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RECENT ADVANCES AND DEVELOPMENTS IN REFRACTORY ALLOYS

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ABSTRACT

Refractory metal alloys based on Mo, W, Re, Ta, and Nb (Cb) find applications in a wide range of aerospace applications because of their high melting points and high-temperature strength. In this paper, we present recent progress in the understanding and applications of these alloys. Recent studies to improve the oxidation and mechanical behavior of refractory metal alloys, and particularly Nb alloys, will also be discussed. Some Re structures, for extremely high temperature applications (> 2000°C), made by CVD and P/M processes, are also illustrated. Interesting work on the development of new W alloys (W-HfC-X) and the characterization of some commercial refractory metals, e.g., K-doped W, TZM, and Nb-1%Zr, continues. Finally, recent developments in high temperature composites reinforced with refractory metal filaments, and refractory metal-based intermetallics, e.g., Nb_3Al, Nb_2Be_{17}, and $MoSi_2$, are briefly described.

INTRODUCTION

Although refractory metals have been used since the early 1900s for special applications in the chemical and electronic industries, it was not until the late 1950s that tonnage quantities of mill products were produced. At that time, the spectrum and range of quality of refractory alloys were comparable to those of stainless steels and superalloys. The production of molybdenum, tungsten, niobium, and tantalum alloy sheet was supported by most of the major US agencies, including the Department of Defense (DoD), the National Aeronautical and Space Administration (NASA), the Air Force Materials Laboratory (AFML), the Atomic Energy Commission (AEC), and the Bureau of Naval Weapons. As a result, a superb technical base for supporting major refractory metal use in nuclear and aerospace applications was developed. Two decisions in the early 1970's altered this picture dramatically. One was that work on nuclear space power systems was terminated in 1973 for an indefinite period. The second was the selection of reusable surface insulation (i.e., ceramic tiles) instead of coated refractory metals for thermal protection of the Space Shuttle.

In a report issued by Klopp [1] in 1974, work on refractory metal alloys before and after these decisions was well documented for one major facility specializing in this area, i.e., NASA's Lewis Research Center. The key issues described by Klopp are the dramatic decreases in funding, professional staff, and specialized facilities for refractory metals that occurred after about 1971-72. In fact, in 1974, the above NASA study was unable to identify any near term missions that would require refractory metal technology beyond the state-of-the-art that existed in 1974. This prediction has turned out to be rather accurate for at least a decade; the continuing work on refractory metals since about 1974 has largely been centered on the use of refractory metals for missile and spacecraft propulsion systems, selected jet engine components, and certain industrial applications.

In the mid 1980's, the above situation changed suddenly for two reasons. First, advanced compact nuclear systems, SP-100, were reconsidered as portable thermal and electrical power sources for possible aerospace applications [2]. Second, the advent of exotic vehicle designs such as the National Aerospace Plane (or derivatives of this concept) demanded the use of very high temperature materials that did not exist. The renewed interest in refractory metals for these applications resulted in advances in refractory metals for structural applications.

For many high-temperature structural applications, refractory alloys based on niobium (Nb), molybdenum (Mo), tantalum (Ta), tungsten (W), and even rhenium (Re) are the materials of choice. This is because, for applications requiring very high operating temperatures, strength levels are required that exceed the capabilities of conventional high temperature alloys such as stainless steels and superalloys. Figure 1 shows some comparative selected data for a number of competing high-temperature materials - including carbon, ceramics, and intermetallics. Each class of materials has inherent limitations which govern its application. In some cases, materials limitations are being solved through the use of engineered materials hybrids such as ceramic-coated refractory metals or ceramics toughened with a ductile refractory metal phase. For many applications, the use of ceramics and intermetallics is limited by technological immaturity. By way of contrast, current understanding and application of refractory metals is based upon nearly 40 years of application experience in high-temperature structures.

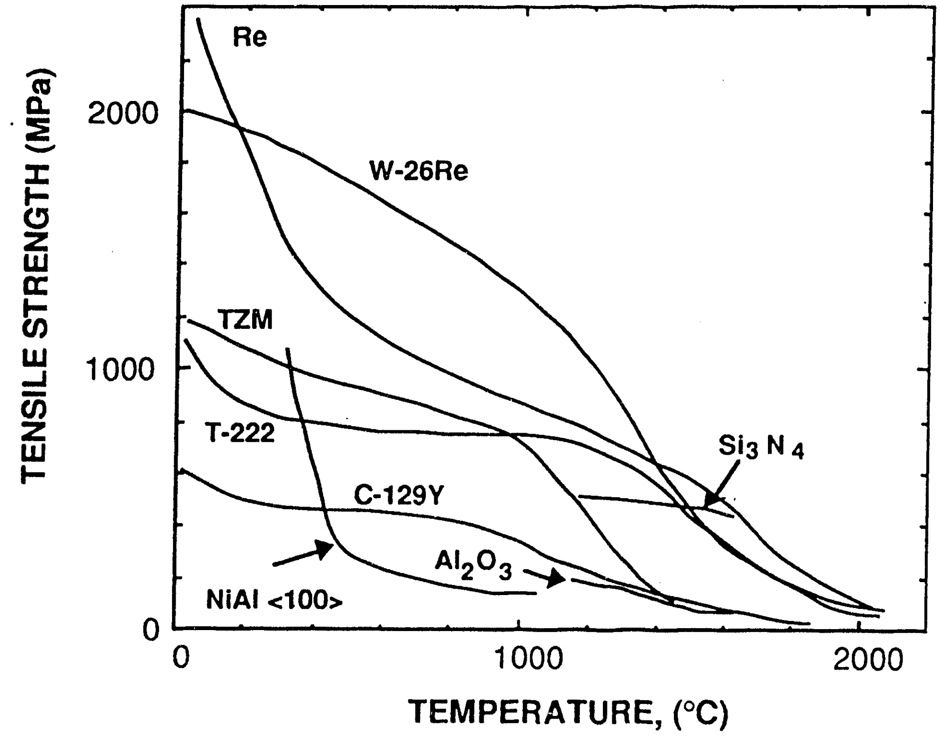

Fig.1 Strength as a function of temperature for selected refractory metals, ceramics, and intermetallics.

Selected data for the principal refractory metals are listed in Table I. As shown the favorable high-temperature strength properties of the refractory metals are often offset by poor room temperature ductility and fabricability (for Mo and W), embrittlement after welding or joining, and in some cases inadequate oxidation resistance. Despite these limitations, refractory metals have been used successfully in a number of demanding high-temperature structural applications — principally in areas of propulsion and energy conversion, such as rockets and re-entry systems [3]. Several refractory materials have also been supplanted in recent years by the demands of aerothermally-heated hypersonic vehicles, proposed high-Mach jet propulsion, and the development of thrust vector controls in advanced fighters.

Table I Selected Data for the Principal Refractory Metals

	Nb	Ta	Mo	W	Re
Melting Point (°C)	2468	2996	2617	3410	3180
Oxide Melting Point (°C)	1490	1772	795	1500	600
Density (g/cm^3)	8.6	16.7	10.2	19.3	21.00
Ductile-Brittle Transition (°C)	-125	-273	30	300	-273
Elastic Modulus (GPa)	110	186	324	405	460

By comparison, the production of alternative high-temperature structural materials (ceramics and intermetallics) has occurred over a much shorter time scale. Although ceramic "mill products" have been available for many years, it is only recently that the purity, density, and microstructural homogeneity of ceramics have allowed their consideration as useful high-temperature engineering structural materials. Key technological advances have included improved toughness, greater availability of product forms, the introduction of ceramic-matrix composites, and gains in the area of superplastic forming. Intermetallic systems are at varying levels of technological maturity. Aluminides of Fe, Ni, and Ti, in particular, are presently under consideration for high-temperature application while a host of other intermetallic systems (e.g. silicides and beryllides) remain at the stage of laboratory examination. Practically all intermetallic systems under investigation today are seen as potential replacements for superalloys. Thus far, no intermetallic materials have emerged to challenge the refractory metals and ceramics for high-temperature (>1350°C) service.

The most recent review on refractory metals was conducted in 1988 [4]. Over the last few years, research has continued in all the major refractory metal groups. Symposia dedicated to the development of tungsten [5] and niobium [6] alloys have been held in the recent past. A special symposium was also organized in 1992 to address the evolution and history of refractory metals [7]. Another special symposium was also organized by the Engineering Foundation in 1993 to address specially on the recent advances in high temperature materials, including refractory metals [8]. In the present paper, we review the recent progress in the development of refractory metal alloys, including those based on tungsten, tantalum, molybdenum, niobium, and rhenium. Intermetallics and composites based on these metals will also be briefly described.

NIOBIUM

Alloys

The most significant technical effort in the field of structural refractory metals was probably the development of rapidly-solidified niobium alloys. This work was primarily triggered by an ARPA (formerly DARPA)-sponsored program on "Development of High-Temperature Metallics for Structural Aerospace Applications" in 1988 [9]. The goal of the program was to develop an intrinsically oxidation-resistant niobium alloy for use at 1537°C (2800°F). In 1991, a special symposium was dedicated to the modern development of high temperature niobium alloys [6]. Various topics related to the application of niobium, including oxidation, strengthening, and niobium-based composites, were addressed in the symposium.

As mentioned previously, the favorable high-temperature strength properties of the refractory metals are often offset by poor oxidation resistance. Traditionally, Nb alloys have to be protected by silicide coatings at high temperatures. An intrinsically oxidation-resistant Nb alloy would be extremely attractive, since niobium is less dense, but stronger, than Ni-base superalloys at high temperatures. The thermodynamic stability of various passivated oxide films are shown in Fig.2. From an oxidation resistance point of view, passive oxides, such as a passive alumina (Al_2O_3) or silica (SiO_2) layer on Nb is desirable for temperatures above 2600°F (1700K). From Wagner's equation [10], in order to form an alumina scale, the critical aluminum content $N_{Al}^{crit.}$ must be

$$N_{Al}^{crit.} = \left(\frac{\pi g^*}{3} N_o^{(s)} \frac{D_o V_m}{D_{Al} V_{ox}}\right)^{1/2} \qquad (1)$$

where $N_o^{(s)}$ is the oxygen solubility in the alloy; D_o and D_{Al} are the diffusivity of O and Al in the alloy, V_m and V_{ox} are the molar volume of the alloy and oxide, and g^* is the critical volume fraction of oxide formed by internal oxidation. In order to develop protective scales therefore, one must increase D_{Al} and decrease $N_o^{(s)}$ and D_o in the alloy. For Nb, the addition of Ti, V, and Cr can produce these effects. Also, V and Cr can stabilize Al_2O_3 at low temperatures. (At low temperatures, Nb-Ti-Al alloys do not form Al_2O_3, but mixed transient oxides.) In fact, an alloy of composition Nb-44%Al-20%Ti-6%V-8%Cr was found to form an Al_2O_3 film at temperatures above 1000°C. Interestingly, similar results were obtained by Wukusick [11] about 30 years ago. The melting point of the new alloy was, however, low (about 1600°C). The low melting point resulted in poor mechanical strengths at high temperatures. Attempts to raise the melting point were made by replacing Nb (melting point ~2500°C) with much higher melting point Ta (melting point ~3000°C). This approach did lead to an increase in melting point, by approximately 300°C. The microstructures of the new Ta-Al-Ti-V-Cr alloys were, however, thermally unstable. By comparison, their Nb counterparts had a relatively stable, two-phase structure.

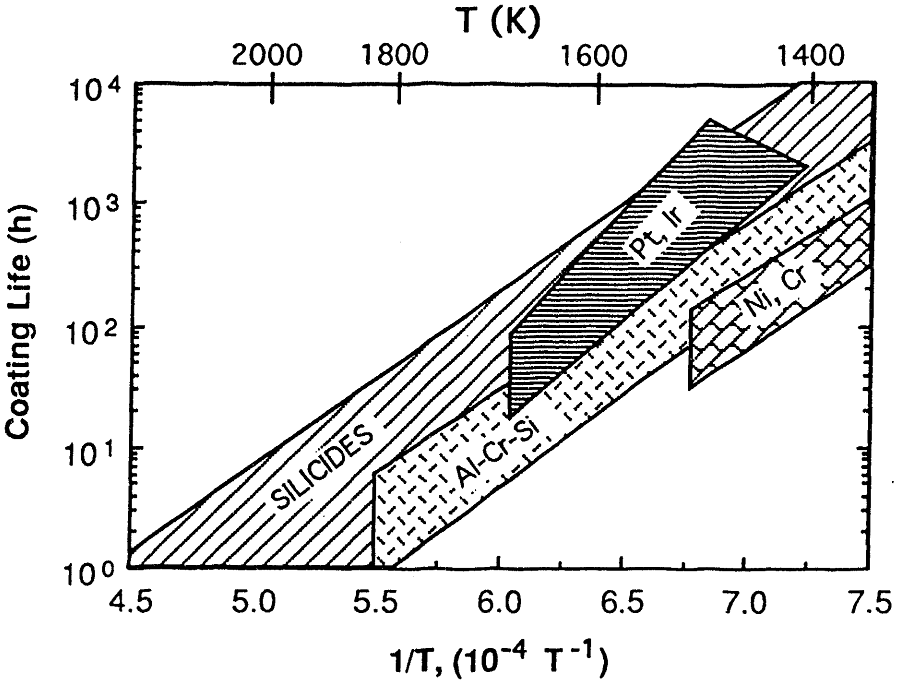

Fig.2 Formation of various oxide films as a function of temperature.

Technical efforts were also made to improve the strength and oxidation resistance of the above Nb-Al-Ti-V-Cr alloys via reinforcements [12]. Reinforcements such as Al_2O_3 and Y_2O_3 were found to be thermally and chemically stable with respect to Nb alloys (composition Nb-(23-25)at%Ti-(38-42)at%Al-3at%Cr-4at%V). In contrast, SiC, Nb_5Si_3, and AlN were found to react extensively with the Nb alloys at high temperatures. The reactions between SiC and Nb_5Si_3, and the Nb alloys resulted in Si formation and, thus, improvement in the oxidation properties of the Nb alloys. These reactions, however, also caused severe detrimental effect on the mechanical properties of these composites. Thermal and chemical instabilities eventually prevented the alloy from insertion into structural applications. Although the ARPA program did not directly result in an application product, the technical progress of the program greatly improved the basic understanding of Nb metallurgy.

Under the sponsorship of the U.S. Air Force, the dispersion strengthening behavior of niobium alloys has been investigated [13]. Dispersions were introduced through either alloying additions, or the additions of carbide, nitrides, and borides. Additions of up to 0.6 at% of refractory metals were found to be necessary to result in a uniform precipitate dispersion of refractory metal compounds. Nonetheless, blocky precipitates were still often observed to segregate preferentially at grain boundaries. The strongest alloys at 1400°C were those with precipitates (nitrides or borides) of the refractory metals Zr and Hf; the commercial alloys with large additions of Mo, Ta, and Zr; and the alloy containing TiN.

Some studies have been carried out to investigate the high-temperature deformation of conventional Nb alloys, and in particular Nb-1%Zr (one of the baseline materials for SP-100) [14]. Systematic investigation of the high-temperature deformation of Nb alloys has been conducted by Wadsworth *et al* [15]. Evidence was presented to indicate that many conventional Nb alloys are Class I solid solutions under creep conditions, as shown in Fig.3. In Class I solid solutions, creep behavior is believed to be controlled by solute drag on gliding dislocations. The law describing creep deformation can be written, in its simplest form, as $\dot{\varepsilon} = K \cdot \sigma^n$ where σ is the true flow stress, $\dot{\varepsilon}$ is the true strain rate, K is a material constant at a given temperature, and n is the stress exponent. In Class I solid solutions, n has a value of 3; this leads to an inherent high strain rate sensitivity of $m = 0.33$ in the equation $\sigma = k \cdot \dot{\varepsilon}^m$ where $m = 1/n$ and $k = 1/K$. The strain rate sensitivity is known to control the rate of neck formation in tensile tests at elevated temperatures. Most ordinary metals and alloys have values of $m \leq 0.2$ and, as a result, show modest tensile ductilities (from 50 to 100%) even at very elevated temperatures. Superplastic alloys have values of m between about 0.4 to 0.6. The high values of m in superplastic metals account for their high tensile elongations. The strain rate sensitivity of $m = 0.33$ found in Class I solid solutions is intermediate between that for pure metals and superplastic alloys, and therefore extended ductility (150 to 600%) is predicted for these alloys. This property is of potential importance to forming of these alloys.

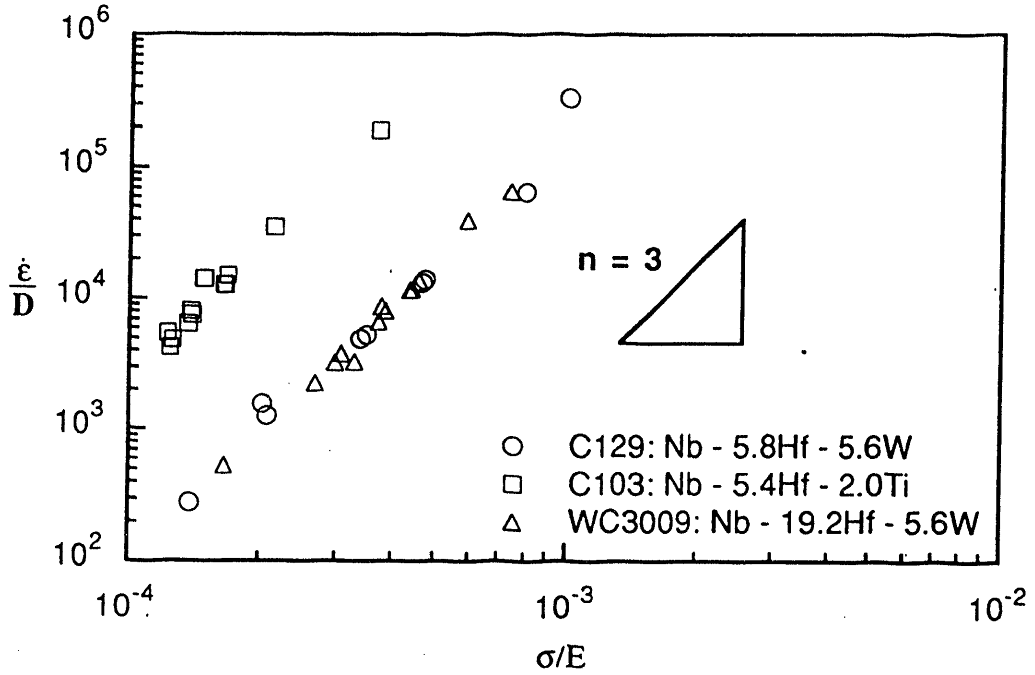

Fig.3 Diffusion-compensated strain rate versus modulus-compensated stress for niobium alloys C103, C129, and WC3009.

Niobium-base and niobium fiber reinforced composites

In seeking high temperature materials, NASA Lewis Research Center has made tungsten fiber reinforced niobium composites using an arc-spray process [16-18]. The mechanical properties (from 1300 to 1600K) of these composites were found to depend upon the W fiber; ThO_2 doped W fiber is more effective than K-doped lamp fiber. The strength difference between the two types of composites was suggested to be attributed to the fiber-matrix interface zone for the two fibers.

Several studies have been performed with the *in situ* 20% Nb-fiber reinforced Cu composites [19-21]. The composite was fabricated via a heavy drawing process; the reduction in area for the drawing process can, sometimes, be as high as 99.7%. Niobium was selected (versus W or Mo) because of its low ductile-to-brittle transition temperature. Experimental results showed that the *in situ* Nb-Cu composites generally exhibit good thermal conductivity and erosion resistance at elevated temperatures. The composites have been suggested for use as combustion chamber liners to replace conventional Cu. The *in situ* processing for Nb-fiber reinforced Cu composites involves spray deposition and subsequent consolidation by vacuum hot pressing or hot isostatic pressing. It is worth mentioning that two-dimensional Nb/Cu composites (laminates) have also been fabricated using a roll-bonding technique [22,23].

The recent interest in the development of structural intermetallics has extended to the niobium-based intermetallics [24-28]. Low-density niobium beryllides, e.g., $NbBe_{12}$ [27] and Nb_2Be_{17} [28,29], have been the emphasis of study in the US. The microstructure of these alloys is quite stable; these niobium beryllides exhibit good creep resistance at elevated temperatures. It has been suggested that creep deformation of these beryllides is controlled by dislocation glide.

Although these beryllides are lightweight and creep resistant at elevated temperature, the room temperature brittleness, as indicated by the DBTT behavior in Fig.4, and the handling problems associated with the toxicity of Be-containing compounds would prevent the alloys from a broad structural application.

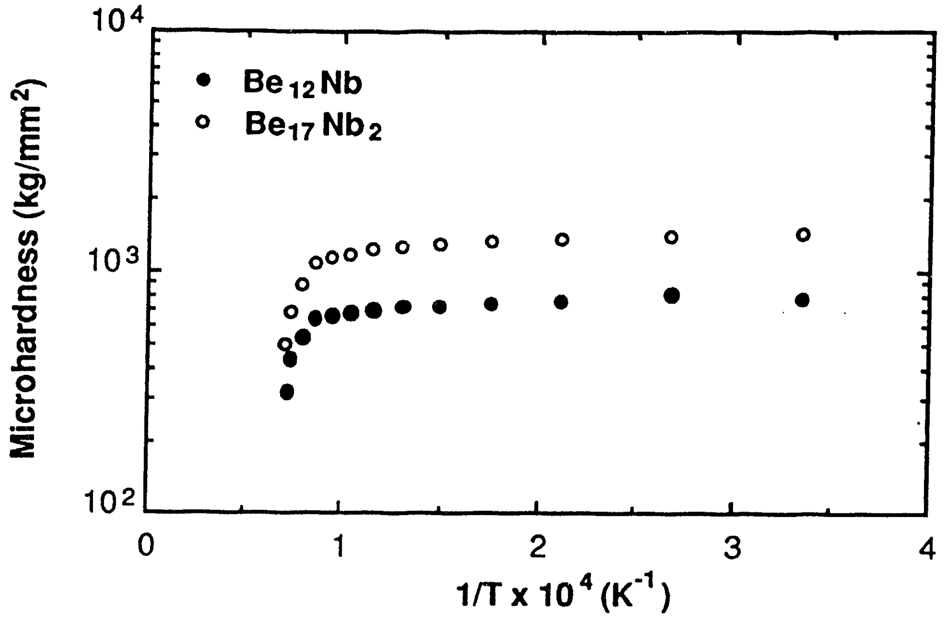

Fig.4 Hardness as function of temperature for various Nb beryllides.

Another Nb-base intermetallic, Nb_3Al (melting point~1960°C), is also currently being studied, particularly in Japan, as a potential extremely-high temperature material [24,30]. Many technical problems (such as extreme difficulty in material preparation, brittleness at ambient temperature, and expected poor oxidation resistance) are associated with using this material for structural applications. Nonetheless, it is important to point out that Nb_3Al is also a superconducting material. Hanada and Saito of Tohoku University [30] have successfully fabricated Nb_3Al by the so-called "Clad-Chop-Extrusion (CCE) Method," which involves cold rolling of clad Nb-Al sheets, followed by chopping and cold extrusion. They have produced good quality Nb_3Al wires by heat treatment of CCE materials at 1000°C. The work was performed under the Japanese MITI project on High-Temperature Ordered Intermetallics.

MOLYBDENUM

Alloys

Luo *et al* [31] investigated the effect of HfC additions (0.5 at.%) on the high-temperature microstructural stability and strength of Mo alloys. The dispersion of HfC in Mo was found to be effective in strengthening Mo; the tensile strength of Mo-HfC is approximately three times greater than that of commercially-pure Mo at 1830°C. The deformation mechanism in Mo-HfC was apparently dislocation glide up to 1530°C, and changed to grain boundary sliding at higher temperatures. In contrast, substructures such as subgrains, dislocation density, texture, and twin boundaries, were all found to be contributing factors to the strengthening of Mo-33 at.%Re at large deformation strains (i.e., various strains) [32].

In another study, potassium doping of molybdenum was carried out to improve high temperature strength; this is a similar approach to that used in K-doped W [33]. Experimental results indicate that doped Mo does offer a better creep strength than undoped Mo. This improved creep strength, together with the fact that Mo has a good thermal conductivity and low expansivity, makes K-doped Mo an attractive material for traveling wave tubes application [34].

There is considerable interest in the production of large-scale molybdenum single crystal sheets for electric components, and as blanket materials for controlled thermonuclear reactors

[35-38]. Secondary recrystallization processing has been used to produce single crystal sheets. The process involves the initial doping of sintered Mo with CaO and MgO and then hot rolling of sheet (~80% reduction in thickness). The rolled sheet is annealed above 2100°C to induce secondary recrystallization. Using the above technique, single-crystal Mo sheets of dimensions 2 mm x 40 mm x 180 mm have been made successfully [36].

In the case of joining, both electron beam welding [39-41] and friction welding [41] of Mo alloys (Mo, TZM, Mo-Nb) have been performed. The effects of impurity contents and their segregation at grain boundaries upon the properties of joints have been examined.

Intermetallics

Recent developments in intermetallics and intermetallic-matrix composites have led to an interest in developing $MoSi_2$ and $MoSi_2$-matrix composites for high-temperature structural applications [42,43]. The major problems associated with using $MoSi_2$ include low-temperature brittleness, dramatic loss of strength at temperatures >1200°C, and low-temperature pest. Many reinforcements have been added to $MoSi_2$ to improve its toughness and strength; reinforcements include ductile refractory metals (e.g., Nb and Ta [44,45]) and ceramic reinforcements, and in particular, SiC [46]. Although there are distinct advantages because of its excellent oxidation and corrosion resistance at high temperatures, molybdenum disilicide ($MoSi_2$) suffers from the "pest" phenomenon during low temperature (400-600°C) oxidation [47-49], as shown in Fig.5. This problem must be overcome before $MoSi_2$ can be widely accepted as a structural material. The development of $MoSi_2$ is extensively discussed in this symposium.

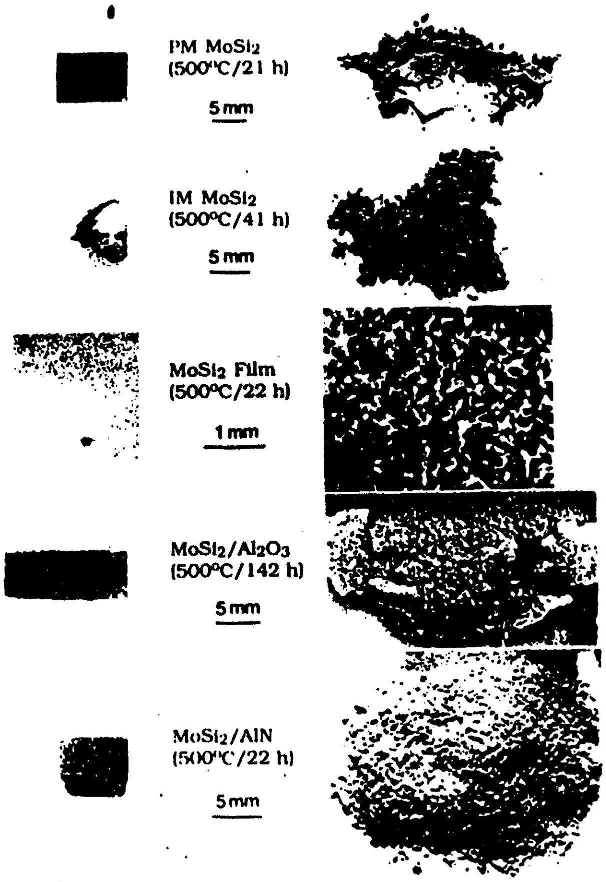

Fig.5 SEM micrographs showing the morphological characteristics of various $MoSi_2$-base materials before and after oxidation at 500°C.

TANTALUM

In contrast to other refractory metals, there has existed only a limited interest in using Ta alloys as structural materials in recent times. Tantalum has been treated as a model material for the evaluation of the performance of shaped charge liners. There was considerable experimental evidence to suggest that the crystallographic texture of the liners played an important role in jet formation and stability [50]. Efforts have been therefore made toward the characterization of the microstructural and textural development in pure tantalum [51,52] and Molybdenum [53] (both have a bcc structure) via thermomechanical processing.

It is of interest to note that the mechanical and structural properties of some Ru-Ta base intermetallic alloys ($L1_0$ structure) also have been investigated [54]. These research alloys were found to have good high-temperature specific strength and a reasonable room-temperature impact resistance. This is part of the technical effort by the US Air Force in seeking alloys for extremely high temperature applications [25,55].

TUNGSTEN

Alloys

There exists continued interest in the microstructure of tungsten rods [56,57] and the growth of creep voids in tungsten wire [58-61], as well as the effect of oxygen on tungsten filament sag kinetics [62]. In the area of alloy development, the Air Force remains interested in improving the room temperature fabricability and high temperature strength of tungsten via alloying. For example, rhenium has been added to thoria-doped tungsten and the alloy exhibits improved high temperature strength up to 2200K [63,64]. In contrast, W-Ir alloys were found to exhibit only a moderate strengthening effect, despite the fact that Ir and Re have a similar electronic structures [65]. In studying dispersion strengthening in W-base alloys, both HfC [64] and ThO_2 [66] have been alloyed to W-Re alloys. In the case of a W-26wt.%Re-1wt%ThO_2 alloy, ThO_2 was found to be effective up to about 2200K. In the case of W-3.6wt%Re-0.26wt%HfC, HfC particles were found to be even more thermally stable; in fact, the effectiveness of HfC extends to a temperature above 2600K [67]. The effectiveness of HfC can be understood according to an early description of carbide precipitation by Wadsworth [68].

Tungsten heavy alloys are penetrator materials which have a high toughness and a high kinetic energy. The uses include armor piercing projectiles as well as perforation devices for rejuvenation of stagnant oil and gas wells. Several recent studies have been performed to characterize the strength and ductility of W alloys as functions of alloy composition, microstructure, strain rate, and temperature [69-75]. The alloys were mainly based on W-Fe-Ni compositions, with various tungsten contents. Work softening effects, resulting from adiabatic heating, were observed to occur at strain rates higher than about 10 s^{-1} [69]. Cracking, and thus fracture, of the W heavy alloys was found to be mainly associated with the presence of a brittle phase at the W/Fe-Ni matrix interface.

Experimental evidence indicated that the performance of metals at high strain rates can be improved by refinement of grain size [76]. As a result, efforts have been made to produce W alloys with grain sizes finer than those of conventional W-Fe-Ni alloys. The approach taken was to minimize tungsten transport during liquid phase sintering. This was attempted by using an alloy matrix, such as Re- or Mo-modified Fe-Ni [77] or Cu [78], which has a reduced solubility for W during liquid phase sintering. Some progress was made, and the grain size of W alloys can now be reduced to the range of 5 μm (compared to 40-50 μm for W-Fe-Ni). Kim and Whang [79] have used a rapid solidification technique to examine the effect of cooling rate on grain refinement of W-Si alloys. The technique is interesting but may be impractical because of the extremely high melting point of W.

Tungsten alloys are conventionally manufactured using powder metallurgy techniques. Although chemical vapor deposition (CVD) has been used to process refractory metals, it has had only limited success in producing structural refractory metals with good mechanical properties. With the great improvement in CVD techniques in recent years, it is now possible to produce very fine-grained (~5 μm) W, as illustrated in Fig.6. The mechanical properties of the CVD W were observed to be similar to those of conventional powder metallurgy tungsten [80]. It is particularly noted that the technique has been used to produce net cone-shape charged liners [81].

Tungsten fiber reinforced composites

It is interesting to point out that W, because of its high modulus (~420 GPa) and excellent high temperature strength, has been investigated in wire form as a reinforcement for Cu and Ni superalloys [16,58]. In the case of W/Ni metal matrix composites, property improvements in the composites were found to be limited, as a result of extensive reaction between Ni and W at elevated temperatures [17]. In the case of W fiber-reinforced Cu composites (W/Cu), the composites were observed to have good thermal conductivity and exhibit excellent erosion properties at elevated temperatures [16,82]. Both W/Cu and Nb/Cu have been suggested as candidates for combustion chamber liners [83]. Although W/Cu possesses better properties than Nb/Cu, the fabrication processes of W/Cu are, however, quite elaborate and therefore expensive.

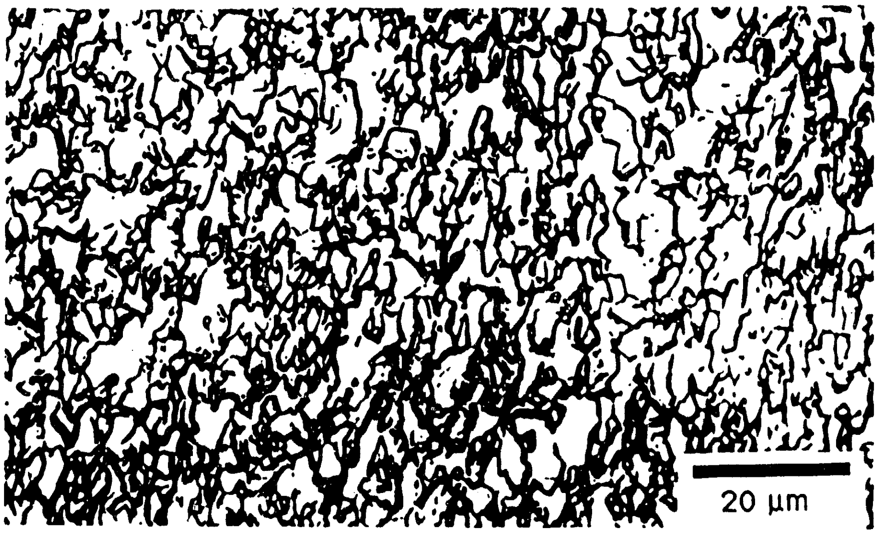

Fig.6 Microstructure of CVD tungsten showing fine grain size.

RHENIUM

Rhenium is the second highest melting point metal (3180°C), only lower than W (3400°C). It is more creep resistant than W and W-Re alloys at temperatures above 1600°C [84]. Also, Re is the only refractory metal that does not form a metal carbide. In fact, it has an extensive solid solubility (12 at.%) for carbon [85]. As a result, Re is expected to be compatible with carbon/carbon composites. These attractive mechanical and chemical characteristics have generated great interest in using Re for extremely high temperature applications, such as rocket thrusters and hot gas valves [81,86]. For instance, Re has been successfully tested for gas valve structures operating at 2200°C under the Lightweight Exoatmospheric Projectile (LEAP) Program, sponsored by the US Air Force. An artistic drawing of the LEAP is presented in Fig.7. To the authors knowledge, this may be the highest operating temperature for an engineering structure. The integrated gas valves of the structure require extensive joining. Brazing was considered impractical because it would reduce the service temperature of the valves. Rhenium can be joined by either electron-beam welding or diffusion bonding techniques, provided the bonding surfaces are properly cleaned. A cross sectional micrograph of a Re joint diffusion bonded at 2300°C with an applied stress of 10 MPa is shown in Fig.8. This joint has a strength of about 130 MPa at 2000°C. As shown in Fig.8, cracks do not propagate along bond interface.

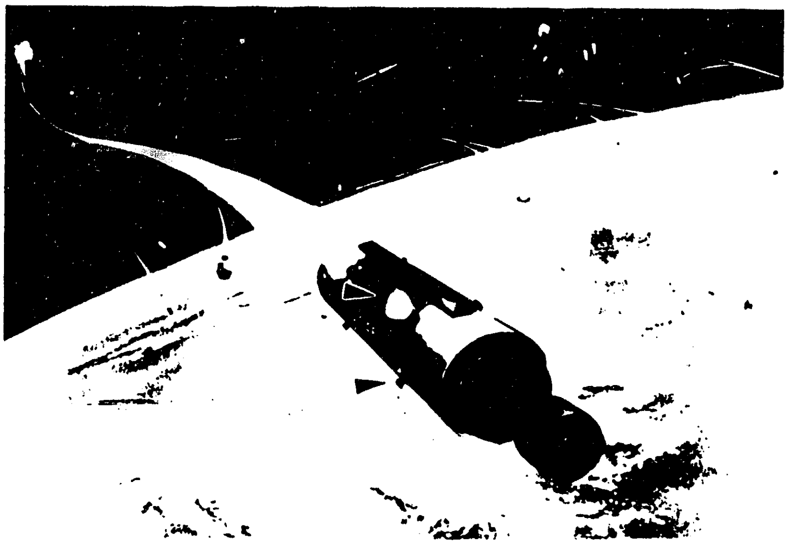

Fig.7 Artistic drawing of Lightweight Exoatmospheric Projectile (LEAP). The hot gas valves (indicated by arrows) operate at 4000°F (~2200°C).

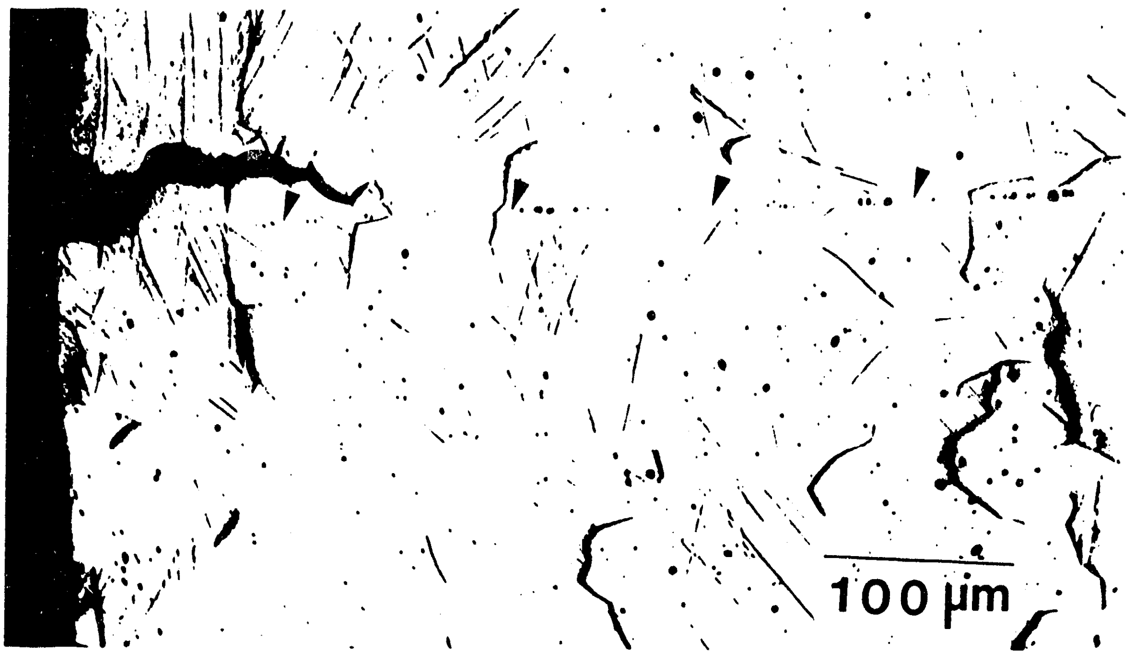

Fig.8 Cross sectional microstructure of a Re joint (indicated by arrows) diffusion bonded at 2300°C with an applied stress of 10 MPa.

Despite the above technological successes, the understanding of Re metallurgy is quite limited. Technical issues, such as oxidation protection, thermomechanical processing, and material availability are just some of the challenges. For instance, oxidation properties of Re are poor, as in the case of other refractory metals [87], although iridium coatings have been used to protect Re from excessive oxidation [86]. Rhenium has good room temperature ductility, but it has a relatively high strain hardening exponent [88]. As a result, Re is difficult to cold work into different shapes. Rhenium can be produced by halide reduction, but it is available only in limited quantity [89]. The cost of Re is, therefore, still high. In view of these technical and economic challenges, Re is not expected to be widely used, except in some special structures.

SUMMARY

The renewed interest in refractory metals for some major aerospace applications has resulted in advances in refractory metals for some structural applications. The major activities are summarized as follows.

1. Niobium - Emphases were on the development of intrinsically oxidation-resistant alloys and their composites. Some interest has been placed on the deformation and thus, the forming characteristics of these alloys.
2. Molybdenum - Thermal stability as well as the mechanical strength of Mo alloys (HfC- or K-doped) have been investigated. The major activity was, however, in the development of $MoSi_2$ and its composites for structural applications.
3. Tantalum - There is only limited interest in using Ta as a structural material; there has been some research work on texture development.
4. Tungsten - Hafnium carbide was found to be the most effective strengthener in W up to temperatures of ~2400°C. In addition, tungsten (and niobium) fiber reinforced copper was investigated as a high-strength, high-conductivity combustion chamber liner material to replace conventional copper.
5. Rhenium - Significant progress has been made in the understanding of Re metallurgy. Some special rocket thrusters and hot gas valves have been manufactured from Re and tested successfully at extremely high temperatures (~2200°C).

The development of other high-temperature structural materials (e.g., ceramics and intermetallics) has also taken place in the recent past. These new materials are, however, lacking technological maturity. By comparison, refractory metals have been available for engineering use for over 100 years and have been used for aerospace hardware for at least 30 years. Some of the refractory metal structures may be gradually replaced by new materials, but certainly not in the immediate future.

ACKNOWLEDGMENT

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