2	0,1-6	Bal	

Table 1. Ni base single crystals compositions

ONERA has patented a 4th generation single crystal superalloy, MCNG, allowing higher temperature capability as investigated by Snecma and Turbo méca [5]. In comparison with a first generation superalloy such as AM1, the time to rupture is multiplied by a factor 2 at 950°C and by 25 at 1150°C. The Larson-Miller diagram compares in figure 5 the creep strength of MCNG ($\rho=8,75\text{g.cm}^{-3}$) alloy to those of the 3rd generation alloys CMSX -10 ($\rho=9,05\text{g.cm}^{-3}$) and René N6 ($\rho=8,97\text{g.cm}^{-3}$) with the reference AM1 ($\rho=8,63\text{g.cm}^{-3}$). The MCNG SX alloy reveals to be quite comparable to the American and Japanese 4th generation single crystal superalloys [6,7] but with the significant advantage of its lower density (8.75 versus 9.2) and a better metallurgical stability.

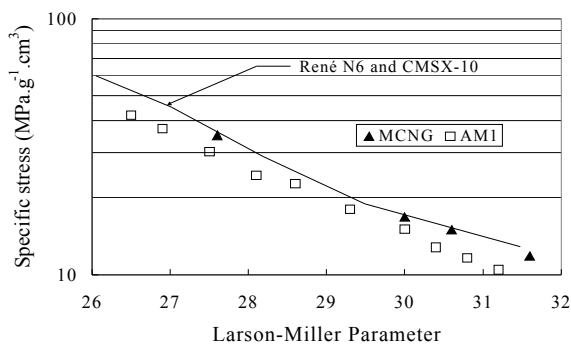


Fig.5. Creep resistance of French SX MCNG

In the last years, several works have been carried on mainly in Japan to increase the temperature capability of Ni base SX through new grades containing up to 5%wt (5th generation) and the TMS196 NIMS alloy [8] exhibits the best creep resistance at 1100°C (rupture life 1526h under 137MPa loading). Quite recently [9] a 6th generation of Ni base SX has been announced (see table1) with still higher rhenium and ruthenium contents (up to 8%wt Re and 6%wt Ru and/or Pt family element such as Pd, Ir or Rh). No data are available on those alloys but notwithstanding their expected good resistance at very temperature, they should exhibit an elevated density (probably above 9.4) and their cost will be definitely an issue due the implementation of Re and Pt family elements. In fact those metals are very expensive with important rate fluctuations since they can be considered as strategic ones due to limited world production: about 40 tons per year for Re which is rare second order by-product of the copper mining and only 30 tons per year for Ru which offers quite limited mining capabilities as all the Platinum Group metals. Aero-turbo-engine manufacturers try today to tailor SX Ni base alloys with no Ru and reduced Re content while keeping good mechanical and environmental properties: for example, GEAE is developing grades [10] derived from René N5 (3%wt Re) with lower Re (René N515 with 1.5%wt) and even no Re (René N500). Likely in Future economical considerations will lead to re-investigate and possibly improve the “old” generations Ni base SX. But for higher temperature use in blades, other technologies or concepts should be thought of as exposed subsequently.

3- Evolution of metallic materials

As shown above, the development of new nickel base superalloys grades with higher performances appears quite difficult. To improve the parts capabilities the efforts of materials scientists are today focused on innovative technologies such as multi-materials and prospective materials. The main research directions are presented hereafter.

3.1 Thermal barrier coatings

A temperature increase on very hot parts such as turbine blades can reasonably be achieved through the implementation of refractory ceramic coatings [11] containing basically yttria stabilised zirconia,

usually noted as Thermal Barrier Coatings (TBC): in that way, the temperature of the metallic substrate remains acceptable although a 30 to 50°C increase of gas temperature (figure 6).



‘Fig. 6. TBC on turbine blade’

The main challenge consists in achieving an adequate adherence between a ceramic coating and a metallic substrate exhibiting quite different elastic moduli and thermal expansion coefficients which induce thermal stresses. A metallic bondcoat between the substrate and the ceramic deposit accommodates these discrepancies but the “weak point” remains the interface between the bondcoat and the ceramic where decohesions can be initiated, inducing spallation of the TBC. Nowadays the Electron Beam Vapor Phase Deposition (EBPVD) process is mastered but numerous efforts are carried out to improve the lives of coated parts and to develop new systems with higher performances.

3.2 Refractory intermetallics

The best Ni base single crystals exhibit acceptable temperature resistances up to 1150°C (even 1200°C for short time) which is about 90% of melting temperatures. To go beyond and new materials families are sought and refractory intermetallics such as refractory metal silicides are potential candidates.

Niobium silicides base alloys seem attractive [12] due to their limited density (about 7,2 to 7,5 compared to 8,8 - 9,2 for last generation SX). 3 phases have to be controlled in those materials (Nb , Nb_3Si and Nb_5Si_3) to get the best compromise between ductility and high temperature resistance as shown on figure 7. Some elements have been added to Nb and Si to improve mechanical and chemical resistance. The “MASC” alloy (“Material And Silicide Composite”) patented by GE can be considered as a reference one [13]. Its composition is as follows (%at): Nb - 25Ti - 8Hf - 2Al - 2Cr - 16Si.

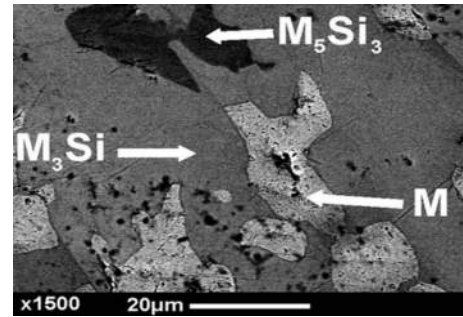
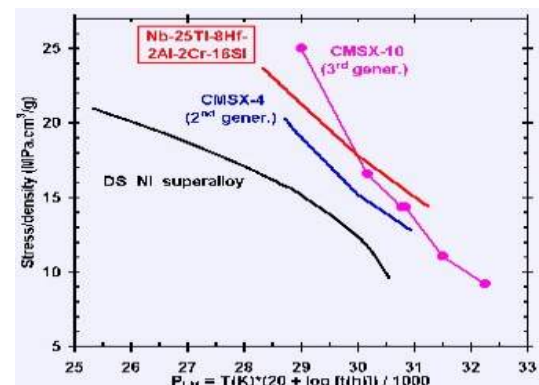


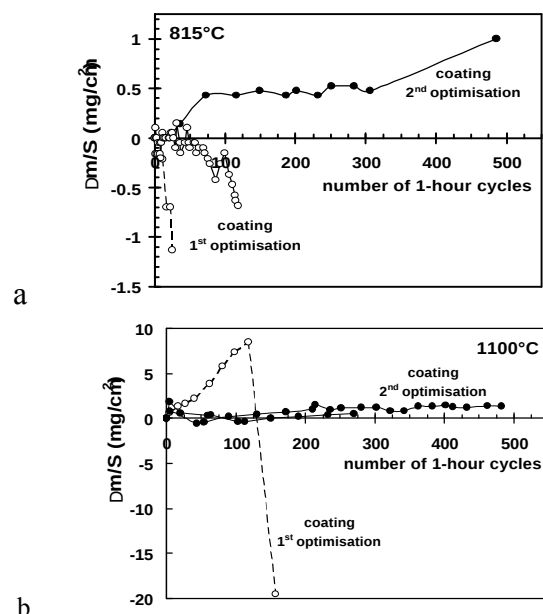
Fig.7. Microstructure of Nb silicide alloy

Creep behaviour (Figure 8) is quite good at very high temperature (>1200°C) but medium temperature mechanical properties need to be assessed and especially toughness.



‘Fig. 8. Creep resistance of NbSi’

Moreover oxidation resistance at intermediate (800°C) and high (1100°C) temperatures is definitely an issue in those materials but some coatings [14] seem quite promising (figure 9).

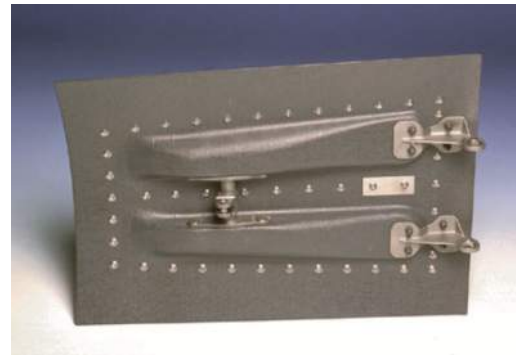


‘Figure 9. Oxidation on coated NbSi at 815 (a) and 1100°C (b)’

An European program on niobium silicides has been launched, “ULTMAT” (“ULtra high temperature MATerials”) with the objective of developing European Nb-Si and Mo-Si base grades in correlation with manufacturing processes [15]: powder metallurgy and ingot metallurgy routes, casting, machining, welding. A cluster of blades have already been cast (figure 10).

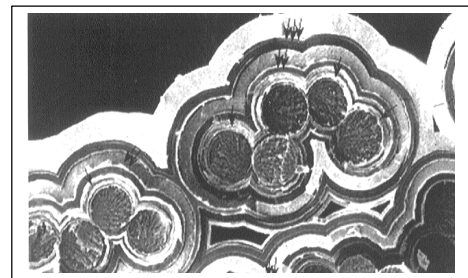


‘Fig.10. NbSi cast blades’



‘Fig.12. SiC-SiC nozzle flap’

Opposite to bulk ceramics these materials are not brittle due to the carbon interphase between fibres and matrix but this interphase is prone to oxidation. An innovative concept of multi-layer self-repairing matrix has been developed by Snecma Propulsion Solide (figure 13) enabling long time use under oxidizing atmosphere.

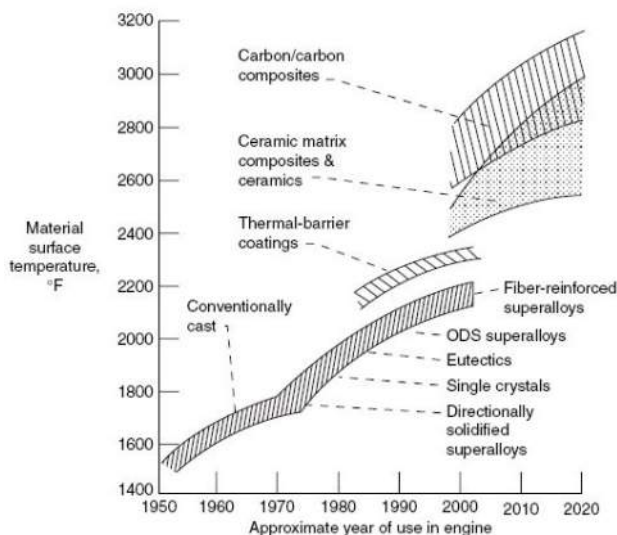


‘Fig.13. SiC self-repairing ceramic matrix around SiC fibers’

4. Non metallic materials

4.1 Ceramic matrix composites (CMC)

Composites with long SiC fibers and ceramic (SiC or C) matrix have been developed (figure 11) for aerospace structures and applications in aero turbo-engines [16] have been implemented as the nozzle flaps shown on figure 12.



‘Fig. 11. High temperature materials development’

Future applications as combustors, turbine vanes and blades are presently studied. (figure 14).



‘Fig.14. CMC aero-turbo-engine parts’

4.2 New Ceramics systems

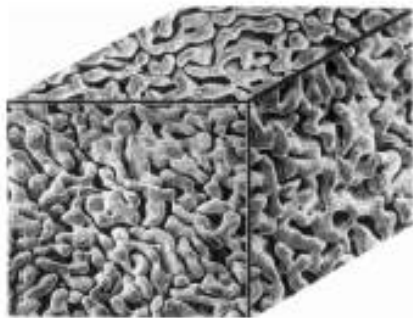
The main drawback of structural ceramics is their intrinsic brittleness and new systems incorporating different ceramics exhibit some “plasticity” while keeping very high temperature resistance are now considered:

- Eutectic ceramics [17] processed through casting and directional solidification of oxides

which could be implemented for uncooled turbine blades;

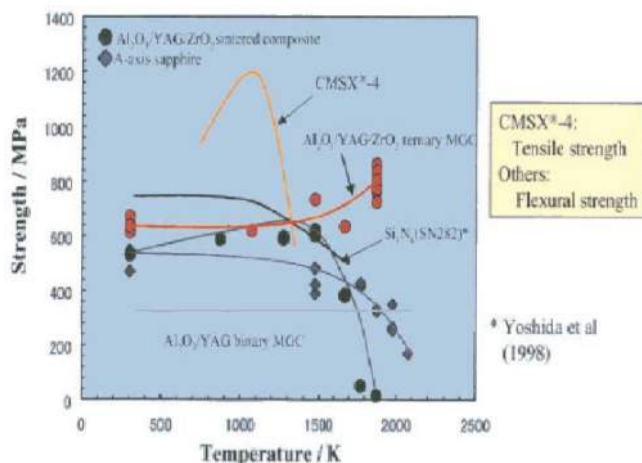
- $\text{MoSi}_2/\text{Si}_3\text{N}_4$ [18] systems with or without oxides reinforcement for possible use in static thermo-structural components.

Eutectic ceramic consist in a combination of 2 or 3 oxides : alumina or zirconia and complex oxides such as perovskite ABO_3 and garnet $\text{A}_3\text{B}_5\text{O}_{12}$ where B is generally Al and A a rare earth element. They have a lower density as compared to SX Ni base superalloys (between 5 and 5.5 vs 8.8 to 9). Their microstructures (figure 15) consist in tortuous shapes phases overlapped each others.



‘Fig. 15. Eutectic ceramic structure’

They exhibit an elevated and nearly constant mechanical resistance between 1200 and 1750°C [19] as shown on figure 16.



‘Fig.16. Eutectic ceramics resistance vs temperature ‘

But these materials need to be thoroughly characterized to define the relevant applications in aero-turbo-engines. Today only small bars are manufactured at laboratory scale in thermal

gradient controlled furnaces and the industrial routes and quality criteria for components are still to be studied.

Si_3N_4 ceramics exhibit good thermo-mechanical properties at high temperature (creep and thermal shocks resistance), an acceptable oxidation resistance, low density (3.2) and expansion coefficient ($2,5 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$). However a higher toughness is required to overcome the issue of foreign object damage and Environmental Barrier Coatings (EBC) are also needed to protect components from environment damage and achieve lifetime performance. MoSi_2 additions enable to improve those two points as shown on tables 2 and 3.

Flexural strength (MPa)	Si_3N_4	$\text{Si}_3\text{N}_4/\text{MoSi}_2$ 90/10
at 20°C	820	780
at 1400°C	730	720
at 20°C after 10000 h at 1500°C	260	509

‘Table 2. Mechanical properties improvement on Si_3N_4 by MoSi_2 addition [18]’

Fracture toughness ($\text{MPa} \cdot \text{m}^{0.5}$)	Si_3N_4	$\text{Si}_3\text{N}_4/\text{MoSi}_2$ 50/50	$\text{Si}_3\text{N}_4/\text{MoSi}_2$ 30/70
at 20°C	6	5	5
at 1000 °C	6	7	10
at 1200°C	6	9	12

‘Table 3. Toughness improvement on Si_3N_4 by MoSi_2 addition [20]’

Important effort both for basic studies and industrial development are to be undertaken before the implementation of parts on engines.

5 . Conclusion

To fulfil the challenge of more and more performing aero-turbo-engines, manufacturers have developed for the last 20 years specific high resistant Ni base superalloys for application in the hottest parts, mainly single crystals (SX) for turbine blades. Those alloys reveal good mechanical properties as well as industrial

affordability and are today commonly used. Meanwhile, studies on successive generations of SX superalloys have been carried out by all turbo-engines manufacturers and today the optimum seems to be reached.

Future perspectives for lighter and highly resistant materials include Nb-Si base intermetallic alloys, ceramic matrix composites and new generation of “ductile” ceramics: they might replace, at medium/long term, Ni base superalloys in the hottest parts with weight saving benefit.

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