Abstract

Nickel-base superalloys exhibit excellent creep strength, oxidation resistance, and fracture toughness. This spectacular combination of properties did not come without effort – it required many decades of basic and applied research. However, nickel-base superalloys are approaching one fundamental limitation – their melting point. Since advanced superalloys melt at temperatures on the order of 1350°C, significant strengthening can be obtained only at temperatures below 1150°C. Presently, attention is focused on three materials systems capable of substantially higher service temperatures: niobium silicides, molybdenum borosilicides, and iridium-base superalloys. Each of these systems has its advantages and disadvantages. The purpose of this review is to provide an objective assessment of these three systems, to point out critical issues, and to suggest topics for further research.

Introduction

Historical Developments

In order to achieve service temperatures higher than those of nickel-base superalloys, materials with significantly higher melting points are required. In the sixties, refractory alloys based on Nb and Mo were considered, but their oxidation resistance was inadequate and no sufficiently effective protective coating systems were found. More recently, systems based on MoSi₂ and NiAl were considered. Although these systems, in particular MoSi₂, have excellent oxidation resistance, their creep strength could not be improved to match or exceed that of nickel-base superalloys. Therefore interest in MoSi₂ and NiAl-
based system has waned. Presently, attention is focused on niobium silicides, molybdenum borosilicides, and iridium-base superalloys.

Requirements for new Materials Systems

**Mechanical properties**

For materials replacing nickel-base superalloys, Bewlay et al. [1,2] suggest as a nominal goal that the creep strength should be greater than 170 MPa at a creep rate of $2 \times 10^{-8} \text{ s}^{-1}$ at 1200°C. This requirement assumes the density of niobium silicide systems, which is typically 7 g/cm$^3$. For materials systems with different density values the required creep strength has to be adjusted accordingly as summarized in Table I. In density-compensated terms, the stress level needs to be above $170/7 \text{ MPa/(g/cm}^3) \approx 25 \text{ J/g}$.

It is desirable that the alloys considered show some degree of metallic behavior to distinguish them from ceramic candidate materials. This requires that they contain at least a small volume fraction of a ductile, metallic phase. Bewlay et al. [3] consider a fracture toughness of 20 MPa m$^{1/2}$ to be the minimum value for critical components.

**Table I: Creep strength goal at a temperature of 1200°C and a creep rate of $2 \times 10^{-8} \text{ s}^{-1}$.

<table>
<thead>
<tr>
<th>Materials System</th>
<th>Density, g/cm$^3$ (typical)</th>
<th>Creep Strength, MPa</th>
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</thead>
<tbody>
<tr>
<td>Niobium silicide</td>
<td>7</td>
<td>170</td>
</tr>
<tr>
<td>Molybdenum borosilicide</td>
<td>9.5</td>
<td>230</td>
</tr>
<tr>
<td>Ir and Pt-Base</td>
<td>20</td>
<td>490</td>
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</table>

**Oxidation resistance**

For the oxidation resistance, Bewlay et al. [1,2] suggest a recession rate of less than 0.25 µm/hour at 1315°C. They derive this goal from the requirement of achieving the oxidation life at 1315°C that 2GSX nickel-base superalloys presently exhibit at 1150°C [2]. Oxidation-resistant coatings, while very important, exceed the scope of this paper and will not be considered. Also, the so-called pesting of refractory metal silicides that can occur at temperatures in the range of 500 to 800°C will not be addressed. This is because even if the pesting problem cannot be solved, one may be able to engineer around it by minimizing the time spent in this temperature range.
Microstructure

For a given volume fraction of the different phases in an alloy, the microstructural scale and morphology are important. Taking, for example, a two-phase system with one phase occurring in the form of individual particles, two extreme cases of microstructures are illustrated in Fig. 1. Let us assume one phase to be oxidation-resistant, yet brittle (Mo$_5$SiB$_2$) and the other to be ductile, relatively weak in creep, and prone to oxidation (Mo). If the Mo occurs in the form of isolated particles (Fig. 1a), the continuous Mo$_5$SiB$_2$ phase provides oxidation resistance. However, little or no ductility is expected, since in a tensile test the Mo$_5$SiB$_2$ matrix would be expected to break in a brittle manner. The isolated Mo particles provide little, if any, ductility and toughening. If, on the other hand, the Mo phase is continuous (Fig. 1b), it can give rise to increased ductility and fracture toughness. However, because of the continuous nature of the Mo phase, the oxidation and creep resistance can be negatively affected.

The size scale of the microstructure is important in two respects. On the one hand, for a given $\alpha$-Mo volume fraction, the fracture toughness is expected to increase when the size of the Mo phase increases [4]. On the other hand, when the width of the continuous Mo phase becomes smaller than the length of dislocation pile-ups predicted from the applied stress and the elastic properties of the Mo phase, the mechanical properties of the material cannot be predicted from the bulk properties of the individual phases. Nickel-base superalloys with microstructures such as that shown in Fig. 2 [5] are a prime example for this effect. They exhibit much higher creep resistance than would be expected from the bulk properties of the individual phases [6]. This is, at least in part, due to the occurrence of small $\gamma$ (Ni solid solution) channels between the $\gamma'$ ("Ni$_3$Al") precipitates.

![Fig. 1. Schematic illustration of possible microstructures.](image)
Subramanian et al. determined the constitutive equation for the compressive creep behavior of $\text{Nb}_5\text{Si}_3$ [7]. The creep strength of $\text{Nb}_5\text{Si}_3$ is more than adequate – the temperature corresponding to a creep rate of $2 \times 10^{-8}$ s$^{-1}$ at an applied stress of 170 MPa is approximately 1350°C, much higher than the goal of 1200°C. A practical alloy, however, requires the Nb solid solution phase ($\alpha$-Nb) in order to provide adequate fracture toughness. Since pure Nb exhibits a ductile-brittle transition temperature (DBTT) of approximately -200°C [8] it is well suited as a toughening phase. Bewlay et al.’s alloys [2] contain $\alpha$-Nb volume fractions varying from 35 to 60%. In cast alloys, the $\alpha$-Nb phase occurs often in the form of individual particles in a continuous matrix. Bewlay et al. have shown that suitable alloying can produce a continuous $\alpha$-Nb phase – the $\alpha$-Nb phase in investment-cast Nb-22Ti-2Hf-4Cr-3Al-16Si, at% (note that compositions will be stated in at% in this paper) is continuous with a volume fraction of approximately 55%. Therefore, the niobium silicide system offers considerable flexibility in its microstructural design.

Niobium silicides containing the $\alpha$-Nb phase exhibit high room temperature fracture toughness values. In Nb-10 at% Si, crack initiation occurs at stress intensities between 5 and 20 MPa m$^{1/2}$ [9]. Also, a steep rise in the crack growth resistance is observed and stress intensities as high as 36 MPa m$^{1/2}$ can be
reached. In more complex Nb-Ti-Si-Al materials, fracture toughness values on
the order of 20 MPa m$^{1/2}$ can be obtained [3].

During oxidation in air, the recession rate of niobium silicides increases
rapidly above 1200°C [1,2]. At 1315°C it is approximately 2.5 µm/h, a factor
10 higher than the goal of 0.25 µm/h. The details of the oxidation mechanism
have not been studied to date, although quantitative relationships for the effect
of alloying additions such as Si, Cr, Ti, Al, and Hf have been developed [3]. In
particular, it is not clear whether the relatively high oxidation rate is due to the
presence of the α-Nb phase, or whether the intermetallic phases present in these
alloys also undergo substantial oxidation. In any case, achieving the required
oxidation resistance while simultaneously achieving the design requirements for
the creep strength and the fracture toughness remains a challenge [2].

Molybdenum borosilicides

Molybdenum borosilicides have attracted considerable interest as a result of
Akinc et al.’s [10] and Berczik’s work [11, 12]. Akinc et al. focused on Mo$_5$Si$_3$
containing Mo$_5$SiB$_2$ and Mo$_3$Si. Thom et al. [13] noted excellent oxidation
resistance of such alloys at 1000°C. Meyer et al. [14] showed that, after an
initial recession of 1 to 2 µm, virtually no further recession occurs after 50 hours
at 1300 or 1450°C. However, since all the three phases involved are brittle, it
would be difficult to engineer adequate fracture toughness values. Berczik
focused therefore on alloys containing not only Mo$_5$SiB$_2$ and Mo$_3$Si, but also a
Mo solid solution phase (α-Mo). Since the Mo phase is expected to be ductile,
at least at high temperatures, these materials exhibit some degree of fracture
toughness, albeit at the expense of oxidation resistance.

Supatarawanich et al. [15] have investigated the oxidation resistance of 6 cast
Mo-Si-B compositions at temperatures up to 1300°C. For Mo-10Si-10B, which
contains between 40 and 50 vol% α-Mo, the recession during cyclic oxidation at
1300°C is rapid during the first few hours: it is approximately 60 µm. This
behavior is commonly observed in Mo-Si-B alloys – Mo is removed as volatile
MoO$_3$ until the surface is sufficiently enriched in Si to minimize further Mo loss.
After the initial loss of material, the recession rate becomes quite low, on the
order of 0.1 µm/h. Thus, if the initial recession can be alleviated, which might
for example be achieved by coating with Si or by a pre-oxidation treatment, the
oxidation resistance of Mo-Si-B alloys may be adequate.

Alur et al. [16] carried out compression tests on powder-metallurgically
processed Mo-6Si-8B over a wide range of temperatures and strain rates. Their
material consisted of Mo$_5$SiB$_2$ particles in a continuous Mo solid solution. The
\(\alpha\)-Mo volume fraction was approximately 65\%. Extrapolation of Alur et al.’s 1200°C creep data from \(10^{-7}\) to \(2\times10^{-8}\) s\(^{-1}\) indicates a creep strength of 140 MPa, which is about 65\% of the target. Cast and annealed Mo-12Si-8.5B contains approximately 40 vol\% \(\alpha\)-Mo particles in a continuous matrix of Mo\(_3\)Si and Mo\(_5\)SiB\(_2\) [17]. Its tensile creep strength at 1200°C and \(2\times10^{-8}\) s\(^{-1}\) is 50 MPa [17], and its (extrapolated) compressive creep strength is 75 MPa [18]. It is not clear at the present time why Mo-12Si-8.5B, which contains a higher volume fraction of intermetallics than Mo-6Si-8B, appears to be weaker in creep than Mo-6Si-8B under these conditions. It is also not clear why Mo-12Si-8.5B has a significantly lower stress exponent for creep than Mo-6Si-8B, namely, \(\sim 3\) vs. \(\sim 7\).

Alloying can increase the creep strength dramatically. Extrapolation of compression test data for a Mo-19.5Nb-12Si-8.5B cast and annealed alloy suggests a creep strength of 260 MPa at 1200°C and \(2\times10^{-8}\) s\(^{-1}\) [18]. It appears therefore that molybdenum borosilicides are capable of reaching the required creep strengths.

The room temperature fracture toughness of molybdenum borosilicides is generally lower than that of niobium silicides. A possible reason for this is the low DBTT of Mo which is near room temperature [8]. Molybdenum borosilicides processed by melting and casting tend to contain discontinuous \(\alpha\)-Mo particles (Fig. 3a). Powder processing involving removal of Si from the powder surfaces prior to consolidation [19] can be employed to process molybdenum borosilicides with a continuous \(\alpha\)-Mo matrix phase (Fig. 3b). For a continuous, coarse \(\alpha\)-Mo phase with a volume fractions on the order of 50\% a room temperature initiation fracture toughness of 12 MPa m\(^{1/2}\) has been observed [20]. Also, R-curve behavior has been observed, with stress intensity factors reaching values as high as 21 MPa m\(^{1/2}\). The fracture goal of 20 MPa m\(^{1/2}\) can therefore be met, but at the expense of the oxidation resistance – this particular material shows no oxidation resistance.
Iridium-base Superalloys

In both Ir-base and Pt-base superalloys, microstructures similar to those of nickel-base superalloys can be obtained. Good examples are Ir-17 at%Nb heat treated for 24 h at 1800°C [21] or Pt-12Al-6Cr-6Ni (at%) [22] homogenized at approximately 1500°C followed by air cooling.

The compressive creep strength of Ir-based superalloys has been determined at 1500°C in vacuum for Ir-17 at%Nb [23] and at 1400°C for Ir-16.3Pt-10.2Nb-2.7Al [24]. Extrapolation of the measured creep strengths to a temperature of 1200°C, assuming the activation energy for self-diffusion in Ir, 438 kJ/mol [25], a stress exponent of 5, and a strain rate of $2 \times 10^{-8} \text{s}^{-1}$ predicts creep strengths of 460 and 170 MPa, respectively. There is considerable uncertainty in these extrapolations. However, it appears likely that the creep strength goal for iridium-base superalloys, a creep strength of 490 MPa at 1200°C and $10^{-8} \text{s}^{-1}$, can be met.

Süss et al. [22] have investigated the creep behavior of Pt-based superalloys at 1300°C. Extrapolation of their 1300°C creep data for Pt-10Al-4Cr and Pt-10Al-4Ru to a strain rate of $2 \times 10^{-8} \text{s}^{-1}$ indicates a creep strength on the order of 1 to 2 MPa. These values are well below the creep strength requirements for turbine applications.

The recession rate of pure iridium at 1315°C in air is on the order of 1 μm/h, whereas that of pure platinum is somewhere between 0.01 and 0.1 μm/h [26]. Unless alloying additions can be found to improve the oxidation resistance of Ir,
Ir-based alloys are marginal with respect to their oxidation resistance. The oxidation resistance of Pt, on the other hand, is well within the requirements. It remains to be seen how the various alloying additions in Ir and Pt-based superalloys affect their oxidation resistance.

The fracture toughness of Ir or Pt-based superalloys does not appear to have been measured to date. While Pt is typically very ductile, Ir can be brittle [27]. Huang et al. [24] tested 5 Ir-base superalloys at 1200°C in compression. Ir-16.3Pt-10.2Nb-2.7Al reached a compressive strain of 14% when the test was stopped. Huang et al. state that this alloy exhibited the lowest (compressive) ductility among the 5 alloys because it had the highest Ir content. Their statement indicates the need to determine the fracture toughness of Ir-base superalloys.

Discussion and Critical Issues

One of the first requirements for assessing whether the temperature capability of a structural high-temperature alloys system suitable for replacing nickel-base superalloys in turbine applications is to determine whether certain key properties can be reached. Important key properties are creep strength, fracture toughness, and oxidation resistance. Once it is reasonably well established that each of these properties is within reach, the next step then is to determine whether all of them can be combined in one particular alloy. It should be kept in mind that even if this goal is not reached, there are potential high-temperature applications other than turbine applications. In other words, the work serves a purpose even though the specific goals may not not reached.

Creep Strength

As far as the creep strength is concerned, niobium silicides, molybdenum borosilicides, and iridium-base superalloys all appear to be suitable. The creep performance of the Pt-based superalloys is inadequate at the present time. However, it should be kept in mind that very little work has been performed on Pt-base superalloys to date, and that there may still be a lot of room for improvement. The creep strength of the much more developed nickel-base superalloys serves to illustrate this. At 1100°C, the 200 hour rupture strength of pure Ni is on the order of 5 MPa [28]. Under the same conditions, the 200 h rupture strength of a third-generation nickel-base superalloy, TMS-75, is almost 30 times higher, namely, 137 MPa [6]. Also, even if the creep strength of Pt-base superalloys does not reach the goal in Table I, they may still be used as oxidation-resistant coatings or as claddings on Ir-base superalloys.
Fracture Toughness

Since the silicide phases such as Nb₅Si₃, Mo₃Si, and Mo₅SiB₂ are all brittle, the fracture toughness of niobium silicides and molybdenum borosilicides is to a large extent controlled by the volume fraction, size scale, distribution, and chemical composition of the α-Nb and α-Mo phases. Since Nb is much more ductile at room temperature than Mo, niobium silicides do have an advantage. However, alloying elements can reduce the ductility and fracture toughness of both the α-Mo and α-Nb phases. Bewlay’s choice of Ti and Hf as major alloying additions is an excellent one in this respect as these elements increase the DBTT only slightly [8]. The DBTT of the α-Mo phase in molybdenum borosilicides is more of a concern. For example, while the Vickers hardness of pure Mo is 212, that of the Mo solid solution in forged Mo-6Si-8B is 474 [16]. One of the reasons for the high hardness of the Mo solid solution is the pronounced strengthening due to dissolved Si (appr. 2.5 at%). For example, 1.9 at% Si increase the hardness number of Mo from 175 to 313 [29]. The hardness increases due to Si are likely to be accompanied by a loss of room temperature ductility and increase in the DBTT.

As compared to Mo, Nb has a high solubility (several at%) for interstitials such as nitrogen and oxygen. These interstitials are detrimental for its mechanical properties. For example, 2000 wppm of O or 200 wppm of N increase the DBTT to room temperature [8]. Because of its lower solubility for O and N, Mo may not be as vulnerable, but interstitials nevertheless remain an issue. In both Mo and Nb-based silicides, the effect of prolonged annealing in oxidizing environments on the mechanical properties of the solid solution refractory phases has not received sufficient attention to date.

In contrast to niobium silicides and molybdenum borosilicides, Ir- and Pt-base superalloys exhibit high-symmetry, cubic fcc and L1₂ crystal structures. Although the fracture toughness of Ir and Pt-base superalloys has not been measured to date, their simple crystal structures suggest that there is potential for obtaining adequate fracture toughness and ductility.

Oxidation Resistance

Presently, the oxidation resistance of niobium silicides is below the goal of a 0.25 µm/h recession rate at 1315°C [2]. Niobium silicide compositions that satisfy this goal do not have adequate strength and/or fracture toughness. The situation is similar for molybdenum borosilicides. They can reach the oxidation goal, but then their fracture toughness is very low, since such alloys contain
negligible amounts of the $\alpha$-Mo phase. It is not clear at this time whether alloys can be found that combine all the requirements at the same time. It may be necessary to grade the properties from fracture-resistant compositions and microstructures in the interior, to oxidation-resistant compositions and microstructures near the surface. Another troubling issue is that the oxidation resistance data presented above were obtained in air. When turbine environments are considered, such data is likely to be overly optimistic. For example, it is well known that the recession rate of silica-based coatings increases dramatically in humid environments at high pressures. In the case of the Ir alloys, the recession rates increase approximately one order of magnitude when testing is carried out in pure oxygen instead in air [26]. This suggests that the recession rates of these alloys increase with increasing oxygen partial pressure. This may become a problem in the high-pressure environment of a combustor. As pointed out by Pint and Wright [30], adequate oxidation resistance is a major obstacle to the application of all of these alloys. It is therefore conceivable that oxidation resistance, and not mechanical properties, is the most important issue determining the use of silicides and platinum-group metals in turbine applications.

**Conclusions**

While niobium silicides and molybdenum borosilicides can deliver adequate creep resistance, fracture toughness, or oxidation resistance, it is not clear at this point whether one particular alloy can reach all of these goals at the same time. In order to achieve adequate oxidation resistance the volume fraction of the $\alpha$-Nb and $\alpha$-Mo phases needs to be kept as low as possible. As a consequence, attention needs to focus on the mechanical properties of these metallic phases. If their ductility and fracture toughness are optimized, adequate fracture toughness values may be obtained with relative small volume fractions. Small volume fractions of the metallic phases would also translate into high creep strengths. Another important issue which has not received much attention to date is the potential embrittlement of the $\alpha$-Nb and $\alpha$-Mo phases in oxidizing environments at high temperatures. If the various goals cannot all be reached in the same alloy, graded microstructures transitioning from a tough, fracture resistant interior to a more brittle, yet oxidation resistant composition and microstructure should be considered.

Iridium-base superalloys deliver adequate creep strength, whereas platinum-base superalloys are much weaker. The oxidation resistance of iridium-base superalloys may be borderline and should be the subject of future research. Similarly, very little information exists on their fracture toughness and ductility.
Before continuing to optimize the creep properties of iridium-base superalloys it is considered critical to examine their oxidation and fracture properties.

Acknowledgements

This work was sponsored by the Office of Fossil Energy, Advanced Research Materials (ARM) Program, and the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Useful discussions with M. P. Brady, J. A. Horton, and H. Bei are appreciated.

References