THE EU-FUNDED “ ULTMAT ” PROJECT: ULTRA HIGH TEMPERATURE MATERIALS FOR TURBINES

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Abstract

The ULTMAT project (started in January 2004 for a duration of 48 months), aims at providing sound technological basis for the introduction of Mo- and Nb-base silicide multiphase alloys, with enhanced high temperature capabilities (up to 1300°C) for applications in aero-engine turbines. The development status of new alloys is presented, focusing on creep and oxidation properties.

1 Introduction

The performances of aircraft and land-based gas turbines engines are evaluated using both technical and sociological metrics. Thus not only technical needs are considered but the economic and environmental issues are addressed, from which the most important are:

- overall power or thrust;
- specific thrust, *i.e.* thrust-to-weight ratio (for aero-engines);
- fuel efficiency, *i.e.* specific fuel consumption (SFC);
- service reliability, *i.e.* the time between outages for turbines, or the time-on-wing for engines;
- emission of CO_2, NO_x and other species (soot, unburnt fuel, CO…);
- external noise emission;
- cost (both installed and of ownership).

Corresponding medium term (year 2010) and long-term (year 2020) [1] goals have been adopted as objectives for the “Aeronautics and Space” thematic priority within the European 6th Framework Programme.

These issues have been continuously addressed by advanced engine architectures and cycle designs, novel combustor designs, optimised aerodynamics and new cooling concepts. But *hot section materials development* (especially for turbine section) 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.

A substantial increase of the *turbine airfoil materials* temperature capability would permit significant performance enhancements. High temperature materials represent one major enablers in the long-term for most, if not all, future engine improvements (Table 1).

Combustor temperature:	+200 K
Compressor exit temperature:	+50 K
Cooling air flow:	-20%
Efficiencies:	+1.5% polytropic
Specific weight:	-20%

Table 1. Technology enablers for an engine with a SFC reduced by 15-20% (goal for 2020) [1].

In this context, the ULTMAT project aims at providing sound technological basis for the introduction of innovative materials, namely Mo- and Nb-base silicide multiphase alloys, which will allow a significant increase (*ca.* 150°C) in airfoil material operating temperature in aircraft/rotorcraft engines over those possible with Ni-base single-crystal superalloys. The increased temperature capability will allow reduction of specific fuel consumption, CO_2 emissions and cooling air requirement, which will lead to a further increase in efficiency and reduction in component weight. Similar gains are anticipated for others applications, such as for aero-derivative land-based gas turbines.

- ONERA (project coordinator)
- Avio S.p.A.
- Electricité de France
- IRC in Materials (University of Birmingham)
- PLANSEE SE - Division High Performance Materials
- Rolls-Royce plc
- Snecma
- Turboméca
- University of Magdeburg
- University of Nancy
- University of Surrey
- Walter Engines a.s.

Table 2. List of the ULTMAT partners.

The consortium (Table 2) has been built up to bring together highly skilled companies, universities and research institutes involved in research and development of high temperature materials for turbine engines.

This paper presents some results obtained at project mid-term, focusing on alloy development for improved high temperature creep and oxidation resistance, but also on alloy processing and fabrication.

2 Alloy systems

Refractory metals (RM) are currently used as components for ultra-high temperature applications in inert atmosphere, taking advantage of their outstanding intrinsic properties (high melting point, very good mechanical and creep strength), making them first choice replacements for Ni-base superalloys in gas turbine engines. However, RM and RM-alloys suffer from severe oxidation problems in air. The sublimation of the oxide occurs already at intermediate temperatures (> 500°C) which excludes any applications at higher temperatures.

By contrast, RM-silicides can be used in air at higher temperature and even (*e.g.* $MoSi_2$, Superkanthal® as well as silicide coatings) up to temperatures of 1650°C in furnace construction or glass industry [2]. But these compounds also suffer from catastrophic oxidation at intermediate temperatures between typically 600°C and 800°C (pesting, see *e.g.* [3] for a recent overview) and exhibit brittleness at ambient [4,5] as well as, for some of them, poor creep strength at elevated temperatures [6].

However, it is the essential objective of future research on RM silicide alloys to manufacture a composite material that takes advantage of *(a)* the beneficial oxidation resistance of the silicides and *(b)* the outstanding mechanical properties of the RM.

RM based metal-intermetallic composites have been developed under US impetus in the 1990's. Two systems show the greatest potential [7], Nb-Si and Mo-Si, as metal-toughened intermetallic-strengthened materials with volume fraction of metallic phase between 35% and 60%. Melting points of these multiphase alloys are in excess of 1750°C (Nb-base) and 1950°C (Mo-base), respectively, being substantially higher than those of Ni-base superalloys.

Both systems are studied within the ULTMAT project. In a first screening step, alloy development focused on the simultaneous improvement of three key properties, namely the high temperature creep strength and oxidation resistance, and the room temperature toughness, to reduce the amount (together with duration and cost) of extensive characterisations. These are planned in a second step on a selection of alloys showing the best compromise in the above mentioned properties.

2.1 Mo-base silicides

Nowotny *et al.* [8] first pointed out that alloys in the ternary system Mo–Si–B might be able to fulfill the above requirements. Berczik [9] followed up this work and patented alloy compositions in the Mo-rich corner (Fig. 1) and a manufacturing route which in essence comprises a rapid solidification step.

A typical microstructure yields a matrix of Mo(ss) solid solution providing good fracture toughness and ductility at temperatures below 600°C and embedded intermetallic compounds of type Mo_3Si and/or Mo_5SiB_2 (T2 phase) for

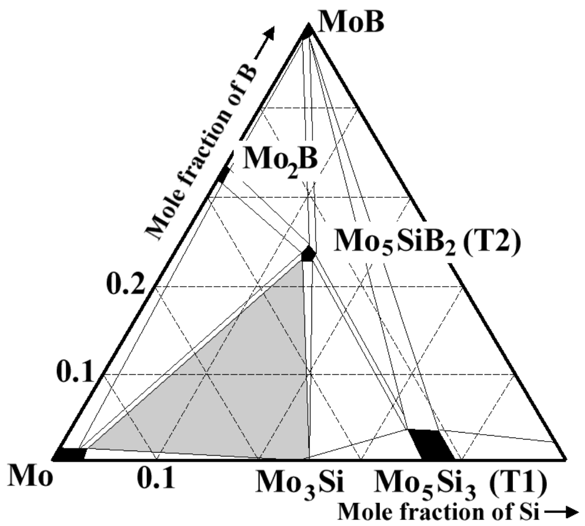


Fig. 1. Mo-rich part of the isotherm section at 1600°C of the Mo-Si-B phase diagram (after [8]). The shaded area is the Mo-T2-Mo_3Si three phase region.

enhancing the creep resistance as well as for providing a silicon and boron reservoir for the formation of a dense borosilicate glass layer on the metal surface. If the latter was formed on the surface at higher temperatures, it suppresses the pesting phenomenon at intermediate temperatures [3].

The alloys studied in the project are basically three-phase Mo-9Si-8B alloy (with addition of alloying elements such as Nb in order to strengthen the solid solution) with volume fractions of about 55% Mo(ss), 30% T2 and 15% Mo_3Si [10].

2.2 Nb-base silicides

Alloys in the binary Nb-Si system exhibit excellent creep resistance, although poor toughness and oxidation resistance. But these last properties can be improved by alloying, leading *e.g.* to the NbTiHfCrAlSi metal and silicide composites (MASC) family developed by General Electric [11,12].

The Nb-base materials consist of a metal solid solution M(ss) (M being *e.g.* Nb+Ti+Hf+ ...) with M_5Si_3 (α or β) and/or M_3Si silicide phases (Fig. 2). Other phases, such as $NbCr_2$–type Laves phases in case of higher Cr contents for better oxidation resistance or hexagonal M_5Si_3 (deleterious for creep resistance) in case of high Ti and/or Hf contents, can also be present.

At high temperature, M(ss) can be considered as the softest phase 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 the soft phase (M(ss)) and/or increasing the silicide volume fraction, the latter by means of increasing the silicon content in the alloy. Higher silicide contents simultaneous improve the oxidation resistance, but decrease toughness and ductility at low and intermediate temperatures. Actually, alloys with silicon content in a wide range have been studied in this project.

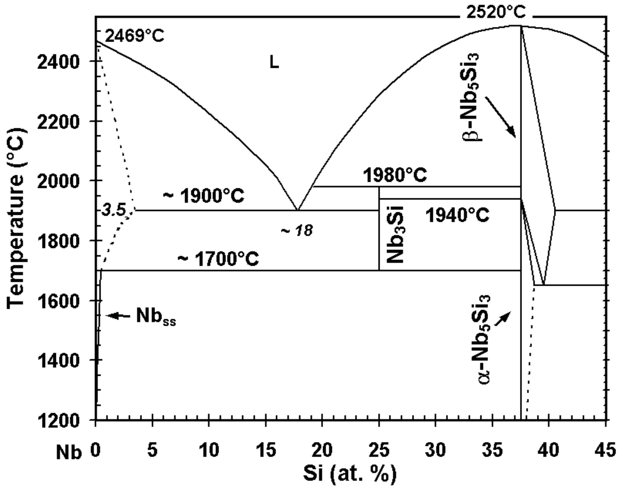


Fig. 2. Nb-rich part of the binary Nb-Si phase diagram (after [13]).

3 Manufacturing

Two processing routes, ingot metallurgy (IM) and powder metallurgy (PM), have been selected at the beginning of the project in order to compare various types of microstructures. Further, for the most adequate route, the possibility of production at industrial scale should be assessed.

3.1 Ingot metallurgy

Vacuum arc melting is mainly used to manufacture small size buttons (up to 500 g) needed to perform the microstructural, mechanical and oxidation characterisations.

Bigger alloy batches, up to 50 kg, are manufactured by plasma melting, after some optimisation of the operating conditions because of the very high melting points of the starting materials, thus enabling a second set of more extensive characterisations.

Manufacturing of shaped parts is the next hurdle to overcome, if the alloys are to go to industrial applications.

Investment casting is the process currently used for production of nickel-base superalloy blades and vanes: it is thus tempting, and encouraging results have already been obtained on similar materials [12], to investigate its ability to be extrapolated to silicide based materials that exhibit melting temperatures higher by several hundreds of degrees.

The main issue is to select a mould composition that can withstand both the high temperature level and the aggressive chemical contact with the melt for relatively long times. First trials to cast cylinders of diameter ranging from 10 to 30 mm have been performed on Nb-base silicide materials, confirming that specific solutions had to be found. Fig. 3 shows that the level of chemical interactions between the melt (and/or the solidified alloy) and the mould is significant, and increases with increasing bar diameter, *i.e.* with decreasing cooling rates and increasing mould/melt contact durations at high temperature.

Further work on casting conditions has led to the successful casting of a cluster of five

Fig. 3. Investment cast Nb-base silicide bars (diameter: 10 to 30 mm) showing the chemical interaction between mould and melt.

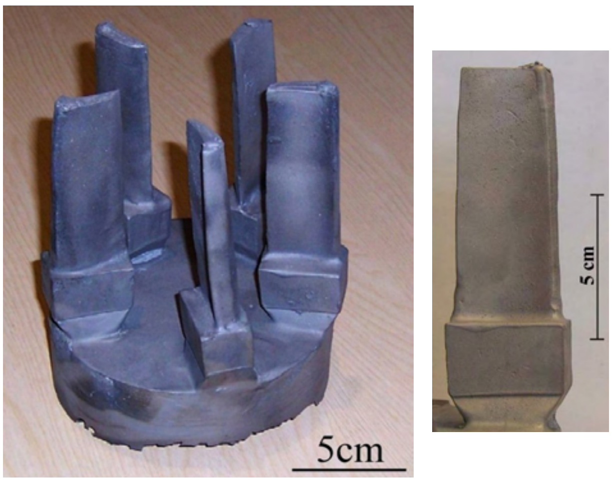


Fig. 4. Investment cast Nb-base silicide blade cluster (left) and blade (right).

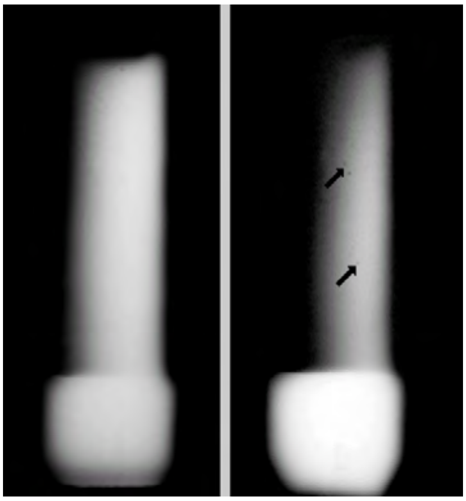


Fig. 5. X-ray radiographs with different exposure time of the same blade, showing reduced casting defect level (pores are shown by arrows).

blades (Fig. 4) exhibiting a very low level of casting defects (Fig. 5) that is expected to be further reduced in the next months.

3.2 Powder metallurgy

According to Fig. 1, processing Mo-rich Mo-Si based alloys with the liquid phase as starting point leads to primary solidification of the Mo(ss) phase surrounded by a network of eutectic Mo + intermetallic compounds phase mixture. The resulting microstructure appears to be brittle up to high temperatures (ductile-to-brittle transition temperatures, DBTT, as high as 1100°C have been reported [14]).

It has been suggested to apply a rapid solidification step, like gas-atomisation, instead of conventional cast metallurgy to end up with a (single-phase) supersaturated molybdenum solid solution which can be properly heat-treated to precipitate the intermetallic phases homogeneously within the metallic matrix [9]. But during argon atomisation sufficiently high quenching rates could not be achieved to produce powders exhibiting complete supersaturation [15].

A typical microstructure, obtained by scanning electron microscopy (SEM), of a ternary Mo-Si-B alloy manufactured by hot isostatically pressing (HIP) gas-atomised powders is shown in Fig. 6.

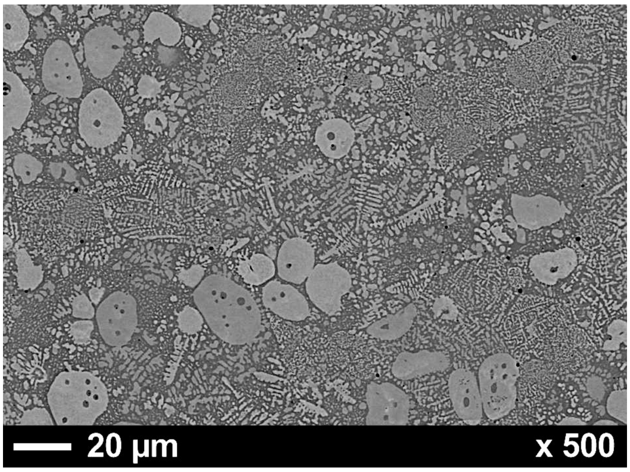


Fig. 6. SEM micrograph in backscattered electrons imaging mode (BSE) of the gas-atomised and HIP'ed Mo-Si-B alloy with Mo(ss) (bright), intermetallics (grey) and silica (dark).

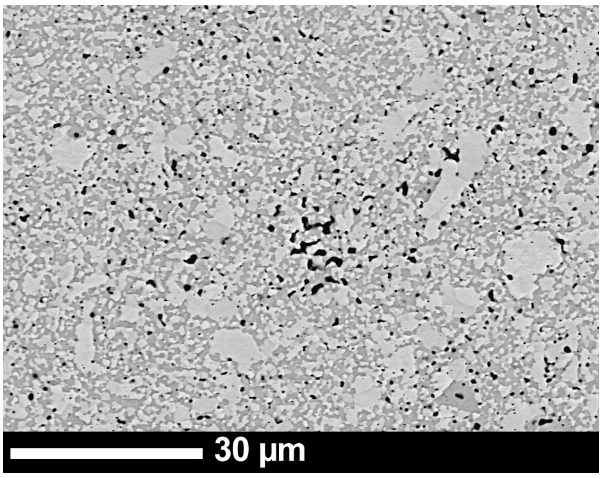


Fig. 7. SEM micrograph (BSE mode) of the MA processed and HIP'ed MoNbSiB alloy with Mo(ss) (bright), intermetallics (grey) and undesired silica (black).

Mechanical alloying (MA) is an alternative technique to produce supersaturated phases or even amorphous phases. This has been applied to a Mo-2.7%Nb-8.9%Si-7.7%B (in at.%) alloy, Nb being added to solid-solution strengthen the Mo matrix [10]. MA in a vertical attritor during 10 h (15 kg batches, under H_2 atmosphere) is sufficient to completely dissolve Nb, Si and B in the Mo matrix, as shown by X-ray diffraction analysis (XRD). The powder was subsequently cold isostatically pressed at 200 MPa and sintered under H_2 at 1450°C. Finally, billets with 50 mm diameter and 200 mm length were obtained by hot isostatically pressing (HIP) the sintered bars at 1500°C under 200 MPa. The microstructure in the HIP'ed state in shown in Fig. 7. The expected phases Mo(ss), Mo_3Si and T2 are present, as proved by XRD, and the residual porosity is below 1%. Because of a relatively high oxygen content (3000 µg/g), some undesired glassy silica inclusions are also visible, the powder handling, at that time, having not been carried out completely under protective atmosphere. Also, some larger-scale areas of Mo(ss) are present which may be due to residual inhomogeneities stemming from the non-optimised MA process.

The average grain size of both Mo(ss) and intermetallics is about 0.8 µm. This ultrafine grained and equiaxed microstructure exhibits superplastic behaviour: Fig. 8 shows that a tensile strain to failure of $\varepsilon_f \approx 400\%$ is obtained at 1400°C for a strain rate ($\dot{\varepsilon}$) of 10^{-4} s^{-1}.

Similarly, at a lower temperature of 1300°C, one obtains $\varepsilon_f \approx 300\%$ at $\dot{\varepsilon} = 10^{-4}$ s^{-1}. This demonstrates the potential for superplastic forming. At present, applicable forming processes appear limited to lower deformation rates ($\dot{\varepsilon} < 0.1$ 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. Generally, the enhanced ductility of the MA processed ultra-fine grained material should favour a defect-free forming of this alloy on conventional refractory metal production facilities.

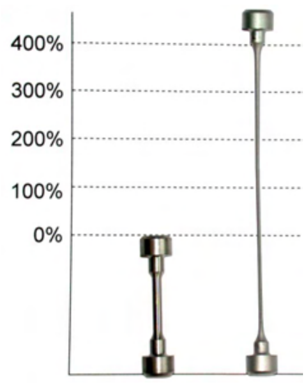


Fig. 8. Comparison of undeformed (left) and deformed (right; 1400°C and 10^{-4} s^{-1}) HIP'ed MoNbSiB tensile sample.

4 Mechanical properties

4.1 Strength

Tensile tests were performed on Mo-Si-B alloys under vacuum at temperatures ranging from room temperature (RT) to 1600°C, and at an initial strain rate of $1.1 \cdot 10^{-4}$ s^{-1}. Three button-head type specimens with 15 mm gage length and 3 mm diameter were tested for each temperature. The data presented in Fig. 9 are the mean values of reproducible measurements with the scatter being within symbol size. 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. Together with the absence of ductility the ultimate tensile strength (UTS) remained at a level close to 500 MPa in the temperature range between RT and 1100°C. Inspection of these samples after testing revealed premature brittle failure within the elastic domain. Crack growth occurred through the continuous network of intermetallics. The presence of significant plasticity at temperatures above 1100°C, however, indicates a substantial potential for the application of hot deformation processes such as extrusion, rolling and forging and for component manufacturing.

4.2 Creep resistance

The creep behaviour is evaluated by compression tests at constant load, in temperatures and

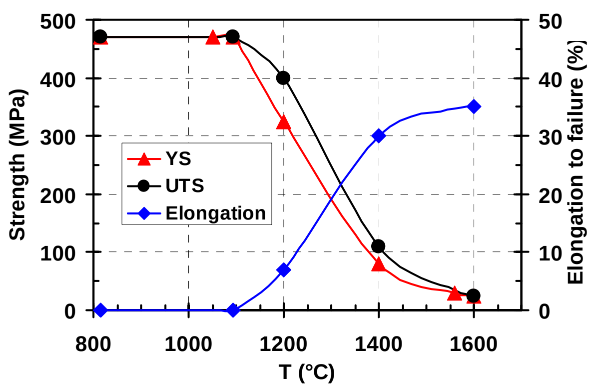


Fig. 9. Dependence of yield strength (YS), UTS, and fracture elongation on temperature of the HIPed Mo-Si-B alloy.

stress ranges of 1050°C to 1315°C and 100 MPa to 400 MPa, respectively. Specimens with dimensions 3 mm x 3 mm x 6 mm were cut and polished on both compression sides. This compression set-up and specimen geometry should ensure a good estimation of the creep law [16]. An electromechanical INSTRON 8562 testing device was equipped with a uniquely designed high temperature furnace, including a laser extensometer for continuous monitoring of creep strain by measuring the displacement of the compression punches, which enables testing under argon atmosphere or low vacuum (< 1 Pa). In order to save specimens and time, the creep tests were carried out under step-wise increase of stress after a steady-state was attained. The holding time at each stress level is adjusted so that steady-state is reached but total strain remains low enough to consider that the cross-section increase is negligible and, in consequence, the constant load test proceeds at constant stress.

A typical creep curve for a Nb-base silicide alloy for a test performed with a 200-300-400-200 MPa stress sequence is represented in Fig. 10: it shows that *(i)* steady state is obtained at all stress levels and *(ii)* the two 200 MPa stress levels give similar creep rates. The accuracy of this type of results is taken as sufficient to allow a reliable screening of alloy compositions and microstructures for both alloy systems.

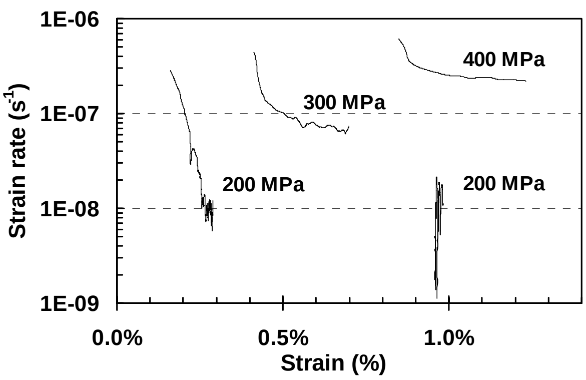


Fig. 10. Compressive creep curve in true strain rate vs. true strain representation indicating steady-state creep (i.e. constant creep rate) of a Nb-base silicide alloy at 1200°C (total test duration: 45 h).

The presence, in HIP'ed Mo-Si-B alloys as shown above, of significant plasticity above 1100°C, if it shows an ability for further hot deformation processing, indicates a poor creep resistance. However, coarsening of the microstructure by an appropriate heat treatment significantly improves the creep behaviour, as exemplified in Fig. 11 [10]. Annealing at 1700°C for 10 hours in vacuum increased the grain size of Mo(ss) and intermetallic from less than 1 µm (in the HIP'ed state) to more than 5 µm. The consequence is a decrease of the compressive creep rate by one order of magnitude at all tested temperatures. The stress exponent remained at a quite low value of 2.3 (given by the slope of the creep rate *vs.* stress curve in bi-logarithmic representation), indicating that grain and interphase boundary sliding processes still play a major role in plastic deformation.

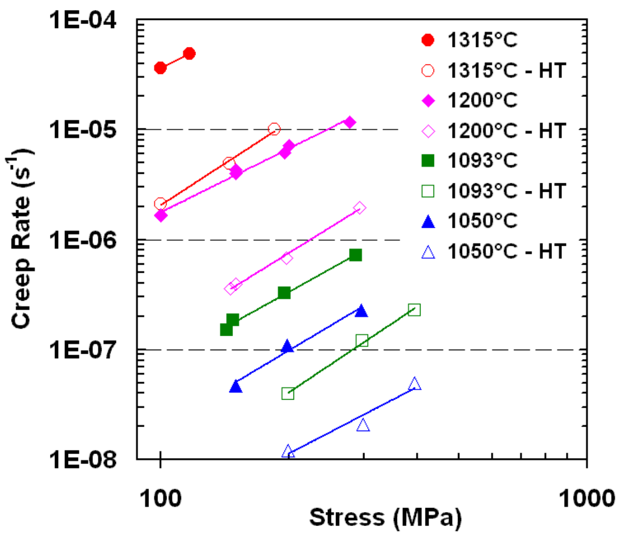


Fig. 11. Steady-state creep rate vs. stress for the HIP'ed (full symbols) and heat-treated (1700°C, 10 h; open symbols) MoNbSiB alloy for temperatures between 1050°C and 1315°C.

5 Oxidation resistance

The oxidation tests are performed in the temperature range 700°C-1300°C in cyclic and isothermal conditions. Two particular temperatures allow characterisation of the oxidation performances of the composite silicide alloys mainly concerning cyclic conditions: 815°C for the pest resistance, and 1100°C for determining the protection capability of SiO_2/B_2O_3 protective oxide layers.

Two examples will illustrate the ongoing activities:

- the influence of Al content in a NbTiHfCrAlSi IM-processed alloy;
- the efficiency of two silicide coatings deposited on a Mo-based silicide PM-processed alloy.

5.1 Alloy oxidation resistance

As shown in Fig. 12, increasing the Al content of the Nb-base silicide alloy increases the resistance to cyclic oxidation at 815°C. At this intermediate temperature, the degradation of pure Nb is known to be pesting, *i.e.* rapid disintegration of the specimen into pieces or powders. For Nb-base silicide alloys with low Al contents (2 and 4 at.%), pesting is still observed but starts after longer times (about 30 to 50 one-hour cycles). The oxide layer formed is mainly constituted with Nb_2O_5, TiO_2 and $CrNbO_4$, as identified by electron probe micro-analysis (EPMA).

By increasing the Al content to 8 at.%, a protective layer is formed during exposure at 815°C, shown in Fig. 12 by a small mass increase and the absence of rapid mass loss. The composition of the protective scale changes, with respect to the 2 and 4 at.% alloys, to a mixture of $CrNbO_4$, SiO_2 and Al_2O_3.

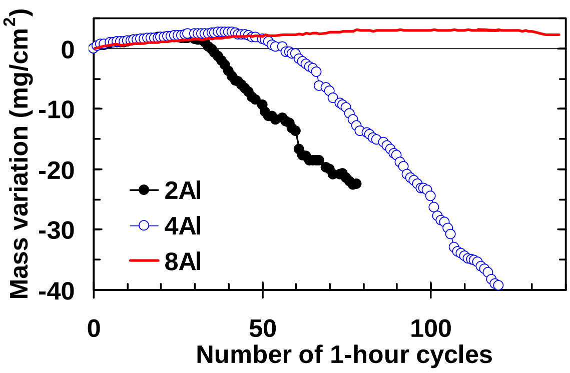


Fig. 12. Cyclic oxidation (1 h cycles) at 815°C of Nb-base silicide alloys of same composition, except for the Al content (given in at. %).

Isothermal oxidation tests at 1100°C led to the determination of the following parabolic kinetic constants: *ca.* 10^{-8} $g^2.cm^{-4}.s^{-1}$ for 2Al and 4Al alloys and *ca.* 10^{-9} $g^2.cm^{-4}.s^{-1}$ for the 8Al alloy, *i.e.* one order of magnitude lower.

5.2 Coating development

The first results of this task yield to promising perspectives. At present, it is possible to propose optimised coating compositions allowing the protection of Mo-base alloys at intermediate (*i.e.* resistant to the pest phenomenon) and at high temperature (*i.e.* under cruise conditions).

Two coatings have been deposited on a Mo-Si-B PM-processed alloy:

- a Fe-Cr-Si based coating deposited by pack-cementation [17];
- a SIBOR® MoSiB coating [18] deposited by atmospheric plasma spraying.

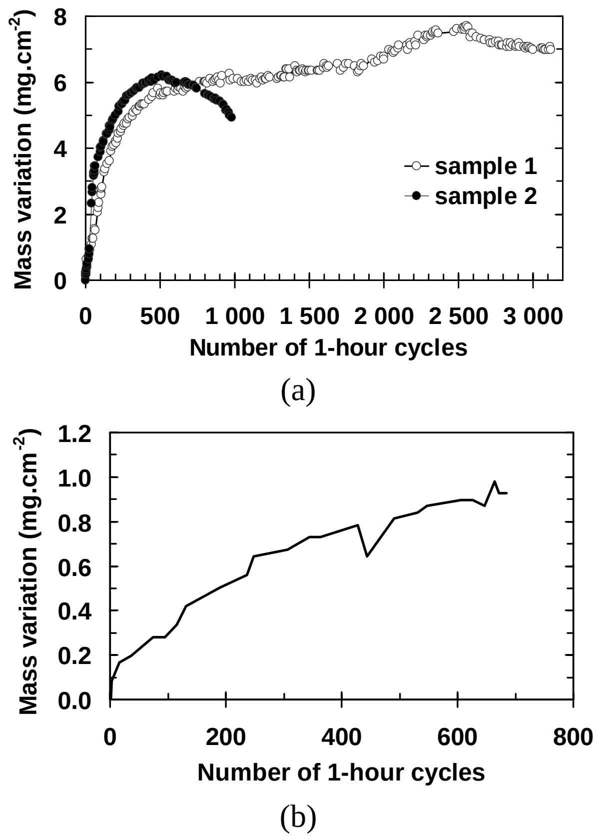


Fig. 13. Cyclic oxidation at 1100°C of coated Mo-base alloy. Coating based on Fe-Cr-Si (a) and SIBOR® coating based on Mo-Si-B (b).

6 Machining

Machining trials, *i.e.* electro-discharge machining (EDM), grinding, turning, milling and drilling, have been performed on Mo- and Nb-base silicide alloys, in order to determine which parameters play a significant role in terms of tool wear and workpiece productivity. This has allowed to define feasible conditions for the main operations required on blades and vanes.

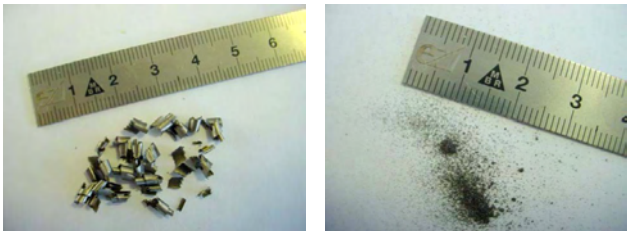
6.1 Mo-base silicides

Mo-base silicides have always shown a brittle behaviour during the trials: the only grinding and drilling operations lead to good results in terms of surface quality, tool wear and easy performing. EDM trials have also shown good results, but a long optimisation phase was necessary to achieve short processing times.

Milling and turning trials have resulted the most challenging, due to the high hardness and brittleness of the alloy: quite good results have been obtained with hard tools and low depths of cut, but the processing time has always been very long, and many fluorescent penetrant inspection (FPI) indications have been found (Fig. 14).

(a) (b)

Fig. 14. Precision machining of Mo-base silicide alloy: from the preform (a) to the firtree mockup (a; height is about 25 mm).



(a) (b)

Fig. 15. Shavings from (a) Nb-base and (b) Mo-base silicide alloys.

6.2 Nb-base silicides

Nb-base silicides have resulted less brittle than the Mo-base silicides: all the machining operations have been easier in terms of surface quality, tool wear and processing time. As an example, with Nb-based silicides, during milling and turning trials high depths of cut (similar to the values obtained with Ni-base alloys) have been achieved, and chippings were obtained; on the contrary, only powder was obtained (Fig. 15) with Mo-base alloys.

With the Nb-silicides alloys, a complete tensile specimen (including threaded heads) was obtained (Fig. 16), in easier conditions as for Mo-base silicide alloys.

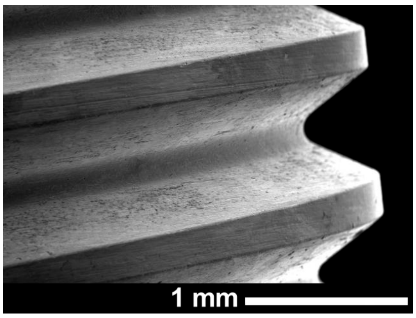


Fig. 16. Machining of the thread of a tensile test specimen (Nb-silicide alloy).

7 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 are promising candidates for such applications. A European industry – university – research centres consortium was built up in the EC-funded ULTMAT project to create a synergy that addresses the scientific and technological challenges and aims at providing a breakthrough solution.

The work performed at mid-project included alloy composition development for Mo- and Nb- base silicides (with focus on high temperature mechanical properties), definition of appropriate processing routes (using powder and ingot technologies), design of oxidation resistant coating systems and investigation of manufacturing techniques.

Acknowledgements

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