

Ultra High Temperature Materials for Turbines

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Administrative Information

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Project execution

1 Project objectives

The ULTMAT project aims at providing sound technological basis for the introduction of innovative materials, namely Mo- and Nb-silicide based multiphase alloys, with enhanced high temperature capabilities (+100°C to +150°C) compared to presently used Ni-base single-crystal superalloys, for application in aircraft/rotorcraft engines and in aero-derivative land-based gas turbines.

The scientific and technological objectives of the project are:

- definition of new compositions for Mo- and Nb-silicide based multiphase alloys with an acceptable balance of mechanical properties and oxidation resistance;
- development, throughout the project, of cost-effective processing technologies, adapted from either powder metallurgy (PM) or ingot metallurgy (IM);
- design of coating systems to improve oxidation resistance;
- building of a property database which will provide data for applications under specific turbine service conditions;
- preliminary assessment of the conditions of implementation of the materials in turbines, mainly machining and joining.

The composition of the consortium is given in Table 1.

Participant name	Activity	Country
Office National d'Etudes et de Recherches Aérospatiales, <i>Coordinator</i>	Aerospace Research Centre	F
Avio s.p.a	Turbine manufacturer	I
Electricité de France	Electricity producer and distributor	F
IRC in Materials, the University of Birmingham	University	GB
Otto-von-Guericke Universität Magdeburg	University	D
Plansee SE - Division High Performance Materials	Refractory products manufacturer	A
Rolls-Royce plc	Turbine manufacturer	GB
Snecma	Turbine manufacturer	F
Turboméca	Turbine manufacturer	F
Université Henri Poincaré Nancy I	University	F
University of Surrey (before 1/9/2006)	University	GB
University of Sheffield (after 1/9/2006)	University	GB
Walter Engines a.s.	Turbine manufacturer	CZ

Table 1. Composition, activity field and country of the partners in the ULTMAT consortium.

2 Work performed

The project has been structured in two phases. The main objective of the first phase was to down-select a limited number of alloy compositions that fulfilled a given set of specifications (in terms of density, mechanical properties, etc.) while the development of coating and processing technologies for both Mo- and Nb-based silicide alloys, using ingot metallurgy as well as powder metallurgy, was started.

The second phase aimed at refining the work on the down-selected alloys, thus allowing the optimisation of processing technologies and coating systems, the set-up of a database of physical, thermal and mechanical properties, the manufacture of turbine airfoils and application specific testing.

2.1 Preliminary work

The first task was however to define (i) the mandatory characterisations that would allow the down-selection of alloy compositions, (ii) the basic quality standards that the developed materials should conform to for industrial application, and (iii) a reference database gathering the properties of the most recent Ni-based single crystal superalloys to which the Nb- and Mo-based silicides are to be compared.

The basic properties of new blades and vanes materials to be used in future turbo-engines, which could operate at temperatures 150°C higher than those allowed by current Ni-based single crystals superalloys, have been defined from updated literature data, and three key requirements have been identified:

- good ductility at room and medium temperatures;
- good high temperature strength and creep resistance, up to about 1300°C;
- good oxidation resistance at intermediate and high temperature.

In order to rapidly check the relevance of an alloy composition, *i.e.* with a limited amount of material and tests, the primary properties to be assessed on basic laboratory scale have been defined: room temperature toughness and strength at 650°C, high temperature compressive creep and cyclic oxidation resistance.

An exhaustive characterisation matrix, in view of generating data to be used by turbine designers, has been defined in a second step regarding:

- physical properties: density, melting temperature, thermal expansion coefficient, elastic modulus, thermal conductivity and specific heat;
- mechanical properties: impact and tensile resistances, tensile creep strength, ductile to brittle transition temperature, high and low cycle fatigue, notch sensitivity.

Complementary characterisations have been eventually proposed: dwell fatigue, crack propagation behaviour, thermal fatigue and negative temperature behaviour.

Basic data referring to three last generation Ni-based single crystal superalloys (CMSX-4, CMSX-10 and MCNG) regarding the above mentioned properties have been established up to 1200°C, to allow comparison with the silicide materials in development.

2.2 Alloy development

Mo-silicide based alloys

The Mo-Si-B alloys studied in the project had Si and B contents leading to a three-phase microstructure as predicted by the shaded field in the phase diagram (Fig. 1). A 1st generation Mo-silicide based alloy with composition Mo-9Si-8B-2.7Nb (at.%), *i.e.* Mo-3Nb-3Si-1B (wt.%), has been defined to allow the start of activities in processing technologies, development of coatings as well as investigation of machining techniques.

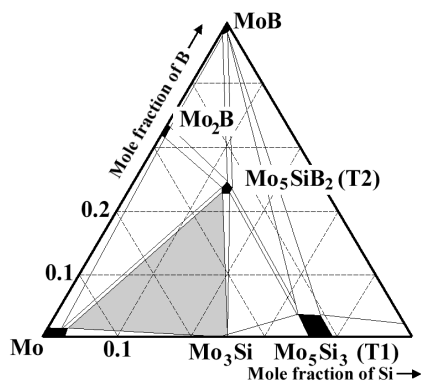


Fig. 1. Mo-rich part of the isothermal section at 1600°C of the Mo-Si-B phase diagram (after [1]).

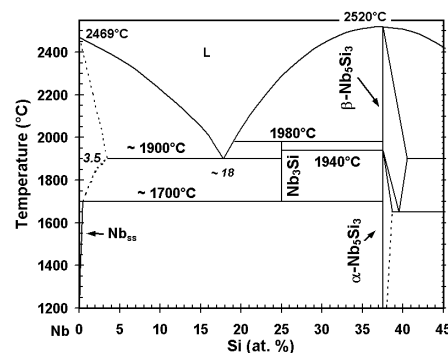


Fig. 2. Nb-rich part of the binary Nb-Si phase diagram (after [2]).

Using the PM route, by mechanical alloying of elemental powder blends followed by CIP¹ and HIP² [3], six billets with diameter 50 mm and lengths between 250 mm and 440 mm for an approximate total weight of 50 kg were manufactured in the first months of the project and

¹ CIP: cold isostatic pressing.

² HIP: hot isostatic pressing.

basic mechanical characterisations have been performed: tensile tests between room temperature (RT) and 1200°C, dynamic impact testing and fracture mechanics tests, compression creep tests up to 1315°C [3,4,5]. For the latter, tests with load increments have been performed, allowing the measurement of the minimum creep rate at various stresses at a given temperature with a single specimen. Special care has been taken to validate the test method on a wide range of stresses and on various test facilities.

Work performed prior to project beginning showed the positive influence of oxide particles on the mechanical properties of MoSiB alloys [6] and a limited set of properties as a function of oxide content in the material was available. The objective of alloy development phase was to collect an additional set of data allowing the selection of an optimised composition of a Mo-silicide alloy, based on the alloy defined in ref 6.

Three candidate oxides were selected: Y₂O₃, La₂O₃ and MgO:

- Ytria was selected as a reference;
- Mo-La₂O₃ alloys are commercially established in the lighting industry for their good workability down to room temperature and their stable microstructure up to 1800°C. Improvements of both parameters could be beneficial for the definition of components made of Mo-silicides;
- MgO was selected due to experimental results available from PLANSEE. Metallic Mg additions were shown to improve the oxidation resistance of Mo-3Si-1B whereas Mg was only detected as oxide in the material. There was no evidence of Mg in the molybdenum solid solution, nor in the intermetallic phases. The primary objective of MgO additions was therefore focused on the improvement of the oxidation resistance.

About twenty alloy batches have been manufactured with the usual route (mechanical alloying of powder blends, CIP, HIP), the selected oxides being added in order to cover a large composition range (0 to 1 wt.%). A basic characterisation of the mechanical properties (in compression at 650°C, 900°C and 1200°C) and of the oxidation resistance in air at 650°C, 1100°C and 1315°C was undertaken.

Statistical methods (Design of Experiment) were used: a D-optimal model was preferred to Taguchi models for its experimental flexibility. The selected factors were oxide species and the corresponding weight fraction, as well as the residual oxygen content in the alloy.

A ranking of the twenty alloys according to oxidation behaviour, ductile to brittle transition temperature and high temperature compression strength was carried out. This has led to the selection of an alloy with composition Mo-3Si-1B-0,1%La₂O₃ (in wt.%).

Nb-silicide based alloys

Alloys in the binary Nb-Si system exhibit excellent creep resistance, although poor toughness and oxidation resistance. But these latter properties can be improved by alloying, leading *e.g.* to the NbTiHfCrAlSi metal and silicide composites (“MASC”) family developed by General Electric [7,8].

The Nb-silicide based materials consist of a metal solid solution M(ss) (M being *e.g.* Nb+Ti+Hf+ ...) with M₅Si₃ (α or β) and/or M₃Si silicide phases (Fig. 2). Other phases, such as NbCr₂-type Laves phases in case of higher Cr contents for better oxidation resistance or hexagonal M₅Si₃ (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. Improvement of the high temperature mechanical properties (mainly creep resistance) can thus be obtained by enhancing the properties of the soft phase and/or increasing the silicide volume fraction, the latter by means of increasing the silicon content in the alloy. Higher silicide contents simultaneously improve the oxidation resistance, but decrease toughness and ductility at low and intermediate temperatures. Large defect-free ingots with high silicon contents are however difficult to manufacture, mainly because of the high melting temperature and the related contraction during cool down, so that these alloys could be manufactured only using arc-melting.

Work has focused on the improvement of the properties of the Mo(ss) phase. Elements such as Al and Cr as well as refractory metals (RM) like Ta, Mo and W were identified to have strong hardening effect to the matrix; from EDS³ measurements, it was found that Al, Mo and W strongly partition to the matrix. The effect of both alloy composition and microstructure, with possible phases being various modifications of M(ss), M₅Si₃ and M₃Si depending on their heavy element content, on oxidation and creep resistance has been established.

Finally, two creep resistant alloy compositions have been selected for further characterisation; patents are currently being filed.

2.3 Development of processing technologies for Mo-based silicide alloys

About 300 kg material were industrially manufactured using a specific powder metallurgy processing route including mechanical alloying, compacting, sintering and extrusion. All processing steps were performed using industrial equipment, hence ensuring that the results of the characterisation could be directly used by engine manufacturers.

The feasibility of the processing route was shown using the 1st generation MoNbSiB alloys. In a second step, the processing parameters were adapted to the 2nd generation MoSiB-La₂O₃ alloy.

The density of the alloy was measured using Archimedes principle. A nearly full density (99.5%, *i.e.* 9.5 g cm⁻³) could be reached after HIPing. The analysis of the microstructure (Fig. 3) shows a duplex microstructure of intermetallic and metallic phases with a fine grain size (~10 μm). The intermetallic phases (Mo₃Si and Mo₅SiB₂) could not be resolved in SEM⁴.

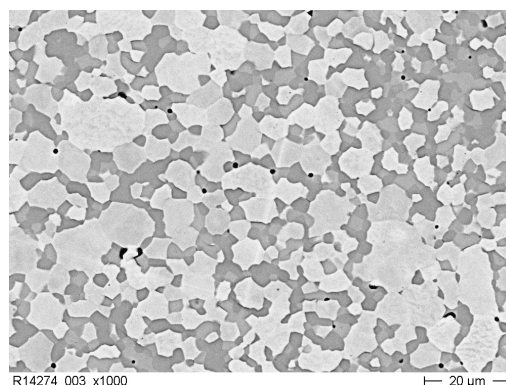


Fig. 3. Typical microstructure imaged using an SEM (back scattered electrons) of sintered 2nd generation Mo- silicide based alloy.

³ EDS: Energy dispersive spectrometry.

⁴ SEM: Scanning electron microscopy.

The chemical composition was measured using ICP-OES⁵ and hot gas extraction (Table 2). The alloying element contents (Si, B and La₂O₃) are close to the objectives. The oxygen, nitrogen and Fe contents (the latter stemming from the attritor milling processing step) could be kept low.

	Mo	Si	B	La ₂ O ₃	Fe	C	H	O (rest)	N
	wt. %			µg g ⁻¹					
Objective	Bal.	3	1	1000	-	-	-	-	-
2 nd gen. MoSiB	Bal.	2.93	0.94	931	252	<5	<1	253	15

Table 2. Chemical composition of the MoSiB-La₂O₃ alloy measured using ICP-OES.

Mechanical properties

High temperature compression tests were performed on cylindrical samples (HIPed state) with a diameter of 4 mm (see Table 3). Very high strength levels were measured at all temperatures. A DBTT⁶ below 650°C could be measured.

	650°C		900°C		1200°C	
	R _m (MPa)	A (%)	R _m (MPa)	A (%)	R _m (MPa)	A (%)
Compression	1696	2.8%	1538	>10%	711	>10%

Table 3. Results of compressive tests measured on cylindrical samples (Ø 4 mm) on HIPed MoSiB-La₂O₃ alloy.

Oxidation resistance

A significant improvement of the weight loss could be observed at 1100°C and 1315°C compared to results on alloys published in the literature or manufactured from atomised powders (Fig. 4), with the same base composition Mo-3Si-1B (wt.%).

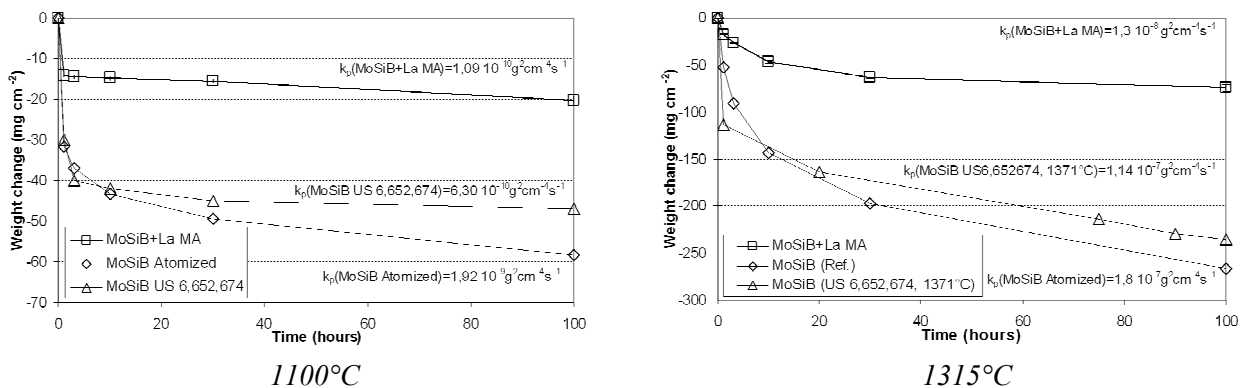


Fig. 4. Results of oxidation tests at 1100°C and 1315°C in air on Mo-3Si-1B (wt.%) alloys: from literature (US patent), obtained from atomised powder and from MA powder (+La₂O₃).

The specific processing route used here allowed a shift of the phase composition (see Table 4) resulting in improved mechanical properties and oxidation resistance. This shift was made possible by decreasing the amount of silicon dissolved in the molybdenum phase while keeping a constant global composition.

⁵ ICP-OES: Induction coupled plasma – optical emission spectrometry.

⁶ DBTT: Ductile to brittle transition temperature.

	Mo _{ss} mean vol.%	Intermetallic phases mean vol.%	Standard deviation	Si content of Mo _{ss} (wt.%)
MoSiB atomised	52.6	47.4	5.7	1.3
MoSiB + La ₂ O ₃ MA	51.4	46.2	1.1	0.4

Table 4 Comparison of the phase volume fraction and composition of Mo-3%Si-1%B alloys processed via atomisation and mechanical alloying (MA).

The industrial availability of MoSiB material was guaranteed within the project and for a future large-scale production. The mechanical properties and the oxidation resistance obtained on laboratory scale material were verified and optimised, outperforming the performance of all material manufactured up to now.

2.4 Development of processing technologies for Nb-silicide based alloys

The development of processing technologies for Nb-silicide based alloys have been achieved through investigation of two routes, PM and IM. To accelerate the maturation of state-of-the-art Nb-silicide-based materials, the development of their processing technologies was based on existing technologies which were further developed in this project to fit the new materials.

Primary fabrication

The feasibility of producing new materials during primary fabrication at a fairly large scale is essential to the maturation of any new material under development. The investigation of primary fabrication of Nb-silicides alloys was carried out using ingot metallurgy and powder metallurgy at the scale of about 50 kg ingot/billet weight.

A few Nb-silicides alloys ingots with different compositions were fabricated using cold hearth plasma arc melting. The ingots were 100 mm in diameter and up to 1 m in length. The results gained from ingot melting investigation show that alloy compositions have a strong effect on the melting process and ingot quality. The factors affecting ingot melting are melting point, silicides phase volume fraction and the plasticity of the metallic matrix, all of which are determined by alloy composition. Alloys with compositions similar to MASC alloy (Nb-25Ti-8Hf-2Cr-2Al-16Si) can be melted using plasma arc melting and no difficulties specific to Nb-silicide alloys were encountered. However, some alloys with alloying elements which increase melting point and silicide volume fraction and induce embrittlement in the matrix phase cannot be easily fabricated into ingots due to insufficient flow during melting and hot tearing during cooling.

Primary PM fabrication of Nb-silicide based alloys was investigated using elemental powder blend technologies. Billets up to 50 kg of alloys based on MASC composition were successfully fabricated by using powder blending, CIPing, sintering and HIPing consolidation. The microstructure of one of the MASC billet is shown in Fig. 5 and it features fine niobium silicides and granular solid solution matrix (the grey phase). It is indicated by the results from the PM MASC billets that this method should be applicable to a wide range of alloy compositions because no coarse niobium silicides dendrites are found in the cast ingots, which contribute significantly to ingot cracking during cooling.

Secondary fabrication

Secondary fabrication technologies (shape casting, extrusion and forging) were applied to Nb-silicides alloys during this project and their suitability was evaluated.

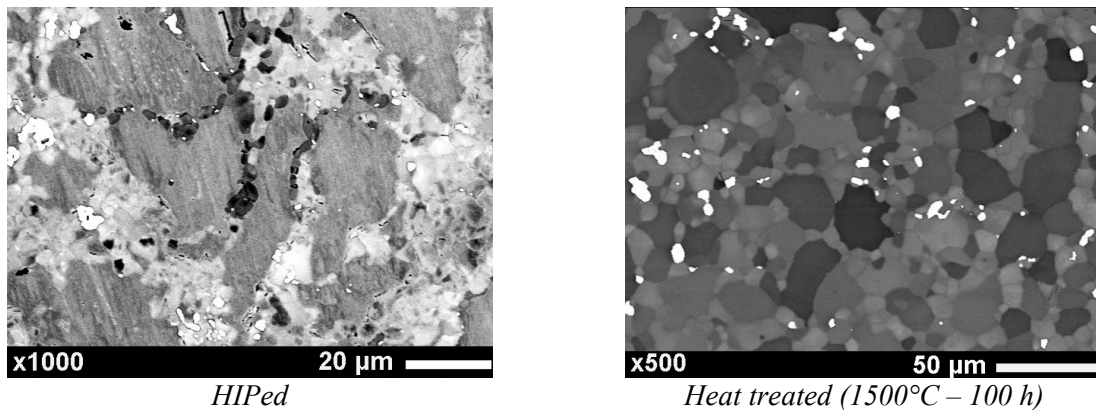


Fig. 5. SEM micrographs of a Nb-25Ti-8Hf-2Cr-2Al-16Si billet fabricated using PM technology.

Shape casting was carried out using investment casting technology and machined graphite mould technology on different shapes and alloys. The effort was focused on investment casting using ceramic moulds due to its flexibility to complicated shapes. The shapes include test bars, generic engine seal segments and generic engine blades. During investment casting, the alloy feed stock was melted in an induction skull melting furnace and poured into a heated ceramic mould. The castability of Nb-silicide based alloys varies with alloy composition; the MASC alloy has the best castability among the alloys investigated (Fig. 5a). The filling of the mould is excellent and near net shape casting has been achieved. The microstructure of the blade after HIPing (1600°C / 150 MPa / 4 h) is shown in Fig. 5b and it is uniform throughout the foil. This blade is one of the cast cluster consisted of four blades and four engine seal segments. It is indicated by the investment casting results that batch production of such blades are possible. The engine seal segment blanks are shown in Fig. 7.

Extrusion is a process to produce simple shapes such as bars. In this project, extrusion was carried out on alloys based on MASC composition fabricated via PM and IM routes. The starting microstructures of the extrusion blocks are different. The one from PM billet had fine equiaxed microstructure and that from ingot featured long silicide dendrites. The extruded bar from PM billet is shown in Fig. 8 and it is smooth and homogeneous. The quality of as-extruded bar from the ingot is not as good as that from the PM billet which is due to the coarse starting microstructure. The fine starting microstructure can tolerate a larger preheat temperature for extrusion.

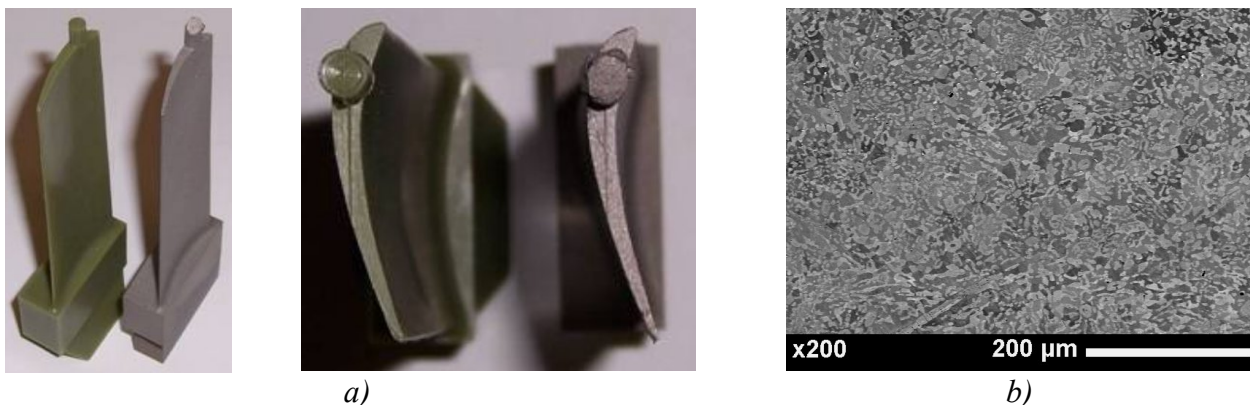


Fig. 6. a) Investment cast Nb-25Ti-8Hf-2Cr-2Al-16Si 120 mm long blade; the left is the wax and the right is the Nb-silicide blade. b) Microstructure of the airfoil after HIPing.



Fig. 7. Investment cast Nb-25Ti-8Hf-2Cr-2Al-16Si generic engine seal segments with different thickness.



Fig. 8. Extruded Nb-silicide alloy based on MASC composition (PM route).

Because of technical problems and various delays, the PM route for Nb-silicide based alloys could not be investigated as thoroughly as initially planned. However, the main trends and solutions for improvement have been identified.

2.5 Building up of a property database

The establishment of a property database for the studied Mo- and Nb-silicide based alloys is a key point in the project, allowing on one side the comprehensive assessment of the candidate alloy systems and on the other side the delivery of a data envelope that can be used by engine designers to integrate RM-silicide based components in future engine.

The alloys differed by composition (within the two Mo- and Nb-based systems of interest) and also by microstructure, due to the various processing routes investigated. The established database contains the physical, thermal and mechanical properties appropriate to the intended application in gas-turbine hot sections.

A flow diagram setting the following data:

- the property to be measured (e.g. room temperature strength);
- the test method (e.g. tensile testing);
- the test conditions (sample geometry, atmosphere, ..);
- the materials to be tested;
- the partners that will perform the tests;
- the date of result delivery.

was issued at the beginning of the project to give to all partners a detailed view of the work to be performed.

To provide a comprehensive overview, a property database was subsequently designed in form of an Excel worksheet with a main sheet collecting the links to all relevant material properties on subsheets. In the course of the 54 months of the project, the properties of certain development alloys (from WP2) and the MASC alloy were added to the database as well as data on comparable alloys available in the open literature. In its final form, the property database especially contains the following information⁷:

- nominal and actual composition of the alloy;
- manufacturing route and main parameters;
- tensile properties at room and high temperatures (up to 1200°C);
- fracture toughness at room temperature;

⁷ however not available for all alloy compositions.

- thermal conductivity up to 1300°C;
- thermal diffusivity up to 1300°C;
- temperature dependence of the dynamic E and G moduli up to 1300°C;
- coefficient of thermal expansion (CTE) up to 1300°C;
- compressive and tensile creep properties in the range 900°C to 1315°C;
- hardness and microhardness;
- room temperature toughness;
- ductile to brittle transition temperature;
- high and low cycle fatigue, notch sensitivity
- oxidation at 815°C and 1100°C / 1200°C / 1300°C.

2.6 Development of oxidation resistant coatings

Insufficient oxidation resistance at medium (*pecking* regime) and high temperature is one the weaknesses of the RM-based silicide materials, compared to superalloys. It is thus of prime importance to characterise the oxidation behaviour and understand the related mechanisms to be able to design and test efficient oxidation resistant coatings.

Basically, the work performed can be divided in two major parts: investigation of the oxidation behaviour of uncoated alloys and design, deposition and testing of oxidation resistant coatings, with emphasis on the Nb-silicide based materials.

Oxidation of uncoated alloys

This part, which constitutes an important contribution to the project, allowed the characterisation of the oxidation behaviour of a number of silicide alloys: Nb-Nb₅Si₃ in situ composites with Ti-Hf-Cr-Al-Ru substitutions and Mo-Mo₃Si-Mo₅SiB₂ with Nb substitution and La₂O₃ addition. The oxidation kinetics have been measured between 815°C and 1300°C.

Concerning the Nb-silicide based alloys, the metallographic characterisations allowed the determination of the degradation mechanisms and showed the effect of respective alloying elements:

- the Nb(ss) phase is the most sensitive to the oxidation and the volume expansion associated with the oxides formation leads to the ruin of the material at 815°C;
- Hf plays a key role as an oxygen “getter”;
- Al is distributed in both typical phases of the alloys and contributes to decrease the oxidation rates, though no specific Al-containing oxide were detected;
- Si seems to be more effective than Al for oxidation protection. Silicon scarcely dissolves in the solid solution matrix but contributes to increase the Cr solubility in Nb(ss) which becomes more resistant to oxidation due to CrNbO₄ formation;
- all the characteristics have been correlated to physico-chemical data.

Development of oxidation resistant coatings

Two approaches have been followed in parallel during the project.

The first one was based on available coatings developed by some partners mainly for the protection of RM alloys, which have been adapted to RM-silicide based alloys and for which the deposition technique has been optimised.

The deposition technique used was predominantly pack-cementation. The operational conditions (masteralloy composition, deposition and annealing temperatures, *etc.*) have been adjusted in order to co-deposit complex silicide coatings on silicide-based alloys, with the

help of gaseous phase composition modelling. A complementary study of the pack-cementation process has been performed in the simplified ternary system Nb-Cr-Si, which has been also investigated through thermodynamic modelling (CALPHAD) and experimental work. The control of the composition (Si, Ti, Fe, Cr, B content, *etc.*) of the successive layers during the optimisation steps has led to outstanding oxidation performances at both intermediate and high temperature thanks to the formation of protective silica-based scales (Fig. 9).

Moreover, microhardness measurements evidenced the necessity to toughen the coating-substrate interface in order to stop any crack that would propagate from the coating to the substrate, where oxidation is catastrophic. This was achieved by allowing an adequate silicide phase to form at the interface.

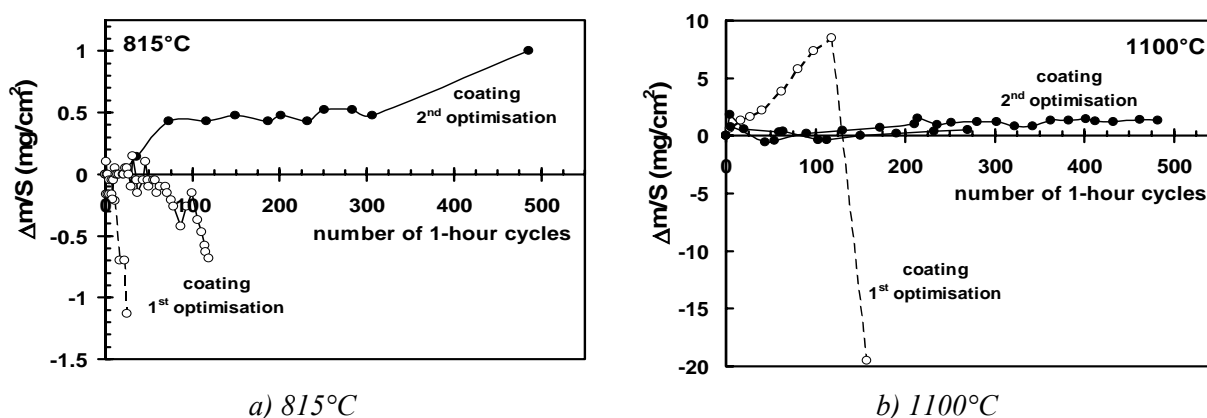


Fig. 9. Cyclic oxidation of coated MASC alloy at a) 815°C, and b) 1100°C, compared with previous coatings.

The second approach was to investigate the possibility to deposit coatings that form alumina scales during oxidation, since it is known that alumina is very efficient in reducing the oxidation rates, at least at high temperature, as it has widely been studied for superalloys. A literature survey showed that RuAl is a promising candidate coating.

The work hence focused on a thermodynamic study of the Nb-Ru-Al ternary sub-system which is part of the complex global Nb-Mo-Si-B-Ti-Hf-Cr-Al-Ru system from which are provided the compositions of the structural materials as well as the coatings. This has been investigated through:

- experimental measurements: high temperature calorimetry for the determination of the formation enthalpies and heat capacities (C_p) of refractory $Nb_{2+x}Cr_{4-x}Si_5$ ($0 < x < 2$) alloys, powder X-ray diffraction to determine the crystallographic structure of a new compound Ru₂Nb, diffusion couples showing that a 2nd order transition takes place between disordered Nb(Ru) and ordered NbRu;
- CALPHAD modelling of the Nb-Ru, Ru-Al, Nb-Ru-Al sub-systems (Fig. 10).

Unfortunately, the unavailability of the adequate deposition facilities made it impossible to obtain acceptable RuAl coatings, so that the experimental investigations were put on hold.

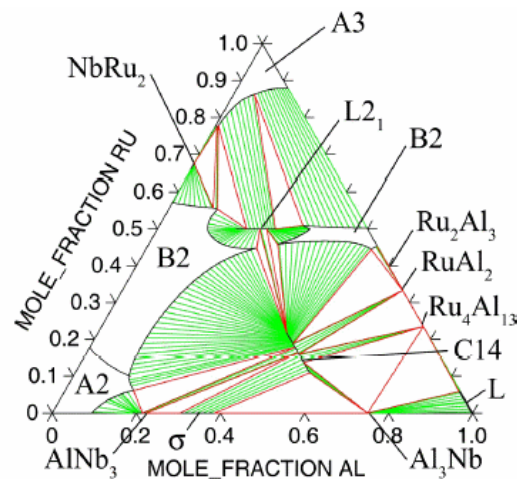


Fig. 10. Calculated isothermal section of the Nb-Ru-Al system at 1100°C.

Concerning the Mo-silicide based alloys, the well-known positive effect of boron has been noticed and the negative effect of a too fine microstructure has been evidenced. It is to be noticed that the SIBOR[®] coating developed for Mo-based alloys provides also very good oxidation resistance to Mo-silicide based alloys.

Finally, the assessment of a database relative to the characteristics of complex Nb- and Mo-silicides has been initiated. These compounds are not widely investigated from a fundamental aspect because of their complex compositions $(\text{Nb}, \text{Ti}, \text{Mo})_x \text{Fe}_y \text{Cr}_z (\text{Si}, \text{B})_p$. The database contains oxidation rate constants at 1100°C, 1200°C and 1300°C, structural data, transition temperatures, thermal expansion coefficients. These compounds are very resistant to high temperature oxidation and can be selected as constituents of protective coatings on Nb- and Mo-silicide based materials.

2.7 Component fabrication technologies

Workable conditions have been defined to perform the main machining operations required on blades and vanes, by performing machining trials on Mo- and Nb- silicide based alloys.

Machining trials have been carried out on the following operations: EDM, grinding, turning, milling and drilling. The first phase of the activity was aimed at understanding which parameters play a significant role in terms of workpiece productivity and tool wear. Subsequently the attention was focused on the optimisation of tool life and surface quality. As a result of this task, a tensile test specimen has been grinded out of both a Mo- and Nb-silicide based rod (Fig. 11).

As a general rule, machining of Mo-silicide based alloys is much more difficult than Nb-silicide based alloys.

Additionally, preliminary joining conditions were investigated for Mo-silicide based alloys. The primary objective was to investigate diffusion bonding, but since brazing is mainly used for joining conventional components, the focus was early set up on brazing technologies.

Brazing alloys based on Ti, Zr and precious metals were tested. PdNi based brazing alloys showed good preliminary results without porosity and good gap filling (Fig. 12).

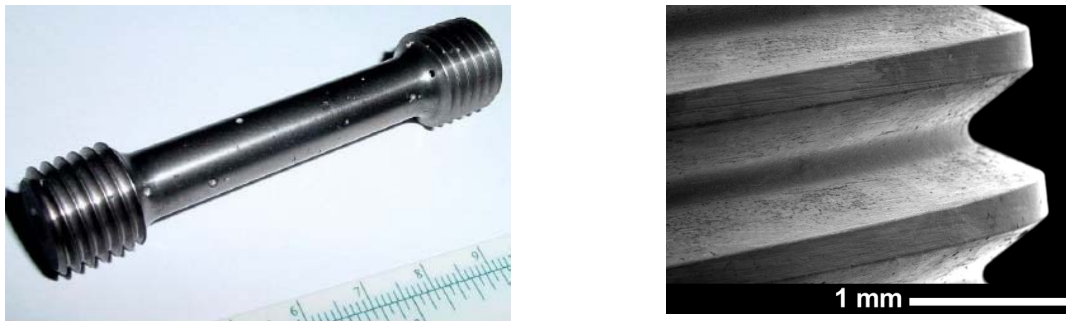


Fig. 11. General view and threaded head of a tensile test specimen (Nb-silicide based alloy), from an investment cast blank (containing some pores).

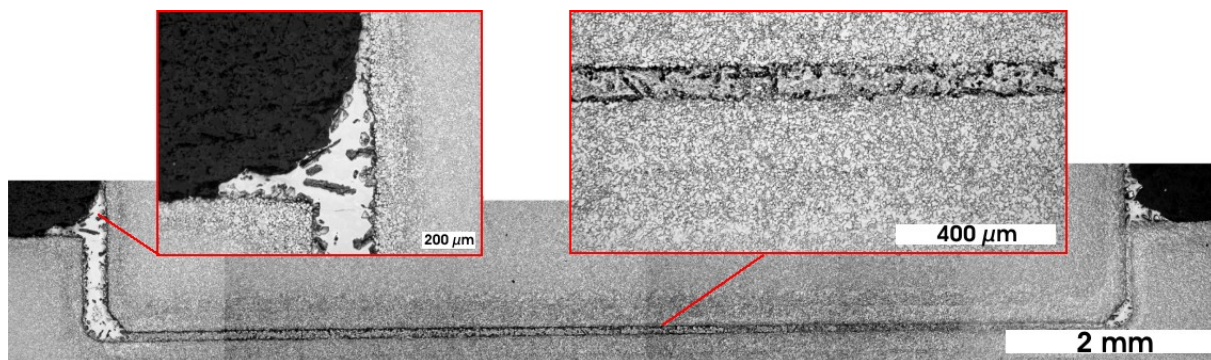


Fig. 12. MoSiB to MoSiB brazing.

2.8 Manufacture of components and testing

Thermal and mechanical calculations have been carried out, in order to have a quantitative evaluation of the benefits of using Mo- and Nb-silicide based alloys in future turbo-engines. This has been performed by industrial partners in a first step on existing turbine hot section components (blade, vane, seal segment) with thermo-physical and mechanical properties as measured in the project (or taken from literature). It was proved, for instance, that Nb-silicide based alloys would be useful to enhance operating temperatures of a non cooled blade or to reduce cooling flow in a cooled one. Nb-silicide based alloys were also assessed for a cooled vane.

A further task was devoted to validate the previously developed manufacturing methods on complex shaped components. Hence, a Mo-silicide based alloy fir tree root specimen was grinded, as well as a fir tree mechanical test sample. Seals were machined from Nb silicide cast parts. Finally, a blade foil was milled.

The last task was aimed at testing Mo- and Nb-silicide based alloys in simulated service conditions. Several coated and uncoated specimens (with uncoated CMSX-4 as a reference) were tested in a burner rig for over 500 one hour cycles, facing burned gas containing Na_2SO_4 . For some of them, an oxidation/corrosion resistance comparable or better than CMSX-4 has been obtained.

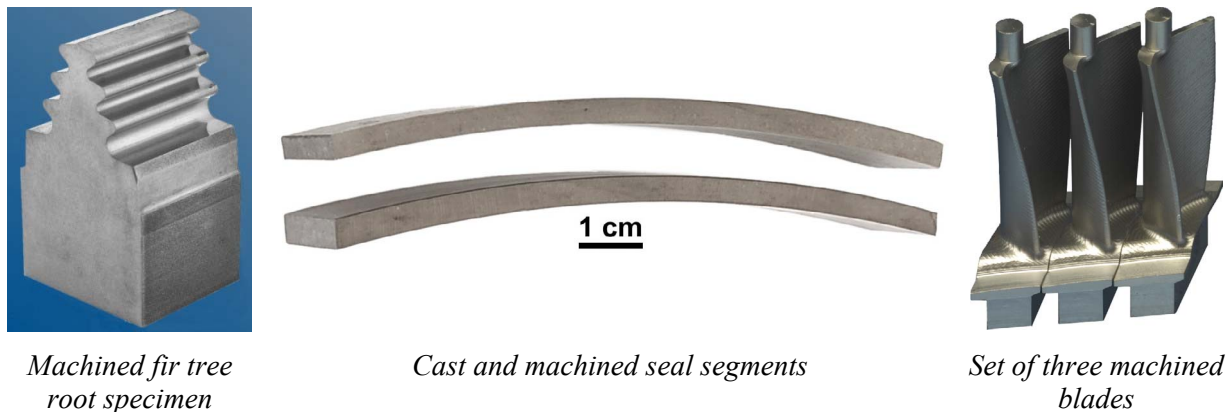


Fig. 13. Examples of machined components (Mo- and Nb-silicide based alloy).

3 Conclusions

ULTMAT is a fast-track programme to evaluate the potential of Mo- and Nb-silicide based materials for high temperature applications. In this field, the research is largely exploratory, with little short time applications. The consortium appeared to be well-balanced and highly relevant to take up the challenge, with four universities, one research centre and seven industrials.

To deal with these scientifically and technically harsh problems, the project has mobilised specific high temperature facilities for manufacturing, processing and characterisation. Breakdowns of facilities were encountered, which could be overcome by redistributing the work among the partners and by sub-contracting.

Significant results have been obtained, even if not sufficiently to develop “products” (but this was not an objective of the project):

- the project has given a precise view of the promises and limitations of Mo- and Nb-silicide based materials, which is a priceless complement to the work performed here and there by individual institutions and companies, and could be obtained only by the synergetic commitment of all partners at European level;
- alloy compositions have been worked out for both alloy systems, following different development strategies:
 - a Mo-silicide based alloy composition is available that provides reasonable mechanical properties and oxidation resistance. This alloy, because of its somewhat higher density, could be used in static turbo-engine components;
 - Nb-silicide based alloy compositions are available, for which patenting is in progress. These alloys exhibit excellent creep resistance, but oxidation resistance is still insufficient for long duration applications;
- an industrial powder metallurgy route has been developed for Mo-silicide based alloys;
- for Nb-silicide based alloys, investment casting has been developed and validated by the manufacture of blades up to 320 mm in length; it has also been shown that this route can only be used for a certain range of alloys (the main parameter being the melting point). The powder metallurgy route could not be investigated as thoroughly as planned, but flawless HIPed materials have been manufactured;

- coating systems have been designed, deposited and tested, focusing on the Nb-silicide based alloys, that exhibit excellent resistance from the intermediate (800°C) to the high temperature (above 1100°C) range;
- a database has been built up, which can readily be used by engine design offices, and also by the partners to further develop the alloy compositions, the protective coatings and the manufacturing processes;
- the machining and joining of both alloy systems has been assessed, and validated with the manufacture of turbine component mock-ups.

In conclusion, the main scientific and technological outcomes of the project are a significant advance in the understanding of synergistic effects of alloying elements on *(i)* phase selection, *(ii)* phase stability, *(iii)* segregation phenomena, *(iv)* phase transformations, *(v)* phase equilibria, *(vi)* oxidation behaviour, *(vii)* microstructure architecture, *(viii)* mechanical properties and *(ix)* oxidation resistance of both alloy systems, and the development of processing routes (IM and PM) at industrial scale.

This knowledge would benefit the metallurgical academic community once publication of papers commences following the filing of a patent. This knowledge would also help industry focus its future efforts and resources in selecting alloys for further development.

Dissemination and use

Results from the ULTMAT project have been presented at about thirty seminars, colloquia and conferences, to national or international audience, and several more are scheduled.

N°	Date	Title
1	14/01/05	<u>Honorary Symposium for G. Sauthoff, Max-Planck-Institute for Iron Research, Düsseldorf (D).</u> “Industrial processing of high temperature structural intermetallics: current state and future trends”
2	30/05-03/06/05	<u>Int. “Plansee-Seminar 2005”, Reutte (A).</u> “High Temperature Deformation Mechanisms of Molybdenum Silicides with Molybdenum and Intermetallic Matrix”
3	25-28/09/05	<u>MS&T Fall Meeting, 14th Int. Symp. Processing and Fabrication of Advanced Materials, Pittsburgh (USA).</u> “Mechanical alloying of Mo-Si-B alloys”
4	06/12/05	<u>Seminar des Instituts für Strukturphysik, TU Dresden (D).</u> “Intermetallische Phasen für Hochtemperatur-Anwendungen: Stand der industriellen Umsetzung”
5	12-16/03/06	<u>2006 TMS Annual Meeting, San Antonio (USA), A. Mukherjee Symp. on Processing and Mechanical Response of Engineering Materials.</u> “Assessment of the Creep Behavior of Molybdenum Silicide Alloys for Ultra-High Temperature Applications”
6	19-21/06/06	<u>AeroDays 2006, Vienna (A).</u> “Ultra High Temperature Refractory Metal Based Silicide Materials For Next Generation Turbines”
7	3-8/09/06	<u>ICAS’2006 International Conference, Hamburg (D).</u> “The EU-funded ULTMAT project: ULtra high Temperature MAterials for Turbines”
8	19-23/09/06	<u>Japan - South Africa - German Workshop and Summer School 2006 High Temperature Alloys, Bad Berneck (D).</u> “Mo-Si-B Type Alloys: Current Status and Future Trends”
9	5-6/10/06	<u>Festkolloquium Prof. Macherlauch 80 Jahre - 40 Jahre Institut für Werkstoffkunde I, Karlsruhe (D).</u> “Beyond Ni-Base Superalloys”
10	2-3/11/06	<u>2nd Symposium on Recent Advances of Nb-containing Materials in Europe, Essen (D).</u> “Superalloys in Snecma Aeroturboengines: Present and Future Evolutions”
11	27/11-1/12/06	<u>MRS Fall Meeting 2006, Symposium “Advanced Intermetallic-Based Alloys”, Boston (USA).</u> “High Temperature Deformation Behaviour of a Mechanically Alloyed Mo-Silicide Alloy”
12	13-16/05/07	<u>PowderMet 2007, Denver (USA).</u> “Mo-based silicide alloys with balanced oxidation resistance and mechanical properties”
13	7-9/06/07	<u>European Research and Innovation Exhibition, Paris (F).</u> “Des Matériaux Résistant aux Hautes Températures pour les Turbines de Nouvelle Génération”
14	10-13/09/07	<u>EUROMAT 2007, Nuremberg (D).</u> “Mechanical Alloying of Mo-Base Alloys for High Temperature Applications”
15		“Study of the Role of Mo and Ta Additions in the Microstructure of Nb-Ti-Si-Cr-Al Silicide Base Alloys”
16		“Properties of Ultra High Temperature Refractory Metal Based Silicide Materials”
17	10-13/09/07	<u>EUROCORR 2007, Freiburg (D).</u> “Oxidation at High Temperature (T1=815°C and T2=1100°C) of New Silicide and Aluminide Coatings for Nb-, and Mo-Alloys”
18	15-17/10/07	<u>EuroPM 2007, Toulouse (F).</u> “Molybdenum alloys for applications under air atmosphere”
19	16/11/07	<u>Tohoku University, Sendai (J).</u> “Beyond Nickelbase Superalloys: Options for developing metallic ultra-high temperature structural materials”
20	19/11/07	<u>Memorial Symposium for the 50th Anniversary of the 123rd Committee, JSPS, Tokyo (J)</u> “Beyond Nickelbase Superalloys: Current status and future trends of Mo-based silicide alloys”
21	22/11/07	<u>Kyoto University, Kyoto (J).</u> “Beyond Nickel-base Superalloys: Options for developing metallic ultra-high temperature structural materials”
22	3-8/01/08	<u>Plasticity 2008, Hawaii (USA).</u> “Superplasticity of multiphase Mo-Si-B alloys”

N°	Date	Title
23	9-13/03/08	TMS 2008 (New Orleans, LA, USA). "Investment casting of Nb/Si-based alloys and Near Net Shape HIPping of Nb/Si powders"
24	4-9/05/08	Creep 2008, Bayreuth (D). "Creep behaviour of Refractory Metal Based Silicide Materials"
25	12-14/05/08	ACMA 2008, Agadir (Morocco). "Materials evolution in hot parts of aero turboengines"
26	8-12/06/08	World PM 2008, Washington (USA). " α -Mo-Mo ₃ SiB ₂ -Mo ₃ Si alloys resistant to high temperature oxidation"
27	23-26/06/08	Aeromat'2008, Austin (TX, USA). "Properties of Mo- and Nb-Based Silicide Materials"
28		"Alloy Development and Processing NbSi alloys to Produce Net Shape Components"

The published papers are listed below:

1. P. Jéhanno, M. Heilmaier, H. Kestler, M. Böning, A. Venskutonis, B. Bewlay, M. Jackson, "Assessment of a powder metallurgical (PM) processing route for refractory metal silicide alloys", Metall. Mater. Trans. A36 (2005) 515-523
2. P. Jéhanno, M. Heilmaier, H. Saage, M. Böning, A. Venskutonis, W. Knabl, "High Temperature Deformation Mechanisms of Molybdenum Silicides with Molybdenum and Intermetallic Matrix", Proc. 16th Int. Plansee Seminar 2005, G. Kneringer, P. Rödhammer, H. Wildner (Eds.), Reutte (A), 841-855 (2005)
3. P. Jéhanno, M. Heilmaier, H. Saage, H. Heyse, M. Böning, H. Kestler, J.H. Schneibel, "Superplasticity of a refractory multiphase Mo-Si-B alloy", Scripta Mater.55 (2006) 525-528
4. S. Drawin et al., "The EU-funded ULTMAT project: ULtra high Temperature MAterials for Turbines", ICAS'2006 Proceedings (2006)
5. P. Jéhanno, M. Heilmaier, H. Saage, M. Böning, H. Kestler, J. Freudenberger, S. Drawin, "Assessment of the high temperature deformation behavior of molybdenum silicide alloys", Mater. Sci. Eng. A 463 (2007) 216-223
6. P. Goud Biragoni, M. Heilmaier, "FEM-simulation of real and artificial microstructures of Mo-Si-B alloys for elastic properties and comparison with analytical methods", Adv. Eng. Mater. 9 (2007) 882-887
7. M. Heilmaier, H. Saage, M. Krüger, P. Jehanno, M. Böning, H. Kestler, S. Drawin, "Current status and future trends of Mo-based silicide alloys for ultrahigh temperature applications", JSPS Report of the 123rd Committee on Heat Resisting Materials and Alloys 48 (2007) 245-259
8. M. Heilmaier, H. Saage, P. Jéhanno, M. Böning, H. Kestler, "Superplasticity of multiphase Mo-Si-B alloys", Mechanics & Mechanisms of Finite Plastic Deformation - Proc. Plasticity '08, A.S. Khan and B. Farrokh (Eds), Neat Press, MD, 184-186 (2008)
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10. M. Krüger, S. Franz, H. Saage, M. Heilmaier, J.H. Schneibel, P. Jéhanno, M. Böning, H. Kestler, "Mechanically alloyed Mo-Si-B alloys with a continuous α -Mo matrix and improved mechanical properties", Intermetallics 16 (2008) 933-941

Exploitable knowledge has been identified in following fields:

- creep resistant alloys with adequate oxidation resistance
- creep resistant alloys
- oxidation resistant alloys
- oxidation resistant coatings
- high temperature micro-indentation
- machining procedures
- casting procedures
- property database

One patent application on alloy composition has been filed.

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