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Advanced Lightweight Silicide and Nitride Based Materials for Turbo-Engine Applications

Refractory metal silicides and nitride-based ceramics combine two properties that may lead to substantial reductions in aircraft fuel consumption: compared to the most advanced nickel-based superalloys presently used in aeronautical turbines, they can withstand higher temperatures and may have lower densities. Niobium silicide-based alloys and silicon nitride / molybdenum disilicide composites are currently being developed for turbine hot section components for both aircraft engines and land-based turbines. This paper presents the processing techniques, the microstructural features and the mechanical and physical properties at low and high temperatures as well as the oxidation behaviour of these materials. Prospects in composition optimisation, manufacturing processes and control of the microstructure for further improvements are discussed.

Introduction

The performances of aircraft/rotorcraft and land-based gas turbine engines are evaluated using both technical and sociological metrics. Thus not only are the technical needs considered, but the economic and environmental issues are also addressed, the most important ones being: overall power or thrust, specific thrust, fuel efficiency, service reliability (reduced maintenance), emission of CO_2, NO_x and other species (soot, unburnt fuel, CO, etc.), external noise emission and cost.

Hot section components in aircraft/rotorcraft and land-based gas turbine engines differ in size and service conditions and within each group there are very different specifications. In general, for military engines, thrust and thrust-over-mass ratio are privileged, while in commercial airline engines it is rather the operating costs. Several land-based turbine types are in operation, from the low power micro-turbines for local (or distributed) power generation up to the grid-connected 345-MW turbines, for which the regime can go from "peaker" (short duration service cycles to accommodate higher electrical power demands on the grid) to the "baseload" (covering the basic grid power demands). In all cases, the desire to reduce owner costs and operating costs, including fuel consumption and maintenance, are technological driving forces that are becoming more and more important.

These issues have been frequently addressed in advanced engine architecture, new cycle and combustor designs, optimised aerodynamics and new cooling concepts. But the development of hot section materials (especially in the turbine) has clearly made a critical contribution to performance gains in turbo-machinery. However, their still limited capabilities with respect to the severe operating conditions and the demands of engine designers often limit further improvements in turbine efficiency. A substantial increase in the temperature capability of turbine materials, especially for the airfoil materials which work in the harshest conditions because they are located directly in the hot gas flow coming from the combustion chamber, would allow for significant performance enhancements. High temperature materials represent one major enabler in the long-term for most, if not all, future engine improvements.

Several new material families are being developed to allow for a significant increase (more than 150°C) in airfoil material operating temperatures. The most advanced materials currently used are Ni-based single-crystal superalloys for which the upper operating temperature limit is 1100°C ~ 1150°C.

In addition to the higher temperature capability, low density is crucial for many applications. Besides the component mass reduction which is of high priority for aircraft/rotorcraft turbines, it also allows for the down-scaling of the disk, since the centrifugal forces created by the lighter blades are lower.

Two new material systems, refractory metal (especially Mo and Nb) based silicide multiphase alloys and silicon nitride based ceramics, show promising properties that would allow for their use in future turbines.

The development status will be presented in this paper for both silicide and nitride based materials with a focus on the work carried out at Onera.

Silicide based alloys

Refractory metals (RM), with their outstanding properties (high melting point, good mechanical and creep strength), are currently used as components for ultra-high temperature applications in inert atmospheres. However, RM and RM-alloys suffer from severe oxidation in air. The sublimation of molybdenum oxide, for instance, occurs already at intermediate temperatures (> 500°C) which excludes any applications at high temperature in air.

By contrast, RM-silicides can be used in air at higher temperatures and even up to temperatures of 1650°C (*e.g.* $MoSi_2$ heating elements). But these compounds also suffer from catastrophic oxidation (pesting) at intermediate temperatures (*ca.* 600°C - 800°C) and exhibit brittleness at ambient temperature. However, the essential objective of the current research on RM-silicide based alloys is to manufacture a composite material that takes advantage of (a) the beneficial oxidation and creep resistance of the silicides and (b) the outstanding mechanical properties of the RM.

RM based metal-intermetallic composites were developed under US impetus in the 1990's. Two systems show the greatest potential [1], Nb-Si and Mo-Si, as metal-toughened intermetallic-strengthened materials with a metallic phase volume fraction between 35% and 60%. The melting points of these multiphase alloys are in excess of 1750°C (Nb-base) and 1950°C (Mo-base), respectively, substantially higher than those of Ni-base superalloys.

Several European universities and research centres, together with major engine manufacturers and a refractory metal supplier, most of them already working on specific aspects of these alloys, pooled their expertise within the European Union funded ULTMAT project, under the coordination of Onera [2]. This project aimed at providing a sound technological basis for the use of these materials in future turbines, with alloy development focused on the improvement of key properties such as high temperature creep strength, oxidation resistance and room temperature toughness, in connection with semi-industrial scale manufacturing and fabrication processes. In parallel with those of the US and European (France, Germany, UK) teams, investigations on RM-silicide based materials are in progress in Japan, China, India and Brazil.

Mo-silicide based alloys

Berczik [3] first patented Mo–Si–B alloys with compositions in the Mo-rich corner (figure 1) and a manufacturing approach which in essence comprises a rapid solidification step. Boron is added to allow for the formation of a dense protective borosilicate glass.

A typical microstructure yields a matrix of the Mo(ss) solid solution providing good fracture toughness and ductility below 600°C, and embedded intermetallic Mo_3Si and/or Mo_5SiB_2 type compounds (T2 phase) for enhancing both creep and oxidation resistance.

Within the ULTMAT project, the studied alloys were basically three-phase Mo-9Si-8B alloy (at.%) [4], with addition of solid solution strengthening elements, with volume fractions of about 55% Mo(ss), 30% T2 and 15% Mo_3Si. Although for these alloys the density is comparable or slightly higher than that of superalloys, higher specific mechanical properties make them attractive for many applications.

Manufacturing and microstructures

Due to the very high melting temperatures (in excess of 2000°C) and the heterogeneous microstructures obtained, ingot metallurgy is now seldom used to study and improve the properties of Mo-Si based alloys. Powder metallurgy (PM), on the other hand, is the manufacturing route that has been privileged. Mechanical alloying (MA) in particular can yield supersaturated or even amorphous powders that can be processed to overcome the brittleness exhibited by conventionally solidified ingots or even PM-processed inert gas atomised powders [5]. This has been applied to a Mo-3Nb-9Si-8B alloy in the ULTMAT project. MA, in a vertical attritor for 10 h, is sufficient to completely dissolve the Nb, Si and B in the Mo matrix. Subsequent heat treatment allows for homogeneous precipitation of the intermetallic phases within the Mo(ss) matrix. The powder was isostatically cold pressed and sintered under H_2 at 1450°C. Finally, billets of 50 mm diameter and 200 mm length were obtained by hot isostatic pressing (HIP) the sintered bars at 1500°C under 200 MPa. The microstructure in the HIP'ed state is shown in figure 2. The expected phases, Mo(ss), Mo_3Si and T2 are present and the residual porosity is below 1%. Some undesired silica inclusions and some larger-scale areas of Mo(ss) are also visible due to a non-optimised MA process.

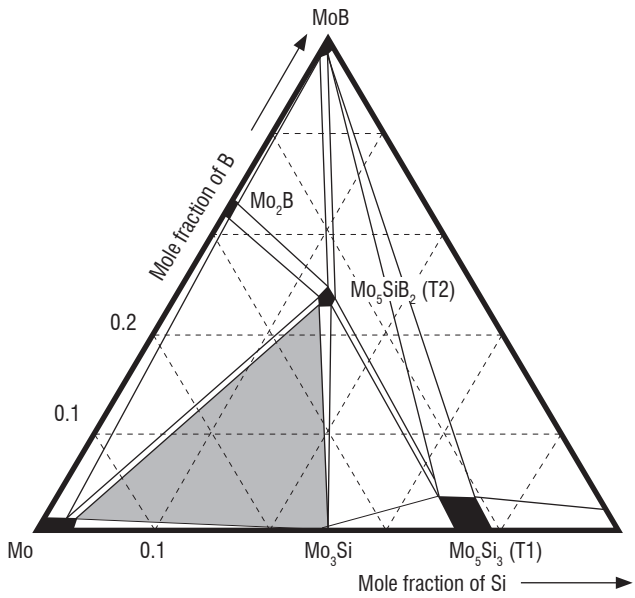


Figure 1 – Mo-rich part of the Mo-Si-B phase diagram at 1600°C. The shaded area is the Mo-Mo_3Si-T2 three-phase region

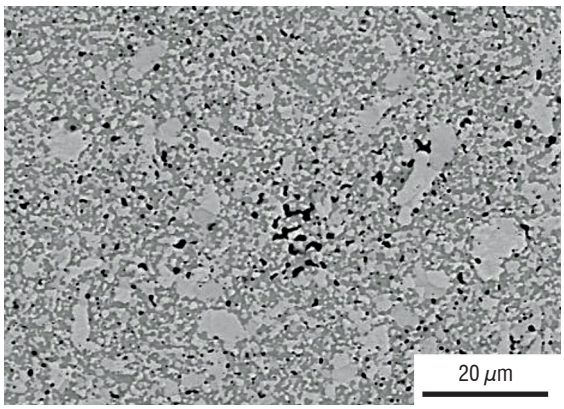


Figure 2 – SEM micrograph of a MA processed and HIP'ed MoNbSiB alloy with Mo(ss) (bright), intermetallics (grey) and undesired silica (black)

Mechanical properties

Tensile tests were performed on Mo-Si-B alloys under vacuum at 20°C to 1600°C [6]. While no significant ductility was measured at temperatures below 1100°C, a total elongation to fracture of about 5% could be observed at 1200°C. The ultimate tensile strength remained close to 500 MPa in the 20°C - 1100°C range. Premature brittle failure within the elastic domain was observed. Crack growth occurred through the continuous network of intermetallics. The ultrafine grained (grain size $\sim 0.8\,\mu$m) and equiaxed microstructure shown in figure 2 exhibited superplastic behaviour: tensile strains to failure of 300% at 1300°C and 400% at 1400°C were obtained for a strain rate of 10^{-4} s^{-1}. This demonstrates the potential for superplastic forming. At present, the applicable forming processes appear limited to lower deformation rates (< 0.1 s^{-1}) which make conventional (fast) hot forming processes like forging or rolling at even higher temperatures still a critical issue for sound wrought processing. Instead, isothermal forging in closed dies may become realistic to manufacture parts with intricate shapes.

The creep behaviour was evaluated by compression tests in temperature and stress ranges of 1050°C to 1315°C and 100 MPa to 400 MPa. The presence of significant plasticity for Mo-Si-B based alloys above 1100°C indicates poor creep resistance. However, the coarsening of the microstructure by an appropriate heat treatment significantly improved the creep behaviour [4], as shown in figure 3. Annealing at 1700°C for 10 h in a vacuum increased the grain size of Mo(ss) and intermetallic phases by almost a factor ten. The consequence was a decrease of the compressive creep rate by one order of magnitude at all temperatures. The stress exponent remained at a quite low value of $n \sim 2.3$, indicating that grain and interphase boundary sliding processes still play a major role in plastic deformation.

Oxidation resistance

Mo-Si-B alloys tend to form a protective borosilicate scale when exposed to high temperatures. They undergo "pesting oxidation" at intermediate temperatures (600°C-850°C) when excessively slow scale formation kinetics allow Mo to oxidise to volatile MoO_3. Pesting can however be avoided by a preliminary short high temperature oxidation treatment that builds up the protective scale. Protective coatings are nevertheless needed to increase the Mo-Si-B alloy lifetime. Figure 4 shows that a SIBOR® plasma sprayed coating [7] provides excellent protection at intermediate temperatures. The good behaviour of both a SIBOR® coating and a pack-cementation FeCrSiB coating was confirmed in a burner rig test at 900°C, 1000°C and 1100°C where lifetimes of over 500 cycles were obtained [8].

Recent developments

The main current research topic is the improvement of the ductility of the Mo-Si-B alloys which exhibit a ductile to brittle transition temperature above 600°C. One direction is better control of the silicon content in the Mo solid solution and the micro-alloying with zirconium or Y_2O_3 particles [9,10].

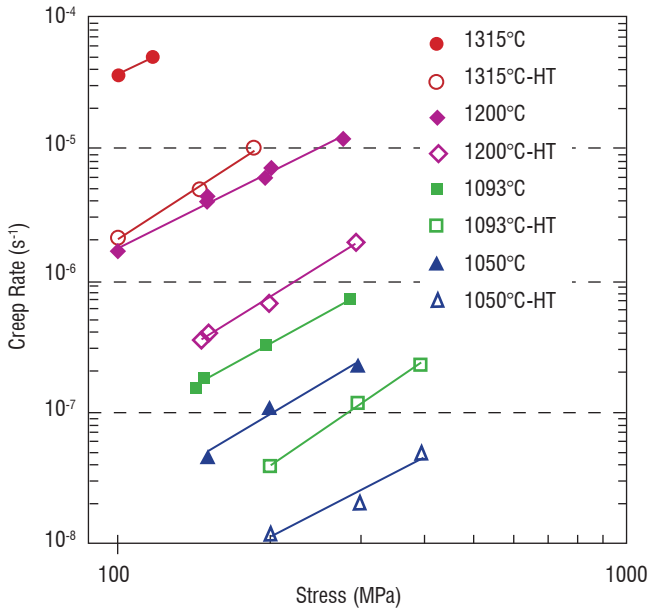


Figure 3 – Steady-state creep rate *vs.* stress for the HIP'ed (full symbols) and heat-treated (open symbols) MoNbSiB alloy in the 1050°C - 1315°C range

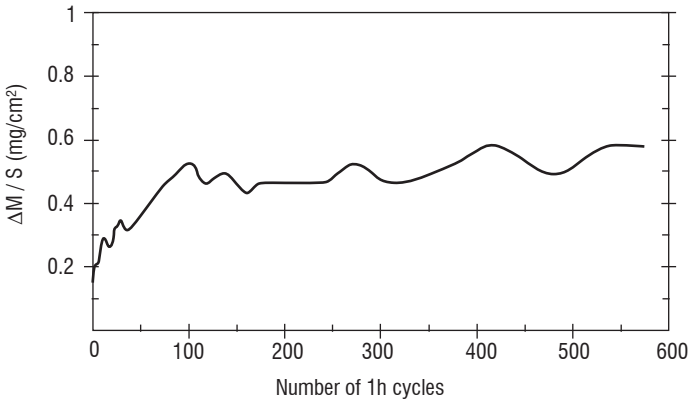


Figure 4 – Cyclic oxidation at 815°C of a SIBOR® coated Mo-Nb-Si-B alloy

Nb-base silicides

Alloys in the binary Nb-Si system exhibit good creep resistance, but poor toughness and oxidation resistance. Their properties can be improved by alloying, leading for example to the NbTiHfCrAlSi metal and silicide composites (MASC) family, as developed by General Electric [11,12]. The Nb-Si based materials consist of a metal solid solution M(ss) (M being *e.g.* Nb+Ti+Hf+...) with M_5Si_3 and/or M_3Si silicide phases (figure 5), with densities in the range 6.5 – 7.9 g/cm³ depending on the composition. Other phases, such as $NbCr_2$-type Laves phases in the case of higher Cr content for better oxidation resistance or hexagonal M_5Si_3 (deleterious for creep resistance) in the case of high Ti and/or Hf contents, can also be present.

At high temperatures, M(ss) can be considered as the softest and the silicide as the most creep resistant phase. Improvement of the high temperature mechanical properties (mainly creep resistance) can thus be obtained by enhancing the properties of M(ss) and/or increasing the silicide volume fraction. High silicide contents simultaneously

improve the oxidation resistance, but decrease toughness and ductility at room and intermediate temperatures. Alloys with silicon content of up to 24 at.% have been studied in the ULTMAT project.

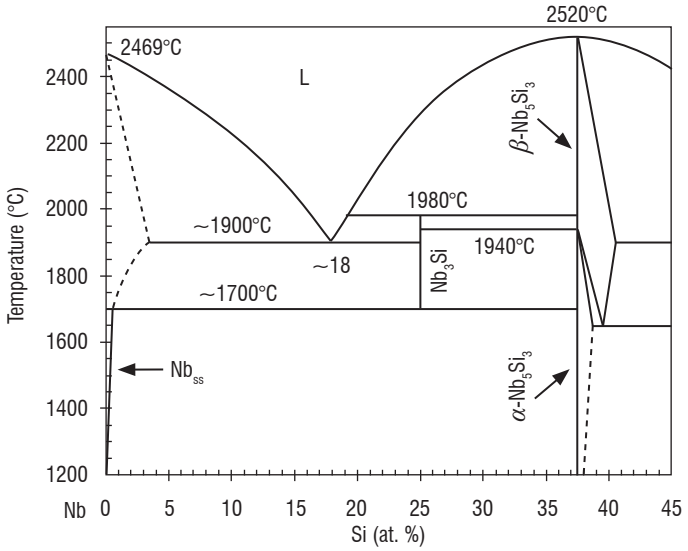


Figure 5 – Nb-rich part of the binary Nb-Si phase diagram

Figure 6 – Investment cast Nb-Si based demo blade (height ~ 120 mm) [2]

Manufacturing and microstructures

Ingot metallurgy (mainly vacuum arc melting, but also Czochralski drawing for directional solidification) is widely used at laboratory-scale to manufacture Nb-Si samples needed for microstructural, mechanical and oxidation characterisations [2,8,11-13]. Unlike Mo-Si-B alloys, complex alloying is required to improve the properties of Nb-Si alloys; the oxidation resistance of the M(ss) phase, for example, is improved by the addition of fairly high amounts of Ti, Cr, Al, which lowers the melting temperature of near-eutectic alloys. The manufacturing of shaped parts by investment casting (figure 6), which requires specific high temperature mould materials with a reduced reactivity with the Nb-Si melt [11,14], becomes possible as an extension of the manufacturing route developed for Ni-based superalloy components.

It remains difficult to improve the mechanical properties because of the heterogeneous microstructure within the ingot. Metallurgical defects (pores, micro-cracks, etc.) are encountered; for high Si-content alloys – exhibiting high melting points – and despite the small mismatch between the coefficient of thermal expansion (CTE) of the M(ss) and M_5Si_3 phases (*e.g.* between pure Nb and a MASC alloy: less than 2.10^{-6} K^{-1}), cracking occurs during cool down in the sometimes several hundred micrometer-long silicide dendrites. This significantly reduces the tensile strength compared with the compression strength [11], since the tensile behaviour is controlled here by the defects. Thermo-mechanical treatments of cast alloys only partially succeeded in improving the properties.

The PM approach offers a possibility of refining and better controlling the microstructure and allows for processing at temperatures far below the melting point. First, investigations were carried out on two-phase Nb-Nb_5Si_3 materials obtained by hot uniaxial pressing (HP) and HIP'ing Nb + Nb_5Si_3 powder mixtures [15], or with reactive hot pressing of Nb + Si powder blends [16]. Alloys with more complex compositions with up to nine elements have to be manufactured using pre-alloyed powders obtained either at lab-scale by crushing and milling arc-melted buttons, or by using the rotating electrode process [11], or inert gas atomisation [5,11]; blending of elemental powders followed by sintering and HIP steps can also be used [2]. Pre-alloyed powder compaction is usually done either by extrusion [11,17] or using emerging processes like spark plasma sintering (SPS) [17]. If the microstructure of the as-extruded alloy is relatively fine, it is coarsened by heat treatment, as shown in figure 7. The mechanical properties of these alloys and the optimisation of the microstructure through powder preparation and heat treatment are currently under investigation.

a) b) c)

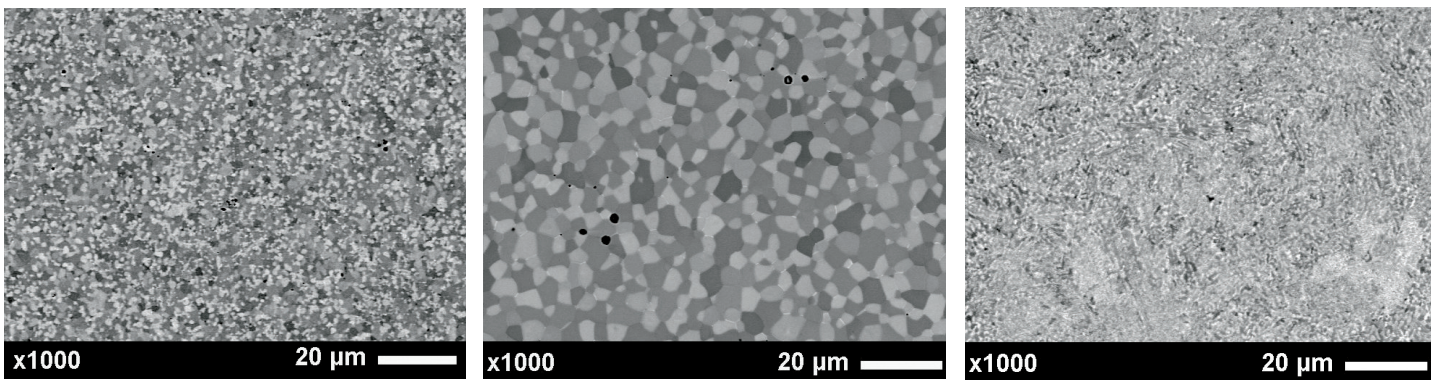


Figure 7 – Microstructure of an Nb-25Ti-8Hf-2Al-2Cr-16Si PM alloy (transverse section) from gas-atomised powders [17]: a) extruded at 1400°C, b) same after heat treatment at 1400°C for 24 h showing an increase of the grain size by a factor 5 to 10, c) as-sintered by SPS at 1325°C

Mechanical properties

The mechanical properties of a range of NbTiHfCrAlSi alloys, including strength, fracture and fatigue behaviour, and creep resistance, were reviewed by Bewlay and co-workers [11,12]. Figure 8 illustrates how alloying improves the fracture toughness of directionally solidified alloys. Alloying with refractory elements results in very high strength and creep resistance. For example, solid solution strengthening of Nb(ss) by Mo and W is very efficient, so that Nb-Mo-(Hf or W)-(16-18)Si alloys exhibit yield strengths at 1400°C higher than 700 MPa in compression [18] (figure 9) and higher than 240 MPa in tension (Nb–18Si–5Mo–5Hf–2C, [19]). These improvements are however obtained at the expense of toughness, ductility (the reported ductile-brittle transition temperatures can be as high as 1200°C [19]) and oxidation resistance.

Creep resistance is one of the major properties to be optimised if high temperature applications for rotating components are the aim. Some results obtained in the ULTMAT project are presented in figure 10, which shows the effect of an increase in Si content, with respect to the MASC alloy (16 at.% Si), and the addition of refractory elements [8]. An improvement in temperature capability of about 150°C can be obtained over the CMSX-4 single crystal Ni based superalloy.

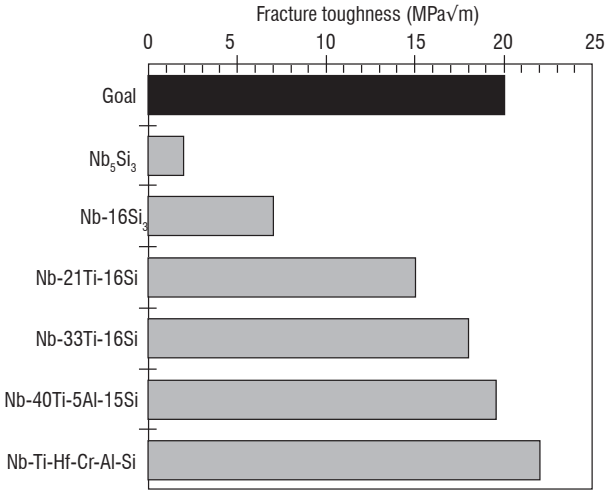


Figure 8 – Fracture toughness of directionally solidified Nb-Si alloys (except Nb_5Si_3), from [12]

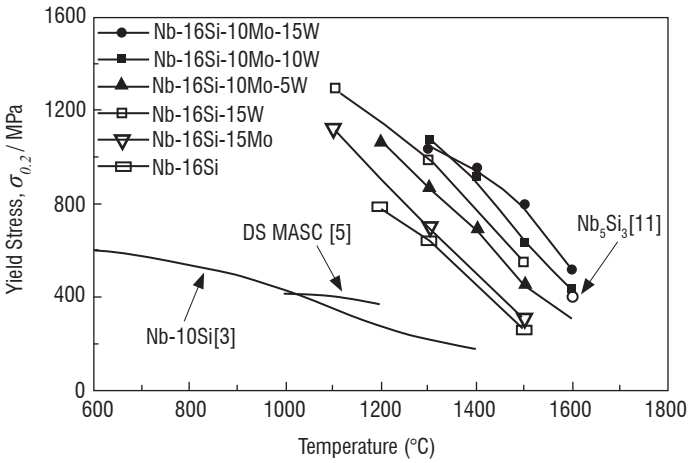


Figure 9 – Compressive yield strength of Nb-16Si-Mo-W cast and heat treated (1700°C, 48 h) alloys compared with single-phase Nb_5Si_3, and two-phase Nb-10Si and Nb-25Ti-8Hf-2Al-2Cr-16Si (MASC) alloys (see references in [18]). Tests were performed in an argon atmosphere

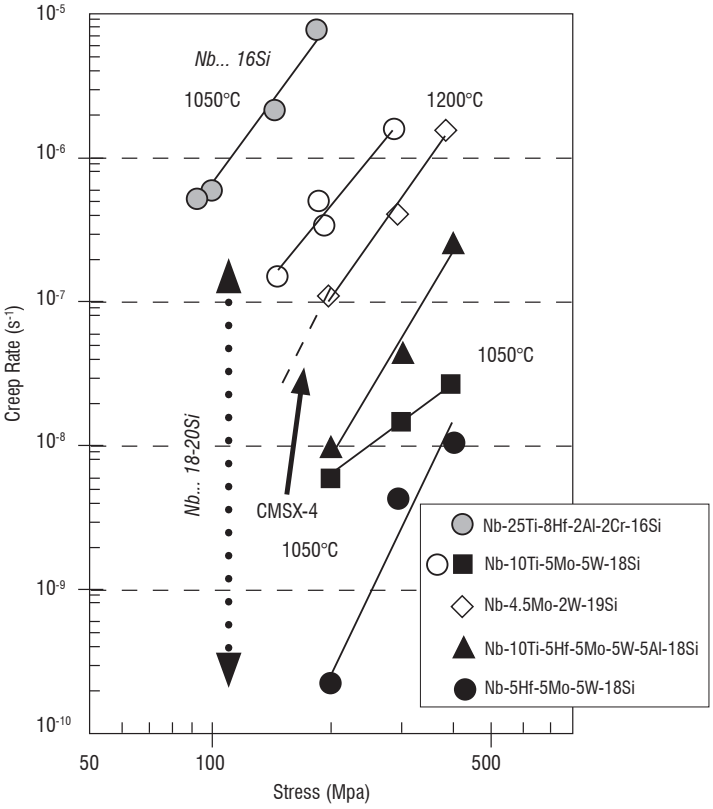


Figure 10 – Compression creep rate as a function of applied stress for Nb-Si based alloys and CMSX-4 [8]

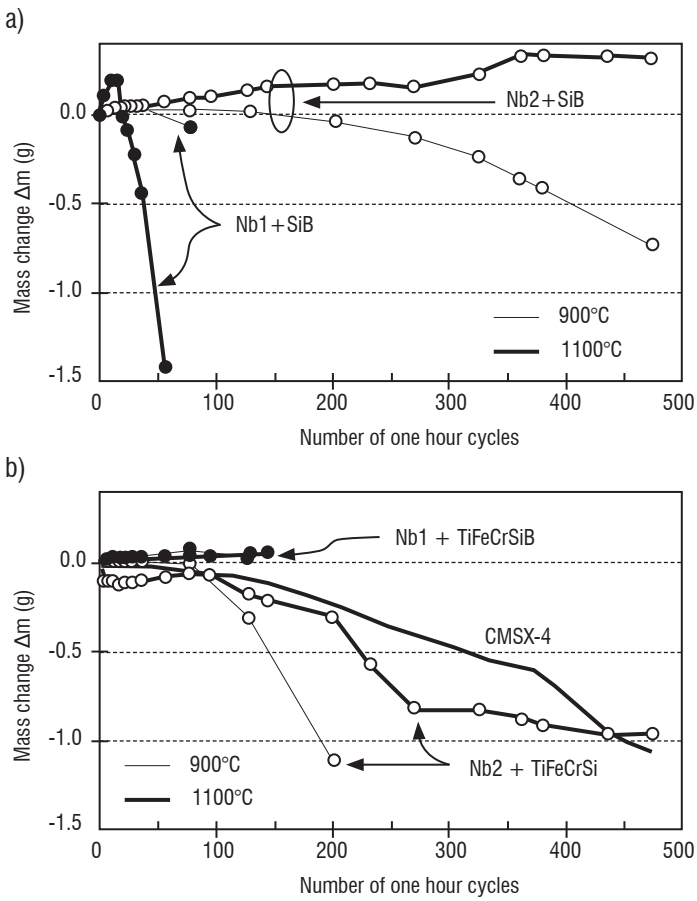


Figure 11 – Mass variation of Nb-Si alloys with various pack cementation coatings in a burner rig test at 900°C and 1100°C, compared with CMSX-4 at 1100°C (1 g corresponds to *ca.* 11 mg/cm²) [8]. Nb1 is Nb-10Ti-5Mo-5W-18Si, Nb2 is Nb-25Ti-8Hf-2Al-2Cr-16Si

Oxidation resistance

Niobium does not form any protective oxide scale and suffers from severe internal and external oxidation above 500°C, so binary Nb-Si alloys do not withstand exposure to air at high temperature. Alloying and protection with an adequate coating is thus required. In addition to high temperature oxidation, Nb-Si binary alloys also undergo a "pest" phenomenon in the range 600-900°C, characterised by a rapid disintegration of the material. Both oxidation regimes have been investigated and protective coatings developed [2,8,11-14,20]. Elements like Al, Cr, Ti, Hf but also Sn (specifically for pesting), Ge and B can be added to improve the oxidation behaviour, either in solid solution (*e.g.* for reduction of oxygen solubility and diffusion in Nb, or oxygen scavenging) or for the formation of oxidation resistant phases such as $NbCr_2$-type Laves phases.

The effect of the microstructure on the high temperature oxidation behaviour has rarely been reported on in the literature. The beneficial effect of a reduced Nb(ss) volume fraction was quickly noticed [12]. It has also been shown that the refined microstructure of PM extruded alloys improves the oxidation resistance at all investigated temperatures (800-1200°C) compared with cast and heat-treated alloys [21].

Conventional cyclic testing in static laboratory air [14] as well as burner rig tests [8] in which samples are exposed to both corrosion by molten salts and oxidation in cyclic conditions have shown in the ULTMAT project that pack-cementation deposited coatings provide excellent protection for both oxidation regimes. The composition of the TiFeCrSiB coating (figure 11) is adjusted to form a continuous glassy borosilicate layer with an adequate viscosity that drastically slows down the ingress of oxygen into the Nb-Si alloy, and is able to fill any crack appearing during cycling.

Recent developments

Current research topics include better control of the microstructure of the Nb-Si based alloys and the simultaneous improvement of the major mechanical properties (creep, toughness, ductility) and oxidation resistance, including the further development of protective coatings. Powder metallurgy-based advanced processes (direct laser fabrication, powder injection moulding, SPS, etc.) are now being considered for the manufacturing of near-net shape components with tailored microstructures. On the European level, the HYSOP project [22] has begun investigating some of these routes and designing advanced coating systems based on multilayer EBC coatings (Environmental Barrier Coatings).

The first applications will probably emerge for intermediate temperatures (900°C – 1000°C) to take advantage of the good specific mechanical properties and the easier handling of the oxidation issues, *e.g.* by the replacement of low pressure turbine Ni based superalloy components by *ca.* 15% to 20% lighter Nb-Si based components.

Nitride based materials

Nitrides are a wide range of compounds made from nitrogen and others elements (see box). Within this chemical family, only a few of them, such as silicon nitride, are refractory ceramics. As shown in the box, this nitride has many attractive properties, and for this reason it is now used in highly efficient small land-based turbines due to optimisation of the composition, microstructure, processing and coatings. Major manufacturers (Solar Turbines, Ingersoll Rand, Honeywell, General Electric, Pratt & Whitney, Capstone-Microturbines, etc.) have had tens of thousands of service hours of experience with them. However, in spite of these numerous advantages, Si_3N_4 is not a "miracle material": it also has some drawbacks, especially difficult and expensive machining due to its hardness and its high electrical resistance ($\sim 10^{14}$ Ω.cm), a lack of long term reliability in severe environments, an insufficient level of fracture toughness to overcome the issue of foreign object damage (when used for engine parts), and sensitivity to corrosion in hot gas environments (H_2O in industrial gas turbines for example).

To increase the high-temperature properties of silicon nitride, several additives (SiC, TiN/TiC, BN, ZrO_2, $MoSi_2$, etc.) have been assessed to form new composite materials. Of these composites, Si_3N_4/SiC and $Si_3N_4/MoSi_2$ based ceramics seem to be the most promising. With the aim of enhancing engine performance (higher efficiency, weight reduction, pollution decrease, etc.), Onera carried out several studies on $Si_3N_4/MoSi_2$ materials. According to the literature, these composites could be used at temperatures considerably higher than those attainable with the currently used superalloys (T > 1200°C). This paper is an outline of the work which has been done on these materials in the Composite Materials and Structures Department.

Silicon nitride / molybdenum disilicide composites

According to previous studies, one way to improve the high temperature properties of Si_3N_4 is to combine this ceramic with $MoSi_2$ [23-26]. Of the non-oxide materials for high-temperature applications, this intermetallic is considered to be one of the most oxidation-resistant at high temperatures (T > 1400°C) [27-29]. This compound has a higher melting point (2030°C) and a lower density (6.2 g/cm^3) than the superalloys, and it also has high electrical and thermal conductivities. It exhibits a high toughness above its brittle-ductile transition at around 1000°C. However, due to its brittle nature at low temperatures, inadequate creep resistance above 1200°C, accelerated oxidation around 500°C (a phenomenon called "pest" oxidation [30,31]) and its relatively high CTE (about 8.5 10^{-6} K^{-1}), the use of $MoSi_2$ as a structural material is limited. Fortunately, as mentioned above, these issues may be offset by combining it with another compound as a composite material. This is the case for the $Si_3N_4/MoSi_2$ composites in particular.

Very interesting properties can be obtained with the synergy of both materials. The addition of about 50 vol.% of Si_3N_4 to $MoSi_2$ leads in particular to the elimination of its catastrophic pest failure (formation of a Si_2ON_2 protective scale), an increase in the mechanical resistance at room temperature (fracture toughness and compression strength) and high temperatures (creep resistance [25]) and decrease of the CTE [32]. On the other hand, the addition of $MoSi_2$ to Si_3N_4 yields better Si_3N_4 material properties: improved mechanical resistance and reliability at high temperatures [33], enhanced high temperature fracture toughness [34] and increased electrical conductivity to allow for electrical discharge machining (EDM) [35].

Processing

Commercially available Si_3N_4 and $MoSi_2$ powders (table 1) were used as precursors, particularly: Si_3N_4 grade M11 and $MoSi_2$ grade B from H.C. Starck. In order to obtain dense materials, several sintering additives were used in different amounts (MgO, $MgAl_2O_4$, Y_2O_3, Al_2O_3 and CeO_2). The preparation of the blends involved three successive stages. First, to reduce particle size distribution and promote intimate mixing, the mixtures were ball milled in a liquid for several hours using Si_3N_4 milling media in a high-density polyethylene tank. Then, rotary evaporation was used to dry the mixtures and minimize segregation. Lastly, the powder blends were sieved to avoid agglomeration.

Box 1 - Introduction to nitrides and silicon nitride

Nitrogen reacts with numerous elements to form many different compounds with a wide range of properties. However, the term nitride is only applied to compounds in which nitrogen is linked with elements of similar or lower electronegativity and has a formal oxidation state of -3 (N^{3-} ions). Furthermore, nitrides can be sub-divided into three general classes: ionic, interstitial and covalent nitrides. Ionic or "salt-like" nitrides are formed with the less electronegative elements, *i.e.* alkali metals, alkaline-earth metals and the metals of Group III of the periodic table, including the lanthanide and actinide series (Li_3N, Mg_3N_2, etc.). Interstitial nitrides formed with the transition metals make up the largest group of nitrides. In these compounds, nitrogen atoms occupy the interstices, or "holes", in the lattice of close-packed metal atoms. The general formulae of these nitrides are MN, M_2N, and M_4N, although their stoichiometries may vary (TiN, HfN, VN, W_2N, Zr_3N_4, etc.). As for covalent nitrides, they are formed with the most electronegative elements such as B, S, P, C and Si. They possess a relatively simple crystal structure and an atomic bonding which is less complex than the interstitial nitrides. Their bonding is mostly covalent by the sharing of electrons and is achieved by the hybridisation of the respective electron orbitals (BN, AlN, Si_3N_4, etc.) [57].

In the categories listed above, only some of the interstitial and covalent nitrides can be qualified as refractory materials (melting point > 1800°C and high chemical stability). This is the case for the nitrides of the early transition metal elements (Groups IV and V) and the covalent nitrides of boron, aluminium and silicon. The refractory nitrides are hard and wear-resistant with high melting points and good chemical resistance. They are important industrial materials and have a significant number of major applications in cutting and grinding tools, wear surfaces, semiconductors, and others.

Among the refractory nitrides, silicon nitride is one of the most interesting. It is also one of the most important non-oxide ceramic materials [58]. This compound has been intensively studied for many years because of its great potential for use in structural applications at room and high temperatures. Thus, many articles have been written about Si_3N_4 [59,60]. It is a hard ceramic with a low density (3.2 g/cm^3), high strength over a broad temperature range, moderate thermal conductivity, a low coefficient of thermal expansion ($\sim 3.10^{-6}$ °C^{-1}), a moderately high elastic modulus, and good fracture toughness for a ceramic. This combination of properties leads to excellent thermal shock resistance, the ability to withstand high structural loads at high temperatures, and superior wear resistance. Si_3N_4 is therefore mostly used in high-endurance and high-temperature applications such as gas turbines, car engine parts, bearings and metal working and cutting tools. Silicon nitride does not melt but dissociates into silicon and nitrogen (N_2 dissociation pressure reaches 1 bar at 1880°C). It exhibits three crystallographic modifications, α, β and γ. The α and β phases are the most common forms and can be produced under normal pressure conditions.

In industry, the most common sintering technology used for Si_3N_4 is gas-pressure sintering. However, several other methods exist to provide different types of materials: Reaction Bonded Silicon Nitride, Sintered RBSN, Sintered Silicon Nitride (pressureless), Hot-Pressed Silicon Nitride, Sinter HIP'ed Silicon Nitride, HIP'ed Silicon Nitride, etc. Moreover, there is a wide range of compositions and microstructures which are affordable depending on the raw materials, the densification technologies and the manufacturing cycles that are used. It is important to notice that the densification of Si_3N_4 is usually achieved through the acceleration of mass transport by the formation of a liquid phase during sintering [61]. Indeed, Si_3N_4 crystals exhibit a low self-diffusion coefficient due to the high energy of the covalent bonds. This liquid phase is an oxynitride liquid formed by the reaction of the sintering additives with the silica existing on the surface of the Si_3N_4 powder particles [62]. After sintering, the additives are located at the grain boundary and in particular in the triple junctions. The grain-boundary phase, which is an amorphous or partially crystallised phase, significantly influences the material properties.

Starting powder	Grade / supplier	Particle size (μm)	Phase	Purity (%)
Si_3N_4	M11 / H.C. Starck	0.54	α > 90 %	> 98
	SN-E10 / UBE	< 0.50	α > 95 %	> 98
$MoSi_2$	B / H.C. Starck	4.72	tetragonal	> 99
	Mo701 / AEE	$1 < d_{50} < 10$	tetragonal	> 99.8

Table 1 – Grade, size, crystallographic structure and purity of the starting powders

The second phase of the process involved sintering the previous powder blends. Three different methods were used: HP, pressureless sintering and HIP [36-40]. In fact, most of the materials were manufactured by HP, which is a standard process often used during development phases and when very limited numbers of parts are required. On the other hand, pressureless sintering in powder beds was chosen to manufacture complex shaped samples, and HIP to improve material microstructure and properties.

A resistance-heated furnace with graphite dies was used to sinter the blends by HP. After some improvements in the mixture compositions, the densification parameters selected were the following:

- Sintering temperature: $1550 \leq T \leq 1650$°C (depending on the amount and type of sintering additives)
- Dwell time at high temperature: t = 90 min
- Uniaxial pressure: P = 25 MPa
- Atmosphere: nitrogen at atmospheric pressure
- Graphite dies: 36 x 36 mm^2, 45 x 45 mm^2 or 6 samples of 50 x 5.2 mm^2 simultaneously

For pressureless sintered materials, powder blends were first pre-packed at 150 MPa by cold pressing and then machined or directly sintered in powder beds under nitrogen pressure (1550°C/90 min/ $P_{N2} \sim 1$ bar). Cold pressing at 150 MPa was also used to prepare the samples (ϕ = 20 mm, L = 30 mm) for HIP'ing in a tantalum can (1800°C/3 h/150 MPa) .

Composition	Sintering additives / weight %	Sintering method	Apparent density / g /cm³	Open porosity / %
50 vols.% Si_3N_4 M11/ 50 vol.% $MoSi_2B$	4 % Y_2O_3 + 3 % Al_2O_3	Pressureless	3.67	0.6
		HP	4.15	0.4
	1 % MgO	HP	4.15	0.6
	7 % Y_2O_3	HP	4.34	0.8
		HIP	4.44	0.4
	10 % CeO_2	HP	4.33	0.5
		HIP	4.51	0.1

Table 2 – Densification level of various $Si_3N_4/MoSi_2$ composites

Microstructure

The density of each material was assessed by the water impregnation method. According to the type and amount of additives and sintering methods used, different apparent density and open porosity values were measured (table 2). For most samples, high densification rates are obtained with open porosity level lower than 1 %. As expected, the lowest values are observed on pressureless sintered materials and the highest on the HIP'ed materials.

Various microstructures have been obtained and in general a fine microstructure with good homogeneity is observed (figure 12). The differences between the microstructures are due to both the type and the amount of sintering aids and to the process used. As already reported in the literature [41], no reaction occurred between $MoSi_2$ and Si_3N_4. In addition, despite the CTE mismatch ($\alpha_{MoSi2} \sim 9.10^{-6}$ °C^{-1} and $\alpha_{Si3N4} \sim 3.10^{-6}$ °C^{-1}), there is good adhesion between the two compounds.

It is important to notice that for HP'ed or pressureless sintered materials, the $Si_3N_4/MoSi_2$ volume ratio is sometimes modified by reactions of $MoSi_2$ with the furnace atmosphere (nitrogen). This is of course avoided when sintering occurs in sealed containers (HIP) or under inert gas (argon). Furthermore, for the composites HIP'ed at 1800°C, the growth of acicular β-Si_3N_4 grains is promoted [42,43]; these grains induce crack deflection, so this type of microstructure is often desirable in order to increase the fracture toughness [44].

Materials properties

Machinability

Materials with hard and brittle compounds often involve machining difficulties and high costs. For the materials processed at Onera, thanks to the low electrical resistivity of $MoSi_2$ ($\sim 10^{-2}$ Ω.cm), the use of EDM seems perfectly possible [35]. Indeed, with 50 vol.% of the conductive phase, the threshold of percolation is easily reached. However, in our work, EDM was successful only with the HIP'ed materials in which the $Si_3N_4/MoSi_2$ volume ratio was retained (figure 13). A similar machinability would be obtained on materials sintered by hot pressing under argon in which the volume ratio is also preserved. This good conductivity level is an important advantage compared with basic Si_3N_4 and has allowed for the development of $Si_3N_4/MoSi_2$ ceramic glow plugs for diesel engines [26].

Mechanical performance

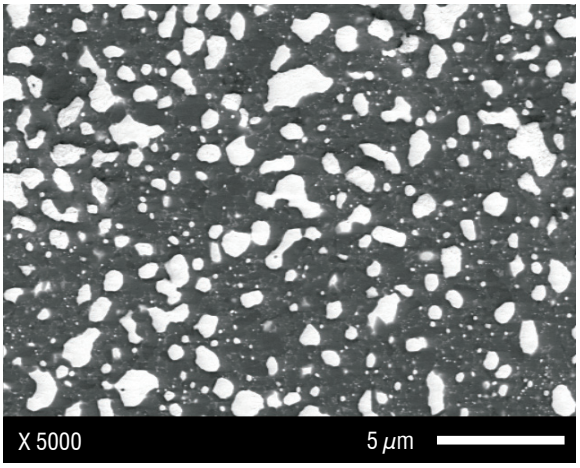
Hardness and fracture toughness

Vickers hardness (HV) and toughness (K_{1c}) have been evaluated at room temperature by Vickers indentation (with a load P = 30 kgf ~ 294 N). The hardness is determined by measuring the surface area A of the indentation mark. The fracture toughness is estimated by using the radial crack pattern formed around the indentation mark [45,46]:

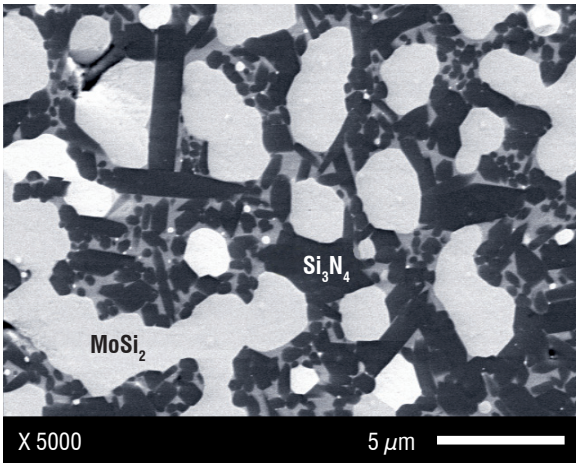
$$HV = \frac{P}{A} = 0.001854 \times \frac{P}{d^2} \quad (1)$$

$$K_{1C} = 0.8854 \times (a \times HV \times E)^{1/2} \times \left(\frac{c}{a}\right)^{-3/2} \quad (2)$$

with HV the hardness (GPa), P the load (N), K_{1c} the toughness (MPa.m$^{1/2}$), $a = d/2$ with d the average diagonal indentation mark length (mm), E the Young's modulus (GPa) and c the crack length from the centre of the indent to the crack tip (mm). Depending on the sintering process and the additives used, different property levels have been recorded (table 3).



$Si_3N_4/MoSi_2$ with 4% Y_2O_3 + 3% Al_2O_3 (HP'ed)



$Si_3N_4/MoSi_2$ with 7% Y_2O_3 (HP'ed)

Figure 12 – Microstructure of two types of $Si_3N_4/MoSi_2$ composites (SEM observations). The phases are $MoSi_2$ (white), Si_3N_4 (black) and the grain-boundary-phase (intermediate grey level)

Composition	Sintering additives / weight %	Sintering method	HV / GPa	K_{1c} / MPa.m$^{1/2}$
50 vol.% Si_3N_4 M11 / 50 vol.% $MoSi_2$ B	4 % Y_2O_3 + 3 % Al_2O_3	HP	15.4 ± 0.4	2.5 ± 0.1
	7 % Y_2O_3	HIP	13.4 ± 0.3	5.2 ± 0.4
	10 % CeO_2	HIP	12.9 ± 0.3	5.1 ± 0.7

Table 3 – Hardness and toughness of Si_3N_4/$MoSi_2$ composites (using E ~ 240 GPa; this low value is used to avoid overestimating the fracture toughness performance of the composites)

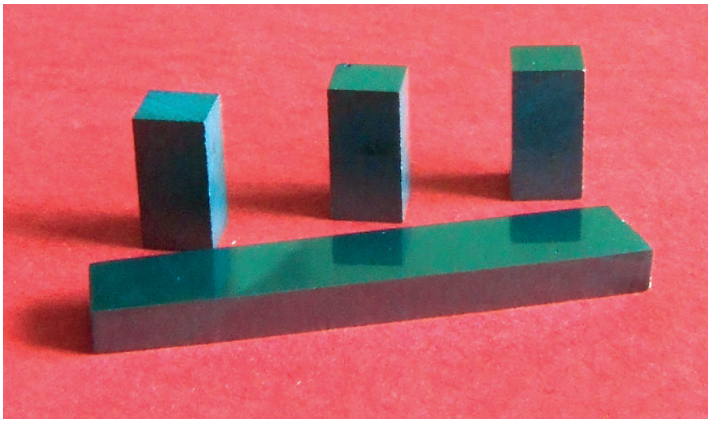


Figure 13 – Pictures of several EDM machined samples after finishing (HIP Si_3N_4/$MoSi_2$ with 10 wt.% CeO_2)

The Vickers hardness is in good agreement with the values found in the literature on similar materials [44]. Table 3 shows that a significant improvement in fracture toughness is possible when adequate processing methods and sintering additives are used; here HIP'ing has led to the in-situ growth of acicular β-Si_3N_4 grains and thus to increased toughness. For these non-optimised materials (composition, processing cycle, etc.), the room temperature toughness levels achieved are remarkable. Due to the presence of $MoSi_2$, they will even increase with temperature as reported in the literature (K_{1c} = 5 MPa.m$^{1/2}$ at 20°C, 7 at 1000°C and 9 at 1200°C) [34].

Several other solutions have also been assessed to form specific β-Si_3N_4 grains containing microstructures to enhance the toughness of Si_3N_4/$MoSi_2$ composites, such as the introduction of β-Si_3N_4 seeds and various SiC reinforcements (Hi-Nicalon fibers, from Nippon Carbon, with or without BN/SiC CVD coating; Sylramic fibers, from Dow Corning; SA3 fibers, from UBE; SiC platelets, from Millenium Materials Inc., Tokawhiskers, from Tokai Carbon, etc.), but with little success.

Flexural strength

The flexural properties of several composites have been studied by using three-point bending tests from room temperature to 1100°C (in air at atmospheric pressure), yielding values for the flexural stress (σ_f) and the modulus of elasticity in bending (E_f). The specimens, three for each condition, have been tested with a crosshead speed of 0.005 mm.s^{-1} and a span length of 30 or 38 mm. In table 4, very satisfactory results are shown for a HP'ed Si_3N_4/$MoSi_2$/4 wt.% Y_2O_3/3 wt.% Al_2O_3 composite. It is important to notice that at high temperatures the values of the apparent Young's modulus are not really relevant (E_f are manifestly reduced by plasticity).

A high flexural strength is still obtained at 1100°C (σ_f > 500 MPa). This temperature is above the brittle-ductile transition temperature of $MoSi_2$ so a decrease in the properties is expected as grain boundary sliding and plastic deformation of $MoSi_2$ particles begin to operate [47,48]. These mechanisms also explain the observed increase in the flexural strain (ε_f = 0.6 % at 1100°C instead of 0.3 % at room temperature).

Creep

Compression creep tests have been conducted in air between 1300 and 1400°C for stresses in the range 50 – 200 MPa on Si_3N_4-$MoSi_2$ HIP'ed composites with Y_2O_3 or CeO_2 additives (sample dimensions: 3 x 3 x 6 mm^3). During the tests, the load was increased in steps after the minimum creep rate was observed at each load. The total strain for each specimen was limited to 10%. The detailed test method was previously reported [49].

The composite containing 10 wt.% CeO_2 was tested at 1300 and 1350°C and the one with 7 wt.% Y_2O_3 at 1300 and 1400°C. For both materials and each temperature selected, the creep rates as a function of stress are shown in figure 14. In addition, in order to compare the previous materials with the literature results, two curves for a HP'ed Si_3N_4-$MoSi_2$ composite with 1 wt.% MgO have been added [50].

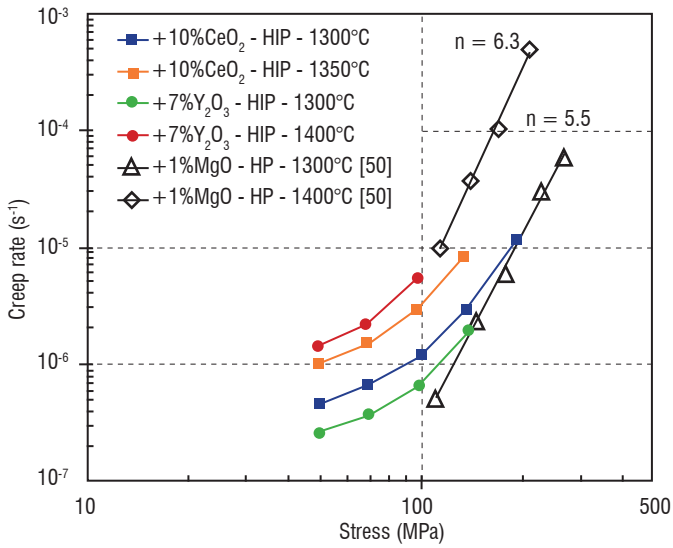


Figure 14 – Stationary creep rate versus stress for various Si_3N_4-$MoSi_2$ composites in the range 1300-1400°C

Composition	Property	Test temperature 20°C	900°C	1100°C
50 vol.% Si_3N_4 M11 / 50 vol.% $MoSi_2$ B + 4 % Y_2O_3 + 3 % Al_2O_3	σ_f (MPa)	910 ± 135	620 ± 80	510 ± 118
	E_f (GPa)	200 ± 5	150 ± 5	100 ± 5

Table 4 – Three-point flexural strength (σ_f) and modulus of elasticity in bending (E_f)

These results indicate that the addition of Y_2O_3 leads to lower creep rates than for CeO_2. In addition, contrary to what is observed on HP'ed materials, the stress exponents (n) recorded on both HIP'ed composites vary with the applied stress. For the latter, n can increase from 1.01 (at lower stresses) to 3.94 (at higher stresses). In the reference materials, the creep rate is controlled by dislocation creep mechanisms (glide and climb). In comparison, in the HIP'ed composites, for the stress and temperature ranges studied, the creep rates are certainly controlled by a combination of several mechanisms: grain boundary sliding, diffusional creep and dislocation creep mechanisms. However, at higher stress, creep behaviours close to that observed on the reference materials (with constant stress exponent $n \sim 5 - 6$) will probably be found.

It is important to point out that the amount of sintering additive in the HIP'ed materials has not yet been optimised (~ 6 vol.% of the Si_3N_4-$MoSi_2$ blend) and that it could certainly be possible to enhance the creep resistance of these composites by reducing the fraction of additive.

Oxidation and thermal shock resistance

$MoSi_2$ based materials can disintegrate rapidly during oxidation at temperatures around 500°C ("pest" phenomenon) [30,31]: the oxidation of polycrystalline $MoSi_2$ leads to the formation of solid MoO_3 and SiO_2 with a substantial volume expansion due to MoO_3 whiskers (or platelets). This results in a mass gain and also in internal tensile stresses which destroy intergranular cohesion:

$$2\ MoSi_2\ (s) + 7\ O_2\ (g) \rightarrow 2\ MoO_3\ (s) + 4\ SiO_2\ (s) \qquad (T < 800°C)$$

Above approximately 800°C, crystalline MoO_3 (melting point: 801°C) evaporates significantly (a mass loss is recorded) and the oxidation is controlled by diffusion of oxygen through the SiO_2 layer [51].
At higher temperatures (900-1100°C), Mo_5Si_3 is formed and then consumed by further oxidation to form SiO_2 and MoO_3 (g):

$$5\ MoSi_2\ (s) + 7\ O_2\ (g) \rightarrow Mo_5Si_3\ (s) + 7\ SiO_2\ (s) \qquad (T > 800°C)$$

$$Mo_5Si_3\ (s) + 10.5\ O_2\ (g) \rightarrow 5\ MoO_3\ (g) + 3\ SiO_2\ (s) \qquad (T > 800°C)$$

However, the SiO_2 layer is a good barrier to oxidation attack because of a low oxygen permeation rate. $MoSi_2$ is hence known to exhibit excellent high temperature oxidation behaviour up to 1600°C.

In this project, the thermal shock behaviour and the long-term resistance under oxidative atmospheres were assessed at 500°C and 900°C under static air at atmospheric pressure for cumulative times of up to 400 h. The latter temperature was chosen for the MoO_3 volatilisation regime.

The oxidation rate was estimated by monitoring the material mass variations versus time and the thermal shock resistance by several quick insertions into and withdrawals of the samples from the furnace.

For each material, more than nine insertion/withdrawal cycles (i.e. at least 18 thermal shocks) were achieved with no problems: all of the samples maintained their integrity and no cracks appeared. As expected, all of the compositions exhibited good thermal shock resistance in the tested conditions.

With regard to the oxidation behaviour, the material mass variations recorded on three different HP'ed composites were reported in table 5 (sample dimensions: ~ 5 x 2 x 20 mm^3). These values are maximum absolute mass variations after 400 h of cumulative treatment.

Regardless of the type of material and the test temperature, the total mass variations are very low ($\Delta M/M < 0.1\%$), showing that the selected materials exhibit good oxidation resistance in the tested conditions, with no "pest" oxidation. This is due firstly to the good densification of the materials (no cracks or pores in the samples) and secondly to the formation of a protective layer.

Outlook

Following up on the previous work, new studies involving the Si_3N_4-$MoSi_2$ composites are included in the HYSOP project [22] to evaluate the potential of applying Si_3N_4-$MoSi_2$ composites in aeronautical turbines (blades, vanes and seal segments). The final objectives are to increase the temperature capability of the turbine materials and to reduce the overall mass of the aircraft in order to reduce fuel consumption and emissions, and help to reduce aircraft operation costs. The Si_3N_4-$MoSi_2$ composite composition will be optimised (nature and quantity of sintering additives, etc.) and advanced processes to manufacture materials with adequate microstructures and properties will be developed (pressureless sintering, Spark Plasma Sintering, HIP). It has already been shown that recent sintering methods (SPS in particular) [52,53] can enhance the mechanical properties of silicon nitride based materials (Si_3N_4 or Si_3N_4/TiN for example). The materials will be characterised (physical, chemical, thermal and mechanical properties, oxidation/corrosion resistance, machinability, etc.) and shaped demonstrators will be manufactured.

It has been demonstrated that one of the major issues for silicon nitride based materials in gas turbines is corrosion resistance [54,55]. Water vapour in particular reacts with the protective silica scale, forming gaseous reaction products such as $Si(OH)_4$. In high pressure and high gas velocity combustion environments, this reaction results in recession of Si_3N_4 based materials. Furthermore, at high temperatures (~1300°C), aggressive deposits such as CMAS (Calcium Magnesium Aluminium Silicate glass) further degrade these materials. Thus,

Composition	Sintering additives / weight %	Sintering method	Absolute weight variation	
			at 500°C	at 900°C
50 vol.% Si_3N_4 M11 / 50 vol.% $MoSi_2$ B	1 % MgO	HP	0.04 %	0.09 %
	4 % $MgAl_2O_4$	HP	0.01 %	0.03 %
	4 % Y_2O_3 + 3 % Al_2O_3	HP	0.06 %	0.05 %

Table 5 – Material mass variations after oxidative treatments under static air, for 400 h

specific investigations will be carried out in order to estimate and reduce these phenomena and protective coatings may be used to fulfil the requirements [56].

Conclusion

The development of new gas turbine hot section materials with increased high temperature capabilities is crucial for the design of future efficient turbines with low CO_2 and NO_x emission levels. Refractory metal silicide based materials and Si_3N_4-$MoSi_2$ composites are promising candidates for such applications.

Extensive work in the United States, Europe and the Far East has led to remarkable improvements in both Mo-Si-B and Nb-Si based materials. Over the past decade, the reduction of engine mass has become as important a factor as extended temperature capability, and it is expected that this will be easily achieved. Nb-Si materials are preferred, although specific attractive mechanical properties can be obtained with Mo-Si-B materials. PM processing is a promising approach that not only allows for refined and controlled microstructures but also considerably alleviates the Si-content limitations encountered in ingot metallurgy (high temperature required for melting, cracking of the silicide dendrites, etc.).

The main tasks that are still to be carried out to ensure the introduction of these silicide based materials into future turbine engines include composition optimisation for simultaneously enhanced mechanical properties and oxidation/corrosion resistance for long service duration, improvement of available protective coatings, control of the microstructure and the implementing of a cost effective industrial manufacturing route.

Silicon nitride based materials have already found applications in small size stationary gas turbines, but their use in turbine engines still requires developments in terms of both mechanical properties and oxidation resistance. The key issues for Si_3N_4-$MoSi_2$ composites are composition optimisation, especially the nature and amount of the sintering aids which have to be kept as low as possible to improve high temperature mechanical properties, control of the microstructure (beneficial effect of the β-Si_3N_4 phase), the reduction of porosity, all in close connection with the manufacturing processes ■

Acknowledgements

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Acronyms

RM (Refractory Metal)
ULTMAT("ULtra high Temperature MAterials for Turbines" project)
PM (Powder Metallurgy)
HIP (Hot Isostatic Pressing)
MASC (Metal And Silicide Composite)
CTE (Coefficient of Thermal Expansion)
HP (Hot uniaxial Pressing)
SPS (Spark Plasma Sintering)
HYSOP ("Hybrid Silicide-Based Lightweight Components for Turbine and Energy Applications" project)
EBC (Environmental Barrier Coatings)
SEM (Scanning Electron Microscopy)
EDM (Electrical Discharge Machining)
CMAS (Calcium Magnesium Aluminium Silicate Glass)
RBSN (Reaction Bonded Silicon Nitride)

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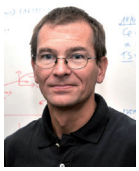

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