

A Review of Very-High-Temperature Nb-Silicide-Based Composites

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The temperatures of airfoil surfaces in advanced turbine engines are approaching the limits of nickel-based superalloys. Innovations in refractory metal–intermetallic composites (RMICs) are being pursued, with particular emphasis on systems based on Nb-Si and Mo-Si-B alloys. These systems have the potential for service at surface temperatures >1350 °C. The present article will review the most recent progress in the development of Nb-silicide-based *in-situ* composites for very-high-temperature applications. Nb-silicide-based composites contain high-strength silicides that are toughened by a ductile Nb-based solid solution. Simple composites are based on binary Nb-Si alloys; more complex systems are alloyed with Ti, Hf, Cr, and Al. In higher-order silicide-based systems, alloying elements have been added to stabilize intermetallics, such as Laves phases, for additional oxidation resistance. Alloying schemes have been developed to achieve an excellent balance of room-temperature toughness, high-temperature creep performance, and oxidation resistance. Recent progress in the development of composite processing–structure–property relationships in Nb-silicide-based *in-situ* composites will be described, with emphasis on rupture resistance and oxidation performance. The Nb-silicide composite properties will be compared with those of advanced Ni-based superalloys.

I. INTRODUCTION

HOT-SECTION materials developments have made substantial contributions to performance improvements of both aircraft engines and land-based gas turbines. In addition, advances in casting technologies for Ni-based superalloy airfoils have provided the evolution from equiaxed microstructures to directionally solidified multigrain and single-crystal components. As a result of the developments in both alloy composition and casting technology, high-pressure turbine blade temperatures have increased by 125 °C in the past ~ 30 years. Metal surface temperatures at the hottest locations on advanced turbine engine airfoils now approach ~ 1150 °C, which is essentially the limit for nickel-based superalloys. Thermal barrier coatings (TBCs) can also provide airfoils with insulation from the hot gas, so that the TBC surface temperatures can be appreciably higher than ~ 1150 °C.

Further increases in the temperature capability of nickel-based superalloys beyond that of the fourth-generation single-crystal alloys will be very difficult to achieve, because most advanced superalloys melt at ~ 1350 °C. Depending on the solidification processing method and subsequent heat treatment, chemical segregation in the superalloy can lead to incipient melting at ~ 1270 °C. In addition, the interaction zone between the bond coat and the single-crystal airfoil can melt at temperatures less than ~ 1250 °C. Thus, there are clear

intrinsic barriers that limit further increases in the application temperatures of nickel-based superalloys. Single-crystal superalloy strength levels may be improved to allow bulk average temperatures in excess of 1050 °C, but any increase toward a 1200 °C metal surface temperature will require substantial gains in TBC damage tolerance and reliability (loss of the TBC leads to an increase in the local metal surface temperature), as well as increases in the melting point of the complex bond coat–substrate interaction zone.

High-temperature materials that can survive above the present temperature limit are required for advanced gas turbines. A new family of materials that have a high melting point, low density, good oxidation resistance to 1300 °C to 1400 °C, and exceptional high-temperature strength are desired. Refractory metals have been considered periodically for turbine applications.^[1–3] Of all the refractory metals, Nb and Mo have been considered as having the greatest potential for turbine applications.^[2–5] Both Nb and Mo have wide solubility for a number of strengthening additions; Nb is inherently ductile at room temperature and has a relatively low density of 8.56 g/cm³ (lower than Ni); Mo has a higher density (10.2 g/cm³) and relatively low ductility at room temperature. Both Nb and Mo have substantial oxidation limitations in their monolithic form, and their refractory metal–intermetallic composites (RMICs) depend on an intermetallic phase to provide the high-temperature oxidation resistance. For the high-temperature applications envisioned for the next advances in jet engines, Nb- and Mo-silicide-based composites are considered to be the most likely candidates.^[6–10] The melting points of the silicide-containing composites based on these systems are in excess of 1750 °C. Densities of the Nb-silicide-based composites are in the range of 6.6 to 7.2 g/cc, while, for the Mo-RMICs, the densities are 8.6 to 9.4 g/cc. The room-temperature fracture toughness of Nb-silicide-based composite systems has been reported as being >20 MPa \sqrt{m} ,^[9–12] while values for

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the Mo-based RMIC are generally $<15 \text{ MPam}^{0.5}$.^[5,13] The differences in fracture toughness are reflected in the fatigue behavior of the RMICs, with the Nb-RMIC showing a metallic $daldN-\Delta K$ response and the Mo-RMIC displaying a response of a ceramic-like nature.^[11-14]

Turbines for either air or surface applications have several system performance requirements. These include fuel efficiency in producing power or thrust (increasing the combustion temperature generally leads to efficiency improvements), weight, and reliability. Reducing the cooling air increases the efficiency, since less of the work done in compressing the air for combustion is lost to cooling. If the airfoil mass can be reduced significantly, the centrifugal stress on the rotor is reduced, and a smaller, lighter rotor can be employed. This can have a major impact on the thrust-to-weight performance of the turbine. An increase in component-temperature capability can generally be exploited by life extension, by a higher combustion temperature, or by a combination of higher combustion temperature and life extension.

For either of these Nb- or Mo-silicide-based innovative systems to be exploited, a balance of properties must be achieved; these properties must be integrated into a workable design, and an affordable method of fabrication of the composites must be possible. The following discussions will concentrate on the Nb-silicide-based composites, whose density, fracture toughness, fatigue behavior, and fabricability show substantial promise. The preliminary creep and oxidation properties indicate that Nb-silicide-based composites could, with further development, be integrated into blade designs with substantial payoffs in weight and cooling-air savings, relative to fourth-generation superalloy blade designs.

There have been several recent extensive reviews of progress in the development of Nb-silicide-based composites,^[2,3] as well as technical articles on the phase equilibria, mechanical properties, and oxidation behavior of alloys in the Mo-Si-B system.^[5,13,15] The aim of the present article is to review the most recent developments that have occurred in the areas of investment casting, creep resistance, oxidation resistance, and coating technologies.

II. Nb-SILICIDE-BASED IN-SITU COMPOSITES

Both Nb- and Mo-silicide-based composites are toughened by a metallic phase with a volume fraction of between 0.35 and 0.6. The basis for the Nb-silicide-based *in-situ* composites is the binary Nb-Si phase diagram, as shown in Figure 1. The Nb-silicide-based composites consist of a Nb-Si solid solution, with Nb_3Si and/or Nb_5Si_3 silicide phases. Typically, compositions from 12 to 25 pct Si have been investigated (all compositions are provided in atomic per cent in the present article, unless otherwise stated). There is intrinsic thermodynamic stability of the phases in these composites, which is a critical requirement for long-term applications at elevated temperatures. In some composites, a small volume fraction (<0.15) of a NbCr_2 -based Laves phase has also been added for improved oxidation resistance.^[2,3] A typical composition is Nb-19Ti-4Hf-13Cr-2Al-4B-16Si. A typical microstructure of this Nb-silicide composite is shown in Figure 2. This composite consists of Nb with a volume fraction of 0.55, large-scale ($\sim 100 \mu\text{m}$) Nb_5Si_3 with a volume fraction of 0.35, and a fine-scale ($\sim 10 \mu\text{m}$) NbCr_2 -type Laves phase with a volume

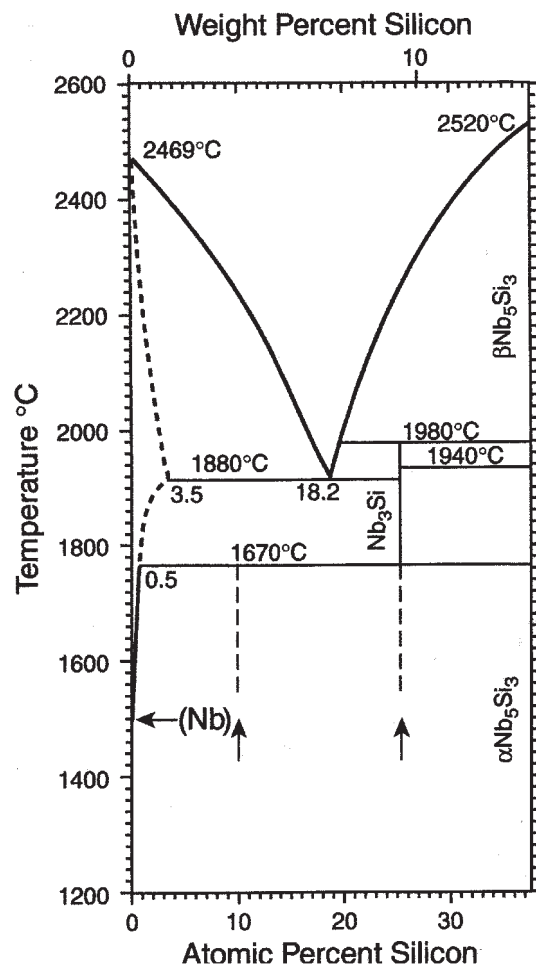


Fig. 1—Binary Nb-Si phase diagram representing the basis for the Nb-silicide-based *in-situ* composites. The range of Si concentrations investigated is shown by the vertical arrows.

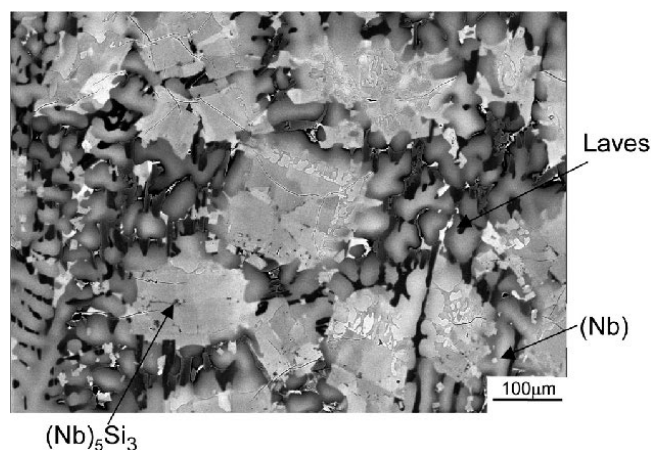


Fig. 2—Typical microstructure (SEM backscattered electron image) of the transverse section of a DS complex Nb-silicide *in-situ* composite consisting of (Nb), Nb_5Si_3 , and a Cr_2Nb type Laves phase. The composite is based on a composition of Nb-19Ti-4Hf-13Cr-2Al-4B-16Si.

fraction of ~ 0.10 . Most of the research programs have focused on developing a fundamental understanding of the mechanical behavior and oxidation resistance of the Nb-RMIC system; there have been essentially no engineering-alloy and

process-development efforts of the form that have been performed for nickel-based superalloys.

In order to establish a balance of mechanical properties that satisfies all of the engineering requirements, alloy development must make engineering trade-offs between high-temperature strength, creep resistance, oxidation resistance, low-temperature ductility, toughness, and damage tolerance. The alloy development must be guided by the design requirements of the particular application under consideration; selection of the airfoil geometry and application environment is a key function. Therefore, a strong coupling of the design community and design requirements with materials development must occur as early as possible in the development cycle. In today's environment, new materials development must be done with full knowledge of the specific design requirements, so that major issues are identified early in the development cycle.

Two of the key properties for airfoil design are the alloy density and elastic modulus, because they have a major impact on the thermal and mechanical design of the rotating elements of the turbine. Table I shows the calculated turbine rotor weight for Nb-silicide composite airfoils (using density and rupture properties reported previously^[9] relative to a current Ni-based superalloy blade and disk configuration. Table I shows that reductions in rotor weight of more than 20 pct can be realized through the substitution of Nb-silicide-based composite airfoils for nickel-based superalloy airfoils in both present and advanced turbine designs.^[16] This type of design-trade study helped to establish the system performance enhancement resulting from the introduction of new materials, such as these high-temperature Nb-silicide composites.

The status of the most recent progress in the material development is reviewed in the present section, with separate discussions of (1) processing, (2) rupture strength, (3) oxidation performance, and (4) coating development.

A. Processing Techniques for Nb-Silicide-Based Composites

Nb-silicide-based composites have been fabricated using a range of processes, including arc melting, ingot casting plus thermomechanical processing,^[2,6,7,12] directional solidification,^[3] vapor deposition, and powder-metallurgy processing.^[3] The reactivity of the Nb alloy melts essentially excludes the use of ceramic-based melting systems. The techniques used previously have all successfully produced laboratory-scale volumes of materials for alloy development and property studies. However, these techniques are not well developed with regard to the production of net-shape airfoils.

Table I. Summary of the Reductions in Rotor Weight—Both High-Pressure Turbine (HPT) and Low-Pressure Turbine (LPT) Weights—That Can Be Realized as a Result of Reduction in Airfoil Weight through the Substitution of Nb-Silicide-Based Composite Airfoils for Nickel-Base Superalloy Airfoils

Rotor Weight Relative to Ni Alloy Baseline	Nb-Silicide Composite
Advanced HPT	saves 20 pct
Current HPT	saves 22 pct
Current LPT	saves 21 pct

From a commercial point of view, investment casting of near-net-shape structures of Nb-silicide composites offers substantial potential because of its proximity to existing airfoil manufacturing practices. To date, investment casting of Nb-silicide composites has received limited attention because of the difficulty of developing the melting capability of the appropriate scale and developing ceramic mold materials capable of withstanding the high melt temperatures. Recently, the feasibility of investment casting thin sheets of selected Nb-silicide composites has been explored using a hybrid arc-melting and drop-casting technique. In this process, the alloys were arc melted using conventional techniques and drop cast into heated ceramic molds. Alumina-based ceramic molds were used in conjunction with low-reactivity face coats. The melt superheat and mold temperature are critical process parameters. The ceramic molds were prepared using conventional slurry techniques, and appropriate mold face coats were developed to minimize mold-metal interaction. Investment-cast plates, with thicknesses from 3 to 8 mm, and simple prototype airfoil shapes have been manufactured using this process. A typical example of a prototype airfoil is shown in Figure 3. A range of Nb-silicide-containing alloys has been investment cast using this approach, including ternary Nb-Ti-Si and multi-component Nb-Ti-Hf-Cr-Al-Si-based compositions.

Figures 4(a) and (b) show the microstructures (backscattered electron images) of two Nb-silicide compositions that were investment cast: a ternary alloy, Nb-34Ti-16Si, and a more complex alloy, Nb-22Ti-2Hf-4Cr-3Al-16Si with small additions of Ge and Sn. Figure 4(a) shows a two-phase composite of Nb and Nb₃Si. The Nb₃Si tP32-type silicide in Figure 4(a) was stabilized by the high Ti concentration. Figure 4(b) shows a two-phase composite of Nb₅Si₃ in an Nb matrix; the Nb₅Si₃ had a volume fraction of ~0.46 and a size of 3 to 40 μm. The Nb₅Si₃ existed as both tI32 and hP16 phases in the microstructure shown in Figure 4(b). The phase distribution and phase compositions in the cast microstructures were similar to those obtained by the other casting processes, such as cold-crucible directional solidification. There was no evidence of any



Fig. 3—Typical investment-cast Nb-silicide composite prototype airfoil based on a composition of Nb-22Ti-2Hf-4Cr-3Al-16Si, with minor additions of Ge and Sn.

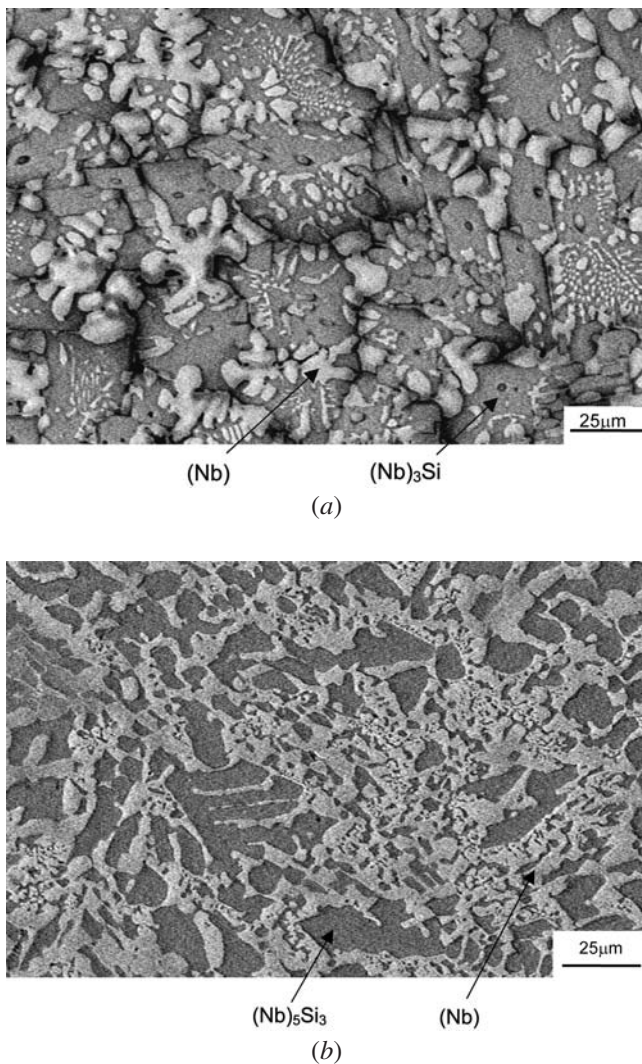


Fig. 4—Microstructures (SEM backscattered electron images) of the transverse sections of two investment-cast Nb-silicide composites based on the following alloys: (a) Nb-34Ti-16Si and (b) Nb-22Ti-2Hf-4Cr-3Al-16Si with minor additions of Ge and Sn.

gross segregation. The bulk oxygen concentration was found to be 670 to 1020 wppm, which is similar to arc-cast Nb-silicide-based composites. Reaction of the mold face coat with Hf in the alloy can lead to HfO_2 particles in the outer regions of the component.

B. Creep Performance

The nominal goal for creep performance is that there must be less than 1 pct creep in 125 hours at temperatures of 1200 °C and stresses of >170 MPa. This goal is shown in conjunction with the oxidation goal in Figure 5. The secondary creep behavior is shown in Figure 5 as a function of stress for both previous, and the most recent, Nb-silicide-based composites.^[2,3] If there is minimal primary creep (typically, there is less than 0.1 pct primary creep in these systems), this corresponds to a secondary creep rate of $2.2 \times 10^{-8} \text{ s}^{-1}$. Primary-creep strains for Nb-silicide-based composites at 1200 °C in tension are shown in Figure 6 for stresses of 35 to 140 MPa. The primary-creep strains of the Nb-silicide-based compos-

ites and those of a typical second-generation single-crystal (2GSX) nickel-based superalloy at 1150 °C are compared; in each case, the primary-creep strains in Nb-silicide-based composites are lower than those in the 2GSX.

The creep behaviors of Nb-silicide-based composites in both tension and compression and at temperatures in the range of 1000 °C to 1200 °C have been described previously,^[2,3] a series of composites has been generated that demonstrated creep rates of $<3 \times 10^{-8} \text{ s}^{-1}$ at 1200 °C and stresses greater than 140 MPa. Detailed fundamental investigations of the effects of alloying additions—such as Hf, Ti, Cr, Al, and Mo—on the creep behavior have also been performed.^[3,17] Creep of Nb-silicide-based composites is controlled by a combined function of creep in the silicide and metallic phases, but at temperatures above 1000 °C, the metallic phase makes only a minor contribution to the creep strength. Creep studies of monolithic Nb_5Si_3 generated from binary and higher-order alloys suggested that creep deformation in Nb_5Si_3 is controlled by diffusion of Nb in the Nb_5Si_3 phase.^[3,18] In this regard, monolithic-phase studies have indicated that complex Nb_5Si_3 -type silicides offer improved creep performance in comparison with complex Nb_3Si -type silicides.^[3]

The density-normalized creep-rupture behavior of a typical Nb-silicide-based composite (based on the composition Nb-25Ti-8Hf-18Si) is compared with the creep-rupture behaviors of directionally solidified and single-crystal Ni-based superalloys in the Larson–Miller plot in Figure 7.^[3,19] The data indicate that the creep-rupture behavior of the Nb-silicide-based composite is similar to that of the third-generation single-crystal superalloy, and that an increase in specific rupture performance results from the substantial reduction in density of the Nb-silicide. However, the rupture life that will be required for application will probably be ~10 times greater than that which has been reported for the Nb-silicide-based composites.^[3,16]

C. Oxidation

Figures 5 and 8(a) describe the typical cyclic oxidation resistance for the uncoated Nb-silicide-based composites. The measured material loss of a typical Nb-silicide composite is shown as a function of temperature. The typical cyclic oxidation testing conditions have been reported previously.^[2,9] The increase (~10 times) in oxidation resistance of the most recent Nb-silicides in comparison with those developed prior to about 1998 is evident.^[3] There are two cyclic-oxidation-resistance goals for Nb-silicide composites: a short-term goal and a long-term goal. The short-term goal is for a loss of $<200 \mu\text{m}$ in 10 hours of test-stand demonstration exposure at 1370 °C. The long-term goal is for a loss $<25 \mu\text{m}$ in 100 hours at 1315 °C. The oxidation goals for these advanced high-temperature materials are derived from the requirement to achieve the oxidation life at 1315 °C that 2GSX superalloys presently display at 1150 °C.^[3,16,19]

The short-term goal is to achieve sufficient oxidation resistance in the uncoated condition to survive a proposed demanding engine test of the form shown in Figure 8(b). The uncoated Nb-silicide-based composites will be required to lose $<200 \mu\text{m}$ in 10 hours of test-stand demonstration exposure at 1370 °C. The present cyclic oxidation behavior satisfies the short-term goal of a hypothetical engine mission shown in Figure 8(b); calculated losses are 100 to 125 μm ,

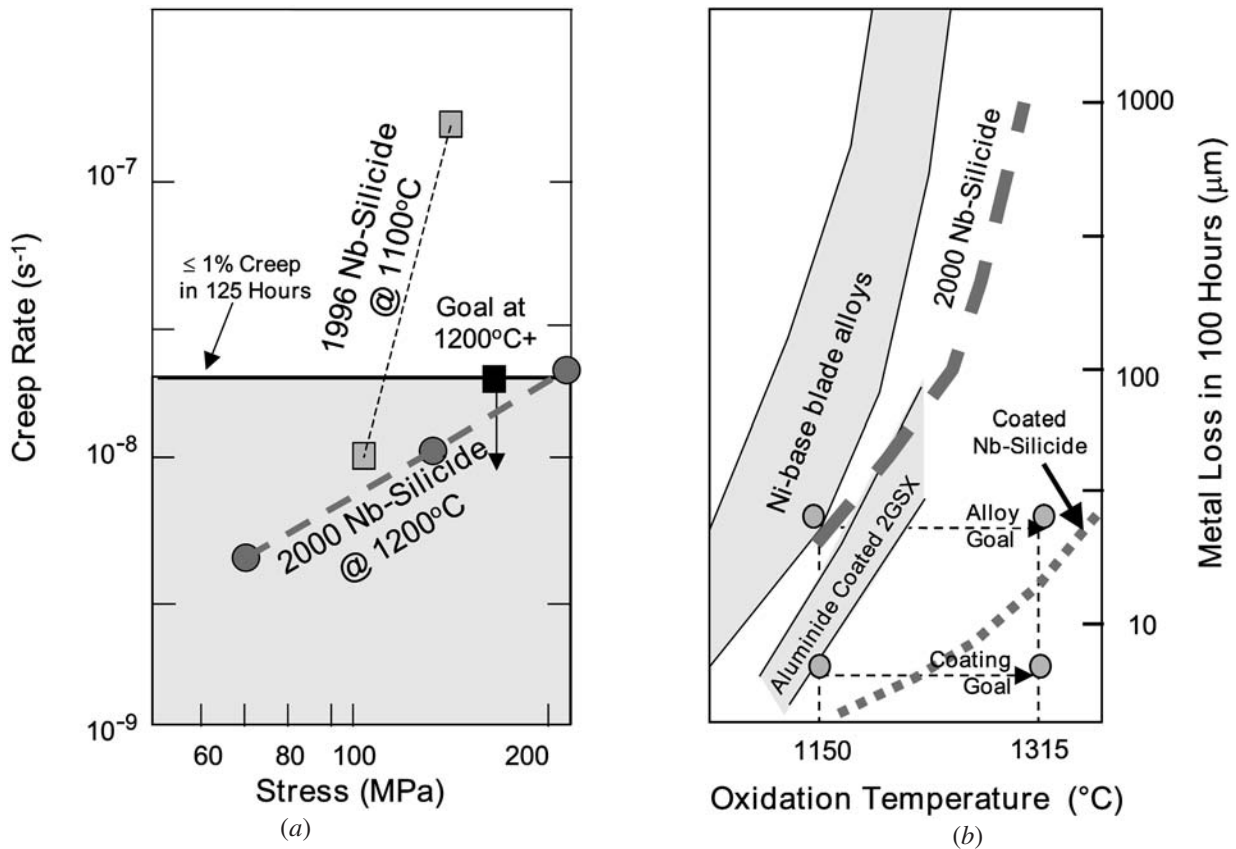


Fig. 5—A broad range of properties, such as (a) rupture strength, (b) cyclic oxidation behavior, and damage tolerance, must be balanced for new materials to be employed in a turbine engine. In particular, a creep strain of <1 pct is desired in 125 h at >1200 °C for tensile stresses of at least 175 MPa (25 kpsi); oxidation losses for the Nb-silicide-based composite and its coatings at 1315 °C must be no more than the losses that superalloys and their coatings experience at 1150 °C. The data for the 1996 Nb-silicide are for a Nb-25Ti-8Hf-2Al-2Cr-16Si alloy, as reported in Reference 9.

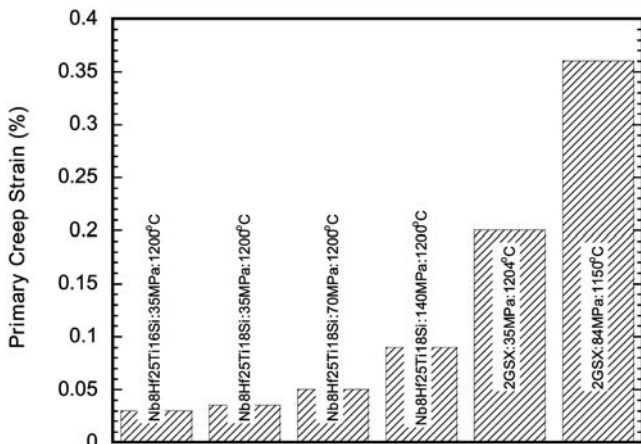


Fig. 6—Primary tensile creep strains for Nb-silicide-based composites (Nb-8Hf-25Ti-16Si and Nb-8Hf-25Ti-18Si) at 1200 °C for stresses of 35–140 MPa. Compositions of Nb-8Hf-25Ti-16Si and Nb-8Hf-25Ti-18Si are shown, as being typical of for Nb-silicide-based composites. Also shown are primary creep strains of a second generation single crystal nickel-base superalloy (2GSX) at 1150 °C. In each case, the primary creep strains in Nb-silicide-based composites are lower than those in the 2GSX.

compared to the allowable material loss of 190 μm. However, the long-term goal (Figure 8(a)) requires a further order-of-magnitude reduction in material loss upon oxidation.

The best current Nb-silicide-based composites possess a temperature capability (<25 μm lost in 100 hours) of ~1200 °C. Achieving the 1315 °C goal and simultaneously achieving the rupture-strength, fatigue, and fracture-toughness goals represents significant challenges. The most recent turbine airfoil applications have developed a greater dependence on coatings because of the high surface temperatures that are presently employed; it is likely that Nb-silicide composites can only be used with a similar coating dependency. For this reason, there has been significant recent effort on the development of both bond coats and TBCs for Nb-silicide-based composites; the performance of the Nb-silicide-based composite with a bond coat is indicated in Figure 5(b).

In recent alloy developments, several design-of-experiment iterations have been performed to characterize the composite oxidation behavior as a function of bulk alloy composition.^[3] The effects of Ti, Hf, Si, Cr, and Al on oxidation behavior have been determined for temperatures from 760 °C to 1370 °C; transfer functions describing these relationships have been reported previously.^[3] The composition-oxidation relationship varies with temperature, and, as a result, the optimization of chemistry for oxidation resistance will need to consider the length of service in each temperature regime. However, optimum oxidation resistance can be achieved for chemistries with Nb: (Ti + Hf) ratios of 1.8 to 2.1 and Si levels of 17 to 19 pct; these composition ranges also offer excellent creep behavior. Both Cr and

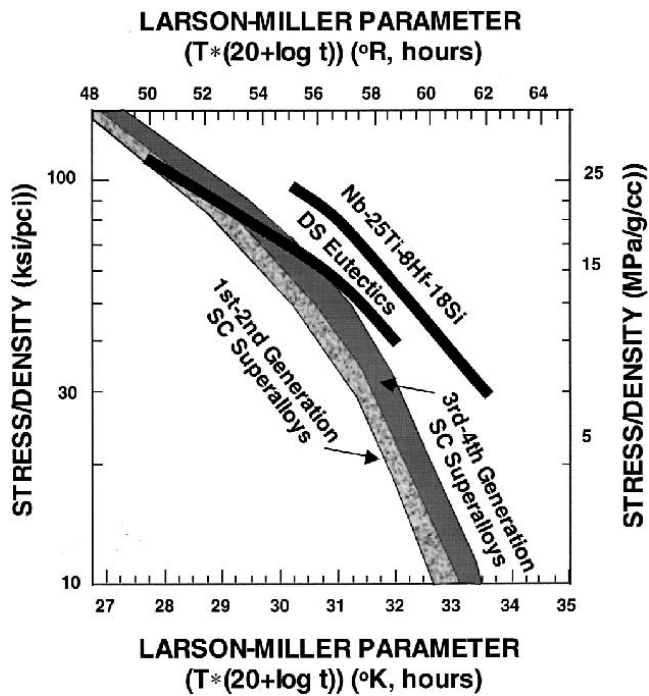


Fig. 7—Density-normalized creep rupture strength of a Nb-silicide composite based on a composition of Nb-25Ti-8Hf-18Si. The data are compared to those for single-crystal superalloys and directionally solidified eutectics using the Larson–Miller parameter ($^{\circ}\text{R}$, hours; and $^{\circ}\text{K}$, hours), (pci refers to pounds/cubic inch).

Al have a strong beneficial role on oxidation behavior. Cr stabilizes the Cr-rich Laves phases at bulk compositions of greater than ~ 5 pct.^[2,3,8]

There have also been several previous studies^[2,3] on the substitution of elements—such as Ge, B, and Fe—for some of the main alloying elements; these include partial substitution of Ge and B for Si and partial substitution of Fe for Cr. The greatest positive effects have been observed for Ge, at levels up to ~ 6 pct. Additions of B (2 to 6 pct) can also be beneficial, but higher levels of B reduce the oxidation resistance. Additions of Fe are almost equally as effective as additions of Cr at levels up to 5 pct, but combinations of Cr and Fe are no more effective than Cr alone for the same total concentrations.

Refractory metals can be susceptible to pesting damage at intermediate temperatures (generally, < 850 $^{\circ}\text{C}$). Pesting is the term that is often employed to describe preferential oxidation at microstructural features, such as grain boundaries, which can lead to self-pulverization in samples cycled from room temperature to relatively low temperatures; it is often coupled with oxygen embrittlement. Additions of Al and Hf are known to reduce the pesting susceptibility of Nb-based alloys, but some Nb-silicide-based composites can still be attacked in this manner. Alloying with tin has been very effective in managing pesting damage, such that it has been essentially eliminated in the temperature regime of 750 $^{\circ}\text{C}$ to 950 $^{\circ}\text{C}$. The addition of tin has minimal effect on oxidation at temperatures above 1200 $^{\circ}\text{C}$.

Pesting behavior has been investigated in a number of Nb-silicide composites using air exposures at temperatures of 980 $^{\circ}\text{C}$, 870 $^{\circ}\text{C}$, and 760 $^{\circ}\text{C}$; typically, the samples were held at the test temperature for 60 minutes, cooled to room tem-

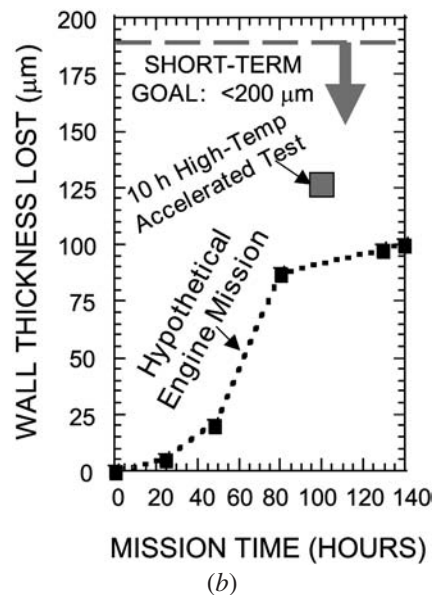
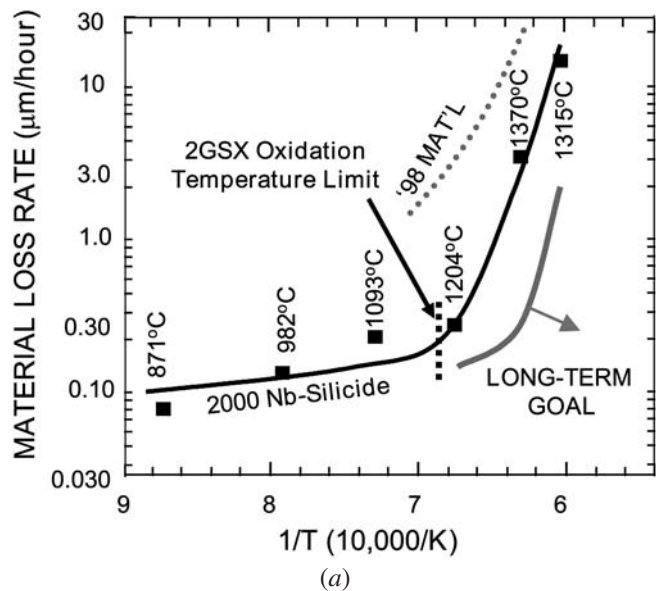


Fig. 8—(a) Measured material loss (cyclic oxidation behavior) of the Nb-silicide composites as a function of temperature, showing the increase ($\sim 10\times$) in oxidation resistance of the most recent Nb-silicides in comparison with those developed in 1998.^[3] (b) The present oxidation behavior satisfies the short-term goal of a hypothetical engine mission (with calculated losses of 100 to 125 μm , compared to an allowable 190 μm of material loss). However, the long-term goal (a) requires another ten fold reduction in material loss upon oxidation.

perature, and then reheated to the test temperature. At the highest temperature, there is essentially no evidence of pesting after 100-hour exposures for a very wide range of alloy chemistries. However, at 870 $^{\circ}\text{C}$, pesting was observed in alloys that did not contain tin. Initial investigations indicated that alloys that contained 1.5 pct tin were essentially immune to pesting, as shown for a series of alloys in Figure 9. Subsequently, a number of different alloys were prepared to investigate the tin effect in more detail.

Table II compares the pesting response (as measured by the degree of cracking around the perimeter of the sample

as a result of the oxidation test) of Nb-silicide composite alloys with and without 1.5 pct tin after 200 hours of exposure at 870 °C. In alloys without tin, cracking was generally evident around essentially the entire perimeter of the 2.5-mm-diameter pins. The cracking was generally restricted to the first 25 to 100 μm, and the cracks propagated through both the silicide and metal phases. Only one tin-free alloy (B3) did not show full-perimeter cracking. In comparison, most of the alloys with 1.5 pct tin showed less than 1 pct cracking around the perimeter of the oxidation pin. The strong beneficial effect of tin was observed at Nb:(Ti + Hf) ratios of 1.25 to 2. In addition, alloys containing tantalum and tungsten with tin (not shown in Table II) behaved in the same manner. Additions of up to 1.5 pct tin were equally effective as additions of 4.5 pct tin. The mechanism by which

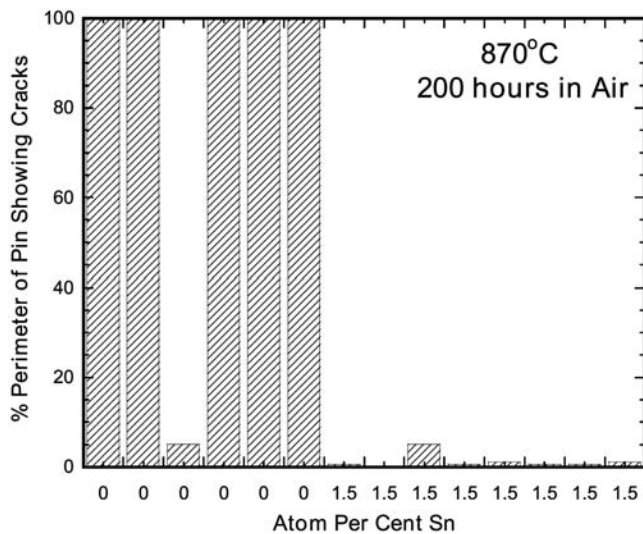


Fig. 9—Low-temperature (870 °C) cyclic oxidation/cracking behavior for Nb-silicide composites of a range of compositions. The alloys that contained tin displayed an extremely low level of damage. The typical composition of an alloy that contained 1.5Sn was Nb-24.5Ti-1.5Hf-6Cr-3Fe-2Al-2B-16Si-6Ge.

tin prevents pitting has not been investigated in detail. Further investigations are required.

Several Nb-silicide composite alloys were also subjected to oxidation at 760 °C for 200 hours. These composites (both with and without tin) showed resistance to pitting for Nb:(Ti + Hf) ratios of 1.5, but more rapid attack was observed for Nb:(Ti + Hf) ratios of 2.5. There are alloy modifications in addition to tin that can also be applied to address low-temperature embrittlement. Protective Nb-silicide coatings are also very effective in both the low-temperature regime as well as the high-temperature regime.

The short-term oxidation goal for Nb-silicide composites has been achieved (losses of <200 μm in 10 hours of test-stand demonstration exposure at 1370 °C). Achievement of the long-term goal (<25 μm in 100 hours of oxidation exposure at 1315 °C) while also maintaining the required balance of mechanical properties is still a challenge. There are also substantial opportunities in employing these Nb-silicide-based composites at temperatures less than the target surface temperatures described in the present article, because they can also offer substantial reductions in airfoil weight and cooling air.

D. Coatings

The fourth-generation single crystal nickel-based superalloys have been developed to provide greater high-temperature strength, but this is typically at the expense of oxidation resistance. Recent superalloy airfoils have, therefore, been designed with a greater dependence on coatings, because of the high surface temperatures that are presently employed. A similar approach is necessary for Nb-silicide composites. As a result, there has been significant recent effort on the development of both bond coatings and TBCs for Nb-silicide-based composites.^[16] A series of high-performance oxidation-resistant coatings have been developed that provide protection for Nb-silicide-based composites at temperatures of up to 1370 °C for more than 100 hours. The coating-deposition technique and subsequent processing are critical to performance. A cross section of a typical silicide coating is shown in both the initial

Table II. Effect of Low-Temperature Cyclic Oxidation/Cracking (870 °C for 200 Hours) of a Range of Nb-Silicide Containing Alloys, as Described by the Percentage of the Diameter of the Pin That Showed Cracking; the Additions of 1.5 Pct Tin Essentially Eliminate Cracking/Embrittlement in Many of the Nb-Silicide-Based Composites

Alloy	Nb/(Ti + Hf) Ratio	Cr + Fe	B	Ge	Sn	Microns of Radius Increase 870 °C	Percent of Pin Perimeter Showing Cracking
B1	1.5	9	2	6	0	25	~100
B9	1.5	9	2	6	1.5	6	0
B2	1.5	9	2	2	0	200	~100
B10	1.5	9	2	2	1.5	0	<5
B3	1.5	12	2	6	0	0	<5
B11	1.5	12	2	6	1.5	0	0
B4	1.5	12	2	2	0	19	~100
B12	1.5	12	2	2	1.5	-12	<1
B13	1.5	9	0	2	0	12	~100
B15	1.5	9	0	2	1.5	6	0
B14	1.5	12	0	2	0	87	~100
B16	1.5	12	0	2	1.5	0	0
B22	1.25	12	2	6	1.5	12	0
B24	2	12	2	6	1.5	12	<1
	2Al	1.5Hf		Si + Ge = 22			

as-coated condition (Figure 10(a)) and after exposure at 1370 °C for 100 hours (cycles) (Figure 10(b)). The cracks that formed in the as-deposited coating are probably due to the brittle nature of the phases in the coating and their different thermal-expansion behaviors. It is important to note that the cracks in the coating rapidly oxidize and effectively blunt and seal the cracks, thereby minimizing oxygen penetration of the substrate. Figure 10(b) shows that the cracks do not propagate with further high-temperature exposure or thermal cycling.

In addition to silicide-reaction-protective coatings, TBCs and associated deposition technologies have also been explored for Nb-silicide composites.^[16] A series of tests have been performed on TBC-coated Nb-silicide composites, including furnace cycling tests (FCTs) and controlled-temperature-gradient tests (jet-engine thermal simulation (JETS)). Test buttons of 25 mm in diameter and 3 mm in thickness were coated with both the silicide bond coat and a TBC and were then subjected to the FCTs to 870 °C

(1600 °F), 1200 °C (2200 °F), and 1370 °C (2500 °F). During the FCT, the specimens were heated to the test temperature for 1 hour in air and then taken out of the furnace and cooled for 10 minutes with fan air. The specimens were then reloaded into the furnace at temperature. These tests were repeated for 100 cycles for each temperature. No internal oxidation of the Nb-silicide composite substrate was observed, and no peeling was observed at any of the test temperatures. In addition, the TBC adhered to the bond coat after the FCT for 100 cycles at all temperatures up to 1370 °C. After exposure at 1370 °C, a layer of thermally grown oxides formed, and there was some internal oxidation on the upper third of the bond coat, indicating that the bond coat still had significant life remaining after the 100-hour exposure. Figure 10(b) shows that very little interaction occurred between the coating and the substrate, reflecting the excellent stability of the silicide bond coat. The coating has also been tested at 1430 °C, but for only 50 hours (cycles). Although there was significant growth of an interaction zone at 1430 °C, the coating was still protective and there was no internal oxidation. The thermal expansion of the Nb-silicide is similar to that of the yttria-stabilized zirconia TBC^[3,20] (unlike the case for superalloys, where the thermal expansion of the superalloy is generally greater than that of the TBC), so interface thermal stresses are reduced, even when cycling up to 1430 °C.

High-temperature gradient testing of the Nb-silicide substrates coated with both bond coats and TBCs has been conducted using a JETS test, as shown in Figure 11. Samples with a diameter of 25 mm and a thickness of 3 mm were coated with a bond coat and a 250- μ m-thick TBC. These coupons were subjected to a high thermal gradient by heating the front face of the TBC with a high-velocity combustion flame and cooling the rear surface of the substrate with a cooling air jet, as shown schematically in Figure 11(a). The temperatures of the front face of the TBC and the rear surface of the substrate were measured using two-wavelength optical pyrometry. By adjustment of the H₂/O₂ gas mixture and the flow rates, the surface of the Nb-silicide-composite substrate was maintained at 1090 °C while the TBC surface was maintained at 1370 °C. The rear surface of the substrate was adjusted from 1090 °C to 1260 °C, and the TBC surface was adjusted from 1370 °C to 1790 °C, as shown in Table III. The bond-coat temperature was estimated for each condition using measured values of the thermal conductivity for the Nb-silicide composite and the TBC. The gradients from the front to the rear of the coupon were, therefore, in the range of 280 °C to 530 °C. The test was run in a cyclic mode: the TBC was exposed to high temperature for 1 hour and then rapidly cooled by rotating the button under a high-velocity cooling jet for 15 minutes. The button was then rotated back into the flame for the next cycle.

A Nb-silicide coupon coated with a bond coat and a TBC was cycled for 10 cycles to a TBC temperature of 1370 °C. Essentially no damage of the TBC and bond coat was detected. This test was repeated at 1510 °C, and a similar result was obtained.

The test was also repeated at higher TBC temperatures of 1650 °C and 1790 °C. At 1790 °C, the TBC separated at the center of the coupon after two cycles, because the TBC became disconnected from the cooled Nb-silicide substrate and bond coat; as a result, the TBC temperature increased, and it peeled away from the center of the coupon while

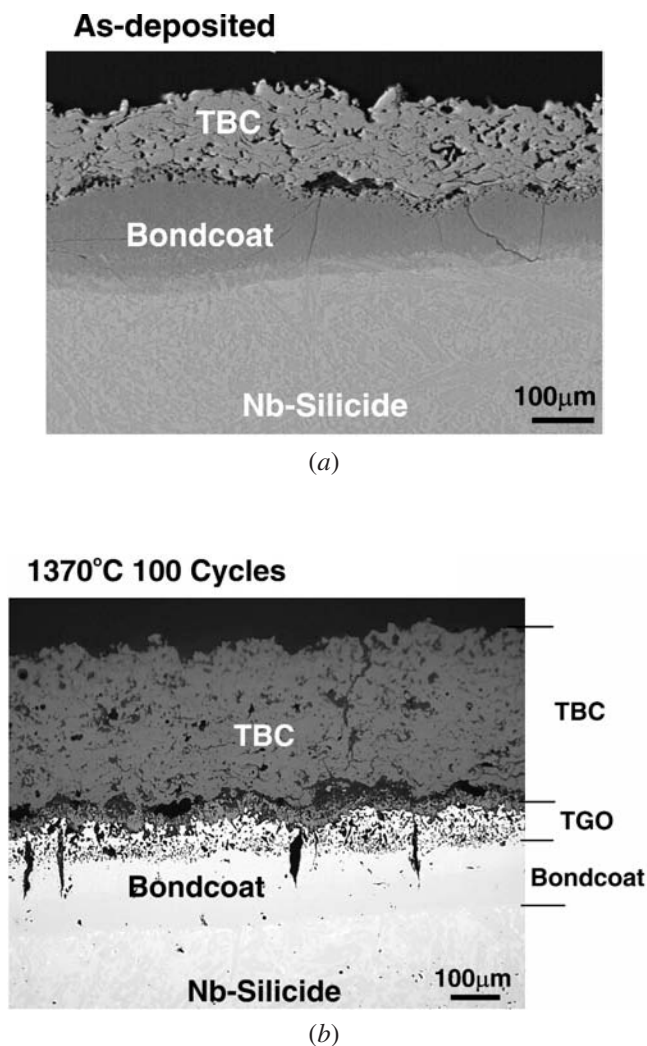


Fig. 10—Micrographs of a silicide-based coating developed for Nb-silicide composites showing the microstructure (a) in the as-deposited condition and (b) after cyclic exposure at 1370 °C for 100 h. The cracks that were observed in the as-deposited coating did not propagate during cyclic exposure.

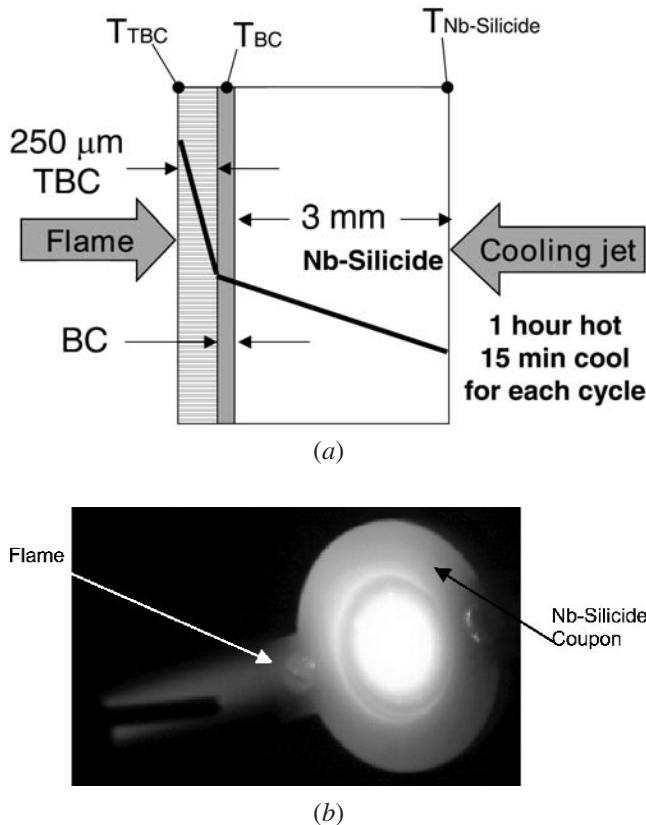


Fig. 11—High-temperature gradient JETS test. (a) A cross section of the sample (including the bond coat and the substrate) and the thermal configuration; the disposition of the hot flame and the cooling jet are shown. (b) The 25-mm-diameter coupon under the hot H_2/O_2 flame. Each test cycle consisted of exposure to the thermal gradient for 1 h followed by a 15 min cool.

Table III. Temperatures of the TBC, BC, and Nb-Silicide as Measured during the JETS Test; the BC Temperature Was Calculated Using Measurements of the Temperatures of the TBC and Nb-Silicide Substrate, Together with Thermal Conductivity Measurements

TBC Temperature (°C)	BC Temperature (°C)	Temperature Nb-Silicide (°C)
1370	1225	1090
1510	1315	1150
1650	1405	1200
1790	1490	1260

remaining anchored at the cooler rim. The photograph of the sample in Figure 11(b) also indicates that there is a very large additional radial temperature gradient; the central third of the diameter is at the maximum temperature, while the rim of the sample is substantially cooler.

The performance of the coated Nb-silicide composite in both the FCT and JETS tests is very encouraging. However, coated Nb-silicide-based composites are still in the early stages of development. Although the coatings developed to date have shown excellent oxidation protection, coating development for the advanced composites requires research on new compositions, as well as coating deposi-

tion technologies. The influence of coatings on the mechanical properties—such as creep, fracture toughness, fatigue, and ballistic impact—of the base composites needs to be examined in detail.

III. SUMMARY

Very-high-temperature Nb-silicide *in-situ* composites are important candidates for future turbine engine components. Nickel-based superalloy airfoils presently have maximum operating surface temperatures of ~ 1150 °C, but advanced turbine designs require airfoils that can operate equally successfully at temperatures above 1300 °C; this high-temperature performance requires further development of materials, such as Nb-silicide-based composites, that possess improved rupture and oxidation resistance. Recent efforts have shown excellent progress in the development of processing techniques, rupture resistance, oxidation resistance, and coatings, including both bond coatings and thermal-barrier coatings.

Hot extrusion, directional solidification, and investment casting have all been used successfully to produce Nb-silicide composites. Recent investment-casting mold developments have shown excellent potential for thin-wall airfoils. The rupture capability of the Nb-silicide composites has been shown to exceed that of 2GSX Ni-based alloys. In addition, the specific rupture resistance is further improved, because Nb-silicide composites have a density ~ 20 pct lower than that of the most recent superalloys. The oxidation resistance of the Nb-silicide composites is sufficient to qualify for near-term engine testing specifications, but further improvements are required to satisfy the long-term design requirements. In addition, the pioneering silicide-coating chemistries and processes for Nb-silicide-based *in-situ* composites have demonstrated excellent oxidation resistance at temperatures up to at least 1370 °C. Thermal-barrier coatings have also been explored, and thermal cyclic oxidation testing in both isothermal and controlled-temperature-gradient testing have shown excellent retention/survivability of TBCs at temperatures up to 1370 °C in an isothermal furnace cycling test and at temperatures up to 1650 °C in a JETS test. There are also great opportunities for exploiting these low-density materials at less than the target surface temperatures, because they offer substantial reductions in airfoil weight and cooling air.

Additional work is required to generate an improved understanding of the mechanisms that control properties such as fracture toughness, fatigue-crack growth, tensile strength, creep performance, and stress-rupture performance, before these alloy systems can be considered for service. There is also a need for further research on the effects of processing, alloy chemistry, and microstructural control on the composite properties. Manufacturing multiphase Nb-silicide components poses significant equipment and process challenges. Process developments are required to enhance Nb-silicide-based composite properties and to establish the capability to manufacture complex articles of these composites. Investment casting of Nb-silicide-based composites offers a relatively low-cost processing approach for fabricating near-net-shape components, such as blades and vanes. However, the casting methods are still in their infancy, and extensive efforts are required to identify high-temperature mold materials and face

coats that are compatible with the parent Nb-silicide-based composite alloy compositions.

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