Chapter 12
Niobium and Other High Temperature Refractory Metals for Aerospace Applications

V.V. Satya Prasad, R.G. Baligidad and Amol A. Gokhale

Abstract Refractory metal alloys based on Nb, Mo, Ta, W, and Re find applications in the aerospace industries because of their high melting points and high temperature strengths. They are generally produced by powder metallurgy technique due to their very high melting points. However, when refining is desired, melting under high vacuum becomes necessary, for which nuggets or powder based electrodes are employed. Niobium is the lightest refractory metal with density close to that of nickel, and exhibits good thermal conductivity. Niobium can be alloyed to improve high temperature strength and oxidation resistance. Applications in nuclear, aerospace, and defence sectors have been reported. The goal of current research in Nb alloys is to simultaneously achieve high strength and workability, and provide protection from oxidation for long-term operation. There is strong research interest in intermetallics also. This chapter will discuss the salient features of refractory metals and alloys in general, and Nb-based alloys in particular.

Keywords Niobium · Refractory alloys · Processing · Mechanical properties · Creep · Applications

12.1 Introduction

Future aerospace applications such as advanced turbojet and scramjet engines to be used in subsonic, supersonic, and hypersonic flights will require materials with ever increasing temperature- and load-bearing capabilities for improved performance

---

V.V. Satya Prasad (✉) · R.G. Baligidad
Defence Metallurgical Research Laboratory, Hyderabad 500058, India
e-mail: vvsatya2004@yahoo.co.in

R.G. Baligidad
e-mail: rbaligidad@yahoo.co.in

A.A. Gokhale
Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India
e-mail: amol_gokhale@yahoo.in

N. Eswara Prasad and R.J.H. Wanhill (eds.), *Aerospace Materials and Material Technologies*, Indian Institute of Metals Series,
DOI 10.1007/978-981-10-2134-3_12

under extreme environmental conditions. The state-of-the-art superalloys can be utilized to a maximum temperature of 1077 °C, and the need for viable materials with higher (1127–2027 °C) temperature capabilities has long been felt. Hence work is being pursued in different directions to develop materials with very high temperature capability [1, 2].

One such area is the development of ceramics and composite materials which have very good high temperature capability. However, designers frequently find that these newer materials cannot be easily fabricated into the shapes required. In other instances, users of high temperature materials are rediscovering that the applicability of advanced nonmetallic and composite materials may be limited by their relatively low thermal conductivity: alloys with good thermal conductivity require less intense air cooling in applications such as turbine hot sections.

Although there are a number of metals that can be considered as refractory by virtue of their high melting points, tungsten, molybdenum, tantalum, and niobium are the promising ones, all of which have body centered cubic (bcc) structures. Rhenium, a hexagonal close packed metal, is also often considered to be a member of this group. The common characteristic of these metals, as shown in Table 12.1 [3], is a high melting point ranging from 2468 °C (Nb) to 3410 °C (W). It would seem natural that these elements would form the bases for high temperature structural materials. Their high temperature strength and Young's modulus are shown in Figs. 12.1 and 12.2 [3].

Unfortunately, all four of the traditional refractory metals have little or no resistance to oxidation in the service temperature range. Niobium and tantalum are the most versatile refractory metals due to their relative ease of fabrication (because of excellent room temperature ductility and low ductile-to-brittle transition temperature, DBTT) and corrosion resistance. The corrosion resistance of niobium is provided by the formation of a very dense and adhesive oxide layer. With the exception of hydrofluoric acid, concentrated hot sulphuric acid and hot alkaline solutions, niobium shows good resistance to aqueous solutions.

In comparison to tantalum the corrosion resistance of niobium is less, but still much better than that of stainless steels or nickel-base alloys used in chemical industries.

Although tungsten finds applications as ballast and nozzle material in rocket systems, its main use has been as core material in antitank penetrators owing to its very high density. All refractory metals find use as alloying elements in nickel-base superalloys since they are beneficial to the creep resistance.

Table 12.1 Properties of common refractory metals

Metal	M.P. (°C)	V.P. (torr) at 2327 °C	DBTT (°C)	Density (g/cm^3)
Nb	2468	4×10^{-5}	< −126	8.75
Mo	2617	6×10^{-4}	27	10.2
Ta	2996	8×10^{-7}	< −248	16.7
Re	3179	1.3×10^{-6}	–	21.0
W	3410	7×10^{-8}	302	19.3

M.P. melting point, *V.P.* vapour pressure, *DBDT* ductile to brittle transition temperature

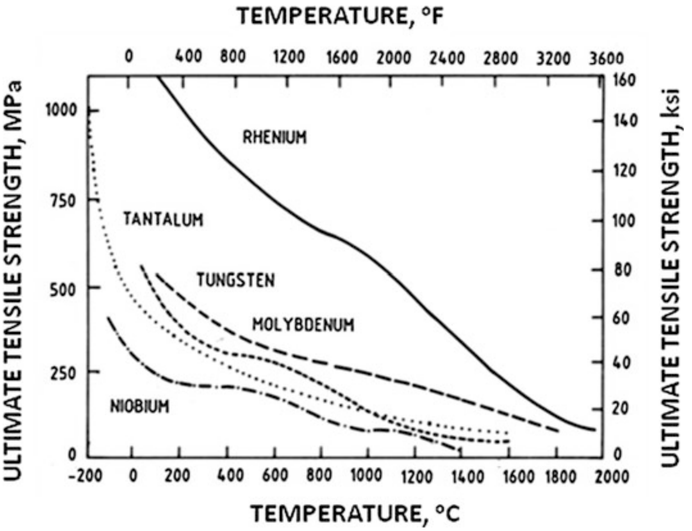


Fig. 12.1 Tensile strength of refractory metals versus test temperature

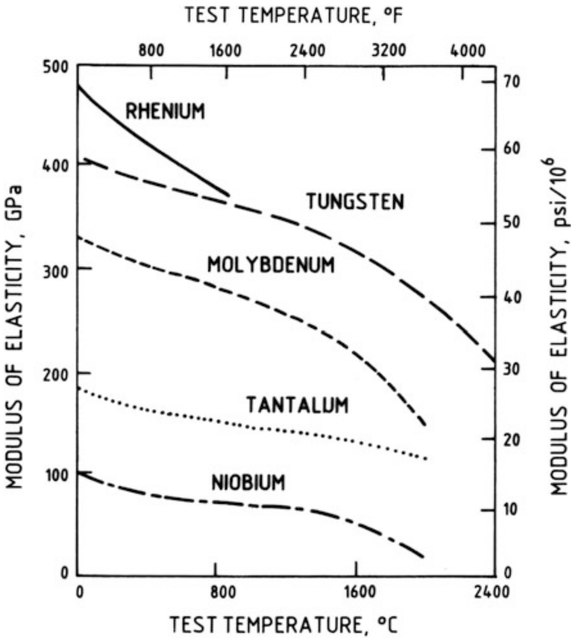


Fig. 12.2 Variation of the modulus of elasticity of refractory metals with temperature

In view of the excellent potential of niobium as an advanced candidate material for aerospace applications, this chapter deals extensively with melting, processing, properties, and applications of Nb alloys and also describes important characteristics of other refractory alloys.

12.2 Niobium Alloys

12.2.1 Nb Alloys and Their Properties

Niobium is a tough, shiny, silver-gray, soft, ductile metal that somewhat resembles stainless steel in appearance. The metal was discovered in 1801 in an ore shipped from Connecticut, more than 100 years earlier, by the English scientist Charles Hatchett, who named it Columbium. The name niobium was adopted by IUPAC in 1950. The important physical properties of niobium metal are listed in Table 12.2. Currently about 1000 tons of niobium is produced per year, of which 95 % is used as additions to steel and nickel-base alloys for increasing strength, while the balance is used either as pure Nb or its alloys.

Niobium is also the lightest refractory metal, with density close to that of nickel, and has good thermal conductivity (65.3 W/mK at 600 °C). Its bcc structure enables a higher solubility of alloying elements, and the metal has excellent formability and weldability, and is not susceptible to low temperature notch sensitivity. However, although niobium is attractive in terms of melting temperatures and room temperature ductility, its applications have been limited because of its poor high temperature strength and oxidation resistance.

Niobium is easily oxidized at about 250 °C. The oxidation takes place rapidly above 500 °C. Its high temperature oxidation resistance and high temperature strength have to be improved for long-term very high temperature structural applications [2]. Nevertheless, it is noteworthy that this metal possesses qualities that cannot be offered by any other type of material. Hence considerable effort has been made to compensate for its disadvantages via engineering design of the components.

Table 12.2 Physical properties of niobium

Properties	
Density at 20 °C (g/cm^3)	8.75
Crystal structure, lattice parameter	Body centered cubic, $a = 3.3 \times 10^{-10}$ m
Melting point (°C)	2468
Boiling point (°C)	4927
Linear coefficient of thermal expansion (K^{-1})	6.892×10^{-4}
Specific heat (kJ kg^{-1} K^{-1})	0.26
Latent heat of fusion (kJ/kg)	290
Latent heat of vaporization (kJ/kg)	7479
Thermal conductivity at 0 °C (W cm^{-1} K^{-1})	0.533
Electrical resistivity (μΩ cm)	15.22

Niobium can be alloyed to improve the oxidation resistance and also the high temperature strength. The problem is that it is not always possible to achieve the desired combination of improvement through alloying without sacrificing some of the other desirable properties. For example, a higher strength, oxidation resistance, and good room temperature ductility combination has not yet been found. Nor has anyone yet achieved the excellent high temperature strength from alloying without sacrificing something in fabricability and weldability.

In searching for ways to increase high temperature strength and creep resistance with satisfactory workability, as well as methods of protection against oxidation at operating temperatures exceeding 1027 °C, significant Nb alloy development activities were undertaken in the 1960s and early 1970s. Several potential alloys were developed [4–6] that may be conveniently divided into low, medium-, and high-strength alloys that have been used for long-term operation at 1000–1200 °C and for short-term operation at 1200–1700 °C.

These alloys were extensively investigated as candidate materials for nuclear applications and structural components in aircraft, space vehicles, rockets, etc.; and are also used for electronic, high energy physics, and chemical process industries. Even in these areas, their applications have been limited by their susceptibility to high temperature oxidation and long-term creep [7]. Efforts to improve the resistance to high temperature oxidation through modification of alloy chemistry have not been successful.

Although protective coating systems were developed to permit the use of Nb alloys in high temperature oxidizing aerospace applications [8], the goal of simultaneously achieving high strength and workability, and providing safe protection for long-term operation remained unsolved. Hence the interest in refractory metallic systems based on Nb declined.

However, the more recent need, since the 1980s, for (very) high temperature materials in aerospace and power engineering has rejuvenated the interest in refractory metallic systems, particularly Nb-based alloys. Two problem areas were identified:

1. In the temperature range 600–900 °C wrought titanium alloys are unsuitable, while nickel-base alloys do not meet specific (i.e. density compensated) strength requirements.
2. In the temperature range 1100–1500 °C wrought nickel-base alloys are unsuitable, whereas alloys based on intermetallics and heat-resistant ceramics, considered as prospective structural materials, do not provide the required strength, ductility or fracture toughness.

Commercial Nb alloys are relatively low in strength and extremely ductile, and can be cold-worked by over 70 % before annealing becomes necessary. Alloying elements such as Mo and W, which are group VIA elements and which go into solid solution with Nb, are the most effective in imparting high temperature strength. However, when added in sufficient quantity to give appreciable strengthening effect, these elements raise the temperature to achieve 10 % reduction in area, see Fig. 12.3, and adversely affect the fabricability and weldability.

Another potent strengthening mechanism characteristic of most of the high strength alloys is the interaction between one of the reactive elements Zr or Hf and

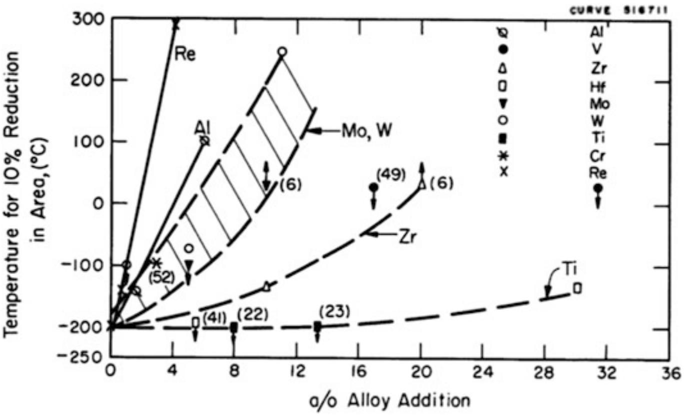


Fig. 12.3 Effect of alloying addition on ductility transition temperature of niobium

C, O, or N to form precipitates. The precipitates are very effective for high temperature strengthening and maintaining ductility after welding. The most common high temperature niobium alloys are listed in Table 12.3 [9, 10]. All are hardened by solid solution strengthening; however, small amounts of second phase particles such as oxides, nitrides, and carbides are present. The size and distribution of second phase precipitate particles can often have a strong influence on mechanical properties and recrystallization behaviour. Typical room temperature mechanical properties of unalloyed niobium and the most common Nb alloys are given in Tables 12.4 and 12.5 [9, 10], respectively.

The WC-3009 alloy listed in Tables 12.3 and 12.5 contains ~0.10 wt% oxygen, which is about five times more than in other niobium alloys. This high level of oxygen is the result of powder processing. It is not deleterious to mechanical properties because oxygen combines with hafnium in the alloy to form stable hafnium oxide precipitates. WC-3009 is unique in that it exhibits an oxidation rate less than one tenth that of most other niobium alloys. When WC-3009 was developed, it was speculated that such an alloy could survive a short supersonic mission even in the event of a protective coating failure.

Table 12.3 Commercial niobium alloys

Nominal composition (wt%)	Commercial nomenclature
Nb-1Zr	Nb-1Zr
Nb-1Zr-0.1C	PWC-11
Nb-28Ta-10W-1Zr	FS-85
Nb-10W-2.5Zr	Cb-752
Nb-10Hf-1Ti	C-103
Nb-10W-10Hf-0.1Y	C-129Y
Nb-30Hf-9W	WC-3009
Nb-46.5Ti	–
Nb-55Ti	–

Table 12.4 Mechanical properties of niobium

Mechanical properties	
Annealed condition	
Ultimate tensile strength	195 MPa
Yield strength	105 MPa
Elongation	30 %+
Reduction in area	80 %+
Hardness	60HV
Poisson's ratio	0.38
Strain hardening exponent	0.24
Elastic modulus	103 GPa
DBTT	−126 °C
Recrystallization temperature	800–1000 °C
Cold-worked condition	
Ultimate tensile strength	585 MPa
Elongation	5 %
Hardness	150HV

Table 12.5 Room temperature tensile properties of commercial niobium alloys

Commercial name of alloy	Alloy composition (wt %)	YS (MPa)	UTS (MPa)	EL (%)
Nb-1Zr	Nb-1Zr	150	275	40
PWC-11	Nb-1Zr-0.1C	175	320	26
FS-85	Nb-28 Ta-10W-1Zr	462	570	3
Cb-752	Nb-10W-2.5Zr	400	540	20
C-103	Nb-10Hf-1Ti	296	420	26
C-129Y	Nb-10W-1Hf-0.1Y	515	620	25
C-3009	Nb-30Hf-9W	752	862	24

All the alloys (except FS-85) are quite ductile at room temperature. The highest tensile strength at room temperature is exhibited by C-3009 (Nb-30Hf-9W), while the highest ductility is shown by Nb-1Zr. The high temperature tensile and creep properties of common Nb alloys are shown in Fig. 12.4. Even though WC-3009 clearly exhibits the highest tensile strength over the entire temperature range, FS-85 has superior creep strength. Its high creep strength is due to its higher melting point, which is due to its high concentration of Ta and W.

Niobium alloys are much less tolerant to impurity pick-up than other reactive metals such as titanium and zirconium. Alloys containing second phase particles that form a continuous boundary between grains can show drastically reduced room temperature tensile elongation. This condition is usually caused by contamination (omit) or improper heat treatment.

The total permissible interstitial oxygen, hydrogen, carbon, and nitrogen contents of niobium alloys are typically one-fifth to one-tenth of those for titanium or zirconium alloys.

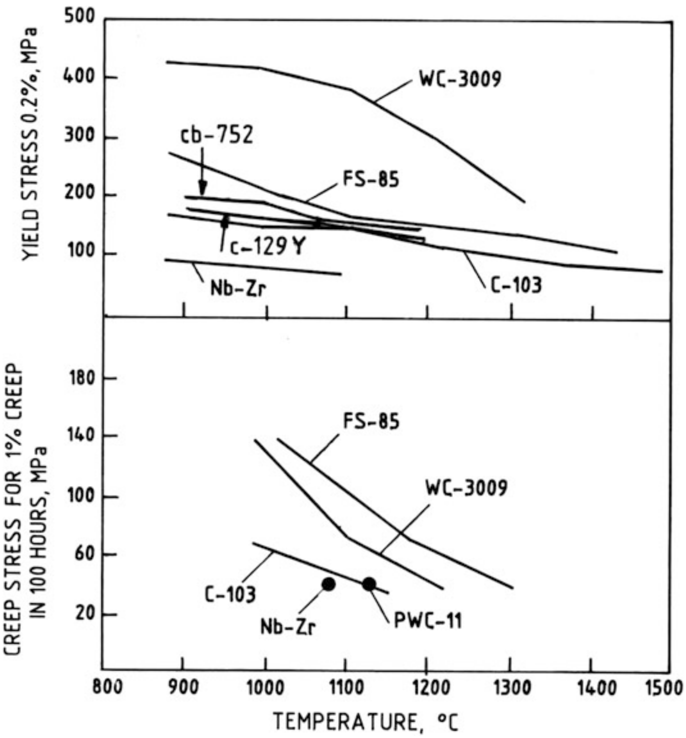


Fig. 12.4 Strength and creep properties of common Nb alloys

Elastic modulus, thermal conductivity, and total hemispherical emissivity are listed in Tables 12.6, 12.7, and 12.8. Generally, smooth and non-oxidized surfaces have much lower emissivity than their oxidized counterparts. Also shown in Table 12.8 is an emissivity value of 0.7–0.82 for silicide coated C-103. This value is for a common Si-20 %Fe-20 %Cr coating applied by the slurry coat and diffusion method.

12.2.2 Production Methods for Niobium

Niobium metal was originally produced by powder metallurgy methods that involved high temperature vacuum sintering and carbon reduction. However, aluminothermic reduction and electron beam (EB) purification became the standard practices since the early 1960s [11, 12].

In aluminothermic reduction, Nb_2O_5 and aluminium powders are first blended together and then reacted exothermically to form crude niobium metal and Al_2O_3 slag. The crude niobium metal typically contains several percent impurities,

Table 12.6 Elastic moduli of commercial niobium alloys

Alloy	Elastic modulus (GPa)	
	20 °C	1200 °C
Nb-1Zr	80	28
FS-85	140	110
C-103	90	64
C-3009	123	–
Cb-752	110	–

Table 12.7 Thermal conductivity of commercial niobium alloys

Alloy	800 °C (W/mK)	1200 °C (W/mK)
Nb-1Zr	59.0	63.1
C-103	37.4	42.4
FS-85	52.8	56.7
Cb-752		

Table 12.8 Total hemispherical emissivity of commercial niobium alloys

Alloy	800 °C	1200 °C
Nb-1Zr	0.14	0.18
C-103	0.28	0.4
C-103 (silicide coated)	0.70	0.82

including aluminium and oxygen. At elevated temperatures many of these impurities have a much higher vapour pressure than niobium metal, because of which they can be purified commercially by EB melting; while the low vapour pressure impurities such as tantalum and tungsten are more difficult to remove. The real impetus to niobium and niobium alloy metallurgy came with the commercialization of the EB Melting Process.

12.2.3 Melting and Refining of Niobium and Preparation of Nb-Based Alloys

It is well established that the properties of wrought refractory metal products depend to a large extent on the purity of the raw material, particularly the interstitial impurity contents [13, 14], which tend to embrittle the alloys. Therefore raw material production methods which result in lower impurity contents are preferred. As such, although Nb-based alloys can be prepared by powder metallurgy (PM) methods, the more common and economic way of preparing the starting material is the ingot metallurgy (IM) route, since it results in lower impurity contents.

Conventional melting and casting techniques are unsuitable for refractory metals and alloys production, since the melting temperatures of these metals are above the working temperatures of common refractories. Vacuum arc remelting (VAR) and

EB melting furnaces are widely used for melting niobium and its alloys. Powders of Nb and other alloying elements are premixed, compacted, and vacuum sintered to produce consumable electrodes for these processes. VAR is suitable for preparation of Nb-based alloys containing alloying elements with high vapour pressure. However, it is necessary to start with high purity Nb, since no refining is possible during VAR. High purity Nb is produced by multiple melting in EB furnaces. Recently, it has been demonstrated that it is possible to produce high purity niobium ingots in one single step of melting by operating the EB melting process under optimum process parameters. Nb-based alloys containing alloying elements with low vapour pressure can be directly EB melted to produce alloys.

The most common alloy additions to Nb are zirconium, titanium, and hafnium. Higher melting temperature elements such as tungsten or tantalum can be added during EB melting. Even though VAR (commonly used for alloy steels, nickel, and titanium alloys) can also be used for niobium, it should be noted that the high melting temperature of niobium requires much higher power levels. It is not unusual to melt 200 mm diameter ingots using 15,000–20,000 amperes of current. Some alloys such as Nb-1Zr are prone to arcing against the crucibles and causing burning of the water jacket. Therefore intensive water cooling is required to minimize this risk.

12.2.4 Processing of Niobium

Niobium can be worked by most metal working processes. However, compared to other more common materials like steel or titanium alloys, niobium alloys have higher flow stresses at hot working temperatures. Processing temperatures of Nb and its alloys are given in Table 12.9 [15].

Breakdown of the generally large-grained ingots by mechanical working is a challenging problem from the cracking point of view, particularly for high strength alloys. Recently, extrusion has become an attractive alternative for alloys with low workability, because of improved glass lubricating and die coating techniques. These reduce frictional stresses and the resultant cracking tendency.

Forging is done for primary breakdown of alloys, although intermediate extrusion is necessary for low workability alloys. Both hammer and press forging techniques are used to produce flat slabs or round billets. Hot forging temperatures for typical commercial alloys range between 650 and 1400 °C.

Heating to the above-mentioned temperatures causes excessive oxidation, and oxygen, nitrogen, and hydrogen can be picked-up, occupying interstitial positions. Thus the alloys are heated using protective coatings or in inert gas atmospheres. Coating protects the alloys during both heating as well as forging, but a certain amount of material must be sacrificed in subsequent grinding or pickling.

Most niobium alloys are either cold rolled or warm rolled (200–370 °C) to produce plates, wires, rods, etc. Cold die forging, spinning, hydroforming, and welding techniques are employed to produce complex shapes.

Table 12.9 Mill processing temperature for niobium and its alloys

Commercial name of alloy	Forging temp. (°C)	Forging total thickness reduction (%)	Extrusion temp. (°C)	Extrusion area reduction ratio	Rolling temp. (°C)	Rolling total reduction in thickness between anneals (%)
Nb	980–650	50–80	1095–650	10:1	315–205; 20	50 breakdown; 90 finish
Nb-1Zr	1205–980	50–80	1205–980	10:1	315–205; 20	50 breakdown; 80 finish
FS-85	1315–980	50	1315–980	4:1	370–205; 20	40 breakdown; 50 finish
Cb-752	1205–980	30	1315–980	4:1	370–260; 20	50 breakdown; 60 finish
C-103	1315–980	50	1315–980	8:1	205; 20	50 breakdown; 60 finish
C-129Y	1315–980	50	1315–980	4:1	425; 20	50 breakdown; 60 finish

During the early 1980s there were several programme aimed at producing niobium alloy parts by more cost-effective methods. Several attempts were made to manufacture niobium alloy net shape parts by investment casting. This method presented some special challenges with respect to extensive metal—mould reaction, and to get enough superheating into the metal to avoid cold laps. While it was demonstrated that casting is possible even for niobium alloys with melting temperatures over 2400 °C, the "as-cast" microstructure is typically less ductile than normal wrought microstructures.

The economic aspects of producing niobium alloy castings were also severely hindered by the loss of metal in the form of gates, skull, and risers. Unlike titanium and nickel alloys, the gates and other casting scrap are not remeltable for niobium alloy production, owing to the metal's low tolerance for interstitial impurities. An investment cast C-103 alloy turbine engine stator is shown in Fig. 12.5. At this time no niobium alloy parts are actually produced by this method.

12.2.5 Applications of Niobium and its Alloys

The largest amount of niobium production is as FeNb in the steel industry, where niobium is used as an alloying element for improvement of the high temperature strength and for providing non-scaling properties during hot working. A special property of niobium is its superconductivity, which was discovered in 1911. For practical use of superconductivity ultrapure niobium is required.

Since niobium is relatively low in density and can maintain its strength at high temperatures, niobium and its alloys are finding high temperature applications. The

Fig. 12.5 Investment cast C-103 stator ring produced by precision casting

most common application of the alloys is in sodium vapour lamps: the Nb-1Zr alloy demonstrates excellent formability, weldability, and long life in a sodium vapour environment. The small tubular shapes of Nb-1Zr in these lamps are made from seamless tubing, which in turn is made by deep drawing sheet metal. Today, the primary application for high temperature niobium alloys is for rocket thrusters and nozzles.

The alloy with the most promising combination of elevated temperature strength and fabrication characteristics is the C-103 alloy. For aerospace applications at 1100–1500 °C, alloy C-103 has been the workhorse of the niobium industry because of its higher strength. Excellent cold forming and welding characteristics enable manufacturers to construct very complex shapes such as thrust cones and high temperature valves. Closed die forgings are also easily produced.

Most of the components in propulsion systems are exposed for relatively short times to temperatures between 1200 °C and 1400 °C. The service environments for propulsion systems are often less oxidizing than the normal atmosphere. However, because C-103 has virtually no oxidation resistance, components are extensively coated with silicides. The coatings contain elements such as chromium, hafnium, iron and nickel in addition to silicon. After the element-mixed coating is applied by spraying or dipping, it is diffused into the alloy at high temperature.

C-103 has also been considered for thrust augmenter (afterburner) flaps in aircraft engines. These flaps are placed at the tail end of the engine to form a high temperature liner in the afterburner section, typically reaching 1200–1300 °C and lasting for $\sim$100 h of afterburner time.

Niobium alloys have also been evaluated for various high temperature components of the (cancelled) US National Aerospace Plane. Hypersonic leading edges and nose cones were fabricated to function as heat pipe thermal management systems. The heat pipe concept was designed to transport extreme heat away from hot spots, such as hypersonic leading edges, to cooler areas, where heat could be expelled by radiation. A typical 500 g niobium heat pipe can dissipate over 10 kW of heat and operate isothermally at 1250–1350 °C.

In addition to these applications, niobium and its alloys are used in more common applications, for example in chemical engineering for heat exchangers, in high temperature furnace construction for heating, and for shielding elements.

12.3 Niobium-Silicide Based Composites

Niobium-silicide based composites are promising candidates for high temperature applications in the next generation advanced jet engines [16–19]. The suction casting method with large cooling rates has been used to produce alloys with refined and large volume fraction eutectic structures [20]. There have been several reviews of development of Nb-silicide based composites [21, 22]. Simple Nb-silicide composites are based on binary Nb-Si alloys; more complex systems are alloyed with Ti, Hf, Cr, and Al.

Alloying strategies have been developed to achieve an excellent balance of room temperature toughness, high temperature strength, and oxidation resistance. The melting point of the Nb-silicide based composites is in excess of 1750 °C. The density is in the range of 6.6–7.2 g/cm^3. The room temperature fracture toughness of the Nb-silicide based composite system has been reported to be >20 MPa/m.

Many of the research programme have focussed on developing a fundamental understanding of the solidification paths, mechanical behaviour, and oxidation resistance of the Nb-silicide based system.

The reactivity of the Nb alloy melts excludes the use of ceramic-based melting crucibles. However, Nb-silicide based composites have been fabricated using a range of processes including arc melting, ingot casting plus thermomechanical processing [21], directional solidification [22], vapour deposition, and powder metallurgy processing [21]. These techniques have successfully produced laboratory scale materials for alloy development and property studies. Directional solidification, investment casting, and hot extrusion have been used successfully to produce Nb-silicide composites. Recent investment mould developments have shown excellent potential for thin wall airfoils, although these techniques are not well developed with regard to the production of net-shaped airfoils.

The oxidation resistance of the Nb-silicides is sufficient to qualify for near term engine testing applications, but further improvements are required to satisfy the long-term design requirements. Additional work is required to generate an understanding of the mechanisms controlling properties such as fracture toughness, fatigue crack growth, and creep performance before these alloy systems can be considered for service. Process developments are required to manufacture actual components of Nb-silicide composites.

12.4 Other Refractory Metals

12.4.1 Tantalum and its Alloys

Tantalum provides a unique combination of properties among refractory metals. Its high melting point (2996 °C), reasonable modulus of elasticity, excellent room temperature ductility, low DBTT, and relatively high solid solubility for other refractory and reactive metals make it an alternative base material for high temperature structural applications.

The most common tantalum alloys are listed in Table 12.10 [15]. Ta-10W is primarily being considered for aerospace applications, while Ta-2.5W is used in heat exchangers and other welded-tube applications where high formability is needed. Other elements that can be added to modify tantalum properties include zirconium, hafnium, molybdenum, niobium, rhenium, and vanadium. The typical tensile strengths of tantalum and tantalum alloys from room temperature to 1800 °C are shown in Fig. 12.6 [15].

High purity Ta is produced by multiple melting in an electron beam melting (EBM) furnace. EBM can also be used for melting Ta-based alloys containing alloying elements with low vapour pressure. Vacuum arc remelting (VAR) is suitable for preparation of Ta-based alloys containing alloying elements with high vapour pressure.

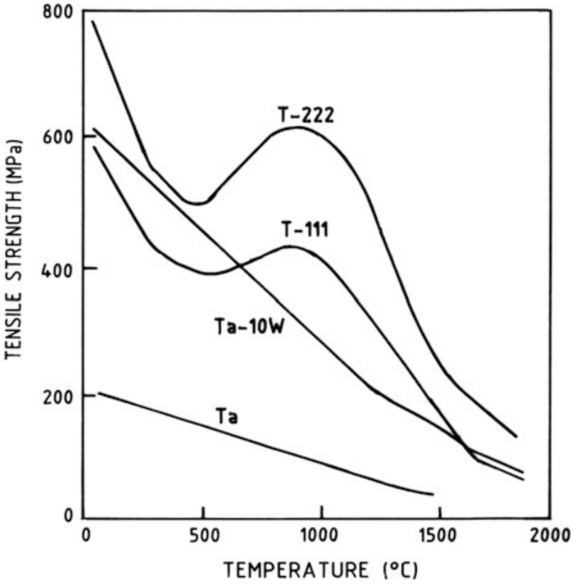
Both hammer and press forging techniques are used to produce flat slabs or round billets. Hot forging temperatures for typical commercial alloys range between 815 °C and 1260 °C. However, heating to temperatures within this range causes excessive oxidation. Therefore these alloys are heated using protective coatings or an inert gas atmosphere. Most tantalum alloys are either cold-rolled or warm-rolled (260–370 °C) to produce plates, wires, rods, etc. Cold die forging, spinning, hydroforming, and welding techniques are employed to produce complex shapes.

It has been reported that the largest (66 %) quantity of tantalum is used in the electronic industry in the form of powder, wire, and furnace hardware for the production of solid electrolyte capacitors. About 22 % tantalum finds applications in cutting tool industries, and only about 2 % is used for nuclear industries and defence applications. Primarily because of its unique combination of ductility and

Table 12.10 Commercial tantalum alloys

Alloy name	Composition (wt%)
	Ta-2.5W
	Ta-7.5W
	Ta-10W
T-111	Ta-8W-2Hf
T-222	Ta-10W-2.5Hf
ASTAR-811C	Ta-8W-1Re-1Hf-0.025C
	Ta-20Ti
	Ta-40Nb

Fig. 12.6 Tensile strengths versus temperature for pure tantalum and typical tantalum alloys



high density, tantalum has become the material of choice for several advanced anti-armour weapon systems. However, because of its very high density, initial efforts to use Ta and its alloys for aerospace applications have not been successful.

12.4.2 Molybdenum and Its Alloys

Molybdenum combines a high melting point with strength retention at high temperatures. Molybdenum also has a high specific elastic modulus, which makes it attractive for applications that require both high stiffness and low weight. The high thermal conductivity, low coefficient of thermal expansion, and low specific heat of this metal provide resistance to thermal shock and fatigue. These properties are also important for electronic applications.

Carbide-strengthened alloys were the first molybdenum alloys to be commercialized, see Table 12.11 [23]. Mo-0.5Ti, the initial alloy, is no longer commercially available. Its high temperature strength and recrystallization resistance were improved by adding about 0.08 % zirconium, resulting in the alloy known as TZM. A higher alloy-content modification of TZM, called TZC, has improved properties and responds to an age-hardening heat treatment. However, TZC has not replaced TZM as the commercial alloy of choice, primarily due to economic considerations.

More recently, alloys strengthened with hafnium carbide (MHC) and combinations of reactive metals carbides (ZHM) have been marketed. Figure 12.7 [23] compares the elevated temperature tensile properties of carbide-strengthened Mo

Table 12.11 Commercial molybdenum alloys

Alloy name	Composition (wt%)
TZM	Mo-0.5Ti-0.08Zr-0.01C
TZC	Mo-1.2Ti-0.3Zr-0.1C
MHC	Mo-1.2Hf-0.05C
ZHM	Mo-0.5-1.5Hf-0.2C

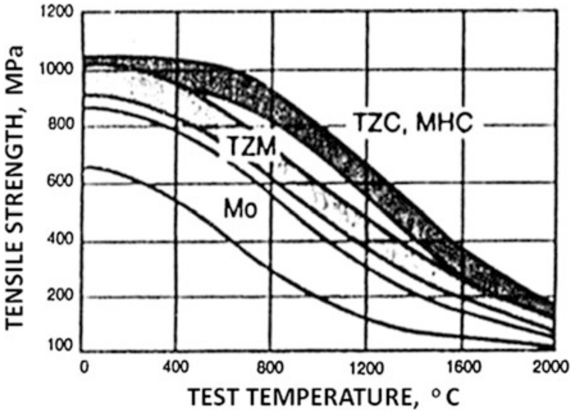


Fig. 12.7 Elevated temperature properties of carbide-strengthened molybdenum alloys

alloys. N.B: Both TZM and MHC are used as tooling materials in the isothermal forging of nickel-base superalloy parts for aircraft gas turbine engines.

Primary consolidation of molybdenum and its alloys can be done by either VAC or powder metallurgy (P/M) techniques. Both mechanical pressing and cold isostatic pressing (CIP) are used to consolidate P/M billets, although most P/M mill products originate as CIP'ed billets.

P/M billets are typically sintered in hydrogen because hydrogen reduces molybdenum oxides and further purifies the material. Vacuum sintering is used by some manufacturers.

Unalloyed molybdenum and TZM can be readily forged with a variety of tools including steam hammers, drop hammers, and hydraulic forging presses using either open or closed dies. Unalloyed molybdenum and TZM are typically forged in the 870–1260 °C temperature range. Billet heating is conducted in commercial gas or oil-fired furnaces. Billets and work pieces will lose weight from volatilization of the oxide at temperatures above 650 °C, but there is no scale formation: weight losses of 1–5 % can be anticipated.

Molybdenum and its alloys are readily extruded to form a variety of shapes including tubes, round to round bars, round to square bars, and round to rectangular bars. Pure molybdenum is typically extruded in the temperature range 1065–1090 °C, and TZM is extruded in the temperature range 1120–1150 °C. Large tubes and rings are fabricated from back-extruded solid billets. Additional ring-forming operations are undertaken via ring rolling. Molybdenum and its alloys can be fabricated in sheet form by conventional rolling and cross-rolling processes, and molybdenum and TZM sheet are typically supplied in the annealed condition.

Molybdenum is important in the missile industry, where it is used for high temperature structural parts such as nozzles, leading edges of control surfaces, support vanes, struts, re-entry cones, heat-radiation shields, heat sinks, turbine wheels and pumps. Alloy Mo-0.5Ti has been used for some aerospace applications, but TZM is preferred where higher hot strength is needed. The service temperatures for molybdenum alloys in structural applications are limited to a maximum of about 1650 °C.

12.4.3 Tungsten and Its Alloys

Tungsten has the highest melting point of any metal (3410 °C) and also the highest density (19.26 g/cm^3). It also has an unusually high elastic modulus (414 GPa) and is the only elastically isotropic metal. The high melting temperature and low vapour pressure of tungsten, along with its ability to be drawn into fine wire, were responsible for its initial commercial application in lamp filaments at the beginning of the twentieth century.

Tungsten has high tensile strength and good creep resistance. At temperatures above 2205 °C, tungsten has twice the tensile strength of the strongest tantalum alloys and is only 10 % denser. However, its high density, poor low temperature ductility, and strong reactivity in air limit its usefulness. Maximum service temperatures for tungsten range from 1925–2480 °C, but surface protection is required for use in air at these temperatures.

Tungsten heavy alloys usually contain Ni and Cu or Ni and Fe. The mechanical properties of tungsten heavy alloys are closely linked to W content, sintering variables, and the amount of post-sintering mechanical working. These alloys are mainly used in counterweights and anti-armor kinetic-energy penetrators. They are also considered for radiation shielding.

Three types of tungsten alloys are produced commercially: W-ThO_2, W-Mo, and W-Re alloys (Table 12.12) [24]. The W-ThO_2 alloy is a dispersed-second-phase alloy containing 1–2 % thorium oxide (thoria). The thoria dispersion enhances thermionic electron emission, which improves the starting characteristics of gas tungsten arc weld (GTAW) welding electrodes. Thoria also imparts creep strength to wire at temperatures above one-half of the absolute melting point of tungsten.

The W-Mo alloys are solid solution alloys. These alloys are used mostly for improved machinability, where strength requirements are somewhat lower than those of W and the W-ThO_2 alloy. W-Re alloys are also solid solution alloys. The W-1.5Re and W-3Re alloys are used to improve the resistance to cold fracture in lamp filaments, especially for lamps subjected to vibrations. These alloys also contain the AKS (alumina, silica, and potassium) dopants to improve the creep

Table 12.12 Commercial tungsten alloys

Alloy name	Composition (wt%)
W-ThO_2	W-1ThO_2
	W-2ThO_2
W-Mo	W-2Mo
	W-15Mo
W-Re	W-1.5Re
	W-3Re
	W-25Re
AKS doped	0.0015 Al, 0.009 K, 0.005 Si and 0.0035 O

strength in filament wire: undoped W-1.5Re and W-3Re alloys are used in thermocouple applications where strength is not the primary concern.

Tungsten is consolidated to full density by three principal methods, two of which are P/M processes. These methods are (i) solid-state sintering and mechanical working (wrought P/M tungsten), (ii) liquid-phase sintering of powders, and (iii) chemical vapour deposition (CVD). Tungsten and tungsten alloys may also be produced by arc casting or EBM, but these methods are not of significant commercial interest. Although tungsten produced by the melting route can have higher purity than P/M or CVD products, the slight improvement in mechanical and physical properties does not justify the added expense and engineering challenge of melting tungsten.

A cold isostatically pressed (CIP'ed) tungsten powder bar is self-resistance heated to around 2500 °C and sintered to 90 % of the theoretical density. The bar is then swaged and drawn into wire; or alternatively the sintered tungsten bar may be forged or rolled into bar or sheet products. Initial hot working is done at temperatures above 1500 °C, since the as-sintered bar is brittle at low temperature because it is fully recrystallized and not fully dense. However, there are more considerations about hot working: the DBTT of fully dense unalloyed tungsten is approximately 3000 °C and the recrystallization temperature is 1700 °C, and so the common thermomechanical processing scheme is to deform the metal at temperatures between the DBTT and the recrystallization temperature. As the amount of deformation increases, both the DBTT and the recrystallization temperature decrease. Hence at room temperature hot-worked tungsten bar is brittle, but heavily worked tungsten wire exhibits significant ductility.

Tungsten and tungsten alloys are used in mill products, as an alloying element in tool steels and superalloys, in tungsten carbide cutting tools, and in a variety of tungsten-based chemicals. In terms of refractory metal consumption, tungsten ranks second to molybdenum, with more than 8500 metric tons consumed annually. Cutting tools account for 59 % of the total; mill products, 26 %; alloying, 9 %; and chemicals and miscellaneous applications, 6 %.

12.4.4 Rhenium and Its Alloys

Rhenium has a very high modulus of elasticity and does not have a DBTT, since it retains its ductility from subzero to high temperatures. Its hardness increases sharply after a small amount of deformation: the work hardening rate is higher than that of any other pure metal. Rhenium products withstand many heating–cooling cycles without losing their strength. Rhenium also has superior tensile and creep rupture strength over a wide range of temperatures [25]: for example, rhenium shows longer rupture life compared to tungsten up to 1800 °C. In addition, rhenium has been found to survive more than 1,000,000 thermal fatigue cycles from room temperature to over 2500 °C without any evidence of failure [25, 26].

Rhenium powder can be produced by the reduction of pure ammonium perrhenate in a stream of hydrogen. The desired properties of the metal powder, such as grain size and surface area, can be achieved by adjustment of the reduction parameters. The rhenium metal powder with added compaction agents is compressed into pellets and then sintered (1000–1500 °C) under an atmosphere of hydrogen. Large workpieces are produced by compressing rhenium metal powders isostatically and then sintering. EBM and zone refining are the methods used to produce rhenium with 99.995 % or more purity [27].

Rhenium has very poor oxidation resistance and therefore cannot be hot-worked when exposed to air. Hence hot working has to be done under vacuum or in a protective atmosphere, or by adopting an encapsulation technique. Because of its very good ductility, rhenium can be cold-worked into wire, rod, sheet, plate, and tubing. Frequent intermittent annealing may have to be performed since, as mentioned above, rhenium work hardens very quickly. Electrical discharge machining, centreless grinding, and welding are manufacturing techniques commonly used for rhenium components.

Platinum-rhenium reforming catalysts are the major rhenium end-use products and account for a significant proportion of rhenium consumption. The higher electrical resistivity coupled with low vapour pressure makes it ideally suited for filament applications. One of the largest applications for rhenium is for mass spectrometer filaments. These are generally available in commercial (99.99 %) and zone-refined (99.995 %) purities.

Besides its intrinsic properties, rhenium is a beneficial alloying addition to other refractory metals and alloys, greatly enhancing their strength. This capability is maintained even when heating above the recrystallization temperature. For example, all aeroengine turbine blades made of second and subsequent generations of nickel-base superalloys contain 3–6 % Re, which significantly improves the creep properties [28]. Rhenium alloys are used in nuclear reactors, semiconductors, electronic tube components, thermocouples, gyroscopes, miniature rockets, electrical contacts, thermionic converters, and other commercial and aerospace applications. Tungsten-rhenium alloys, obtained by vapour deposition, are used to coat the surfaces of molybdenum targets in X-ray tubes. Other rhenium alloys (with tungsten or molybdenum) are used for filaments, grid heaters, cathode cups, and igniter wires in photoflash bulbs. Rhenium has been used as a heat exchanger material for a solar rocket, nozzles for rocket thrusters, and in high temperature thermocouples. Also, rhenium is unique among refractory metals in that it does not form a stable carbide. For this reason, rhenium-coated carbon has been evaluated for rocket nozzles.

The use of rhenium has been restricted by its high density and high cost. For example, the addition of 3 % rhenium to tungsten wire doubles the cost of the wire.

12.5 Indian Scenario

In India a number of organizations have been focussing efforts to develop different refractory metals and their alloys for a variety of applications. Nuclear Fuel Complex, Hyderabad, has been engaged in the production of aluminothermically reduced niobium from the ore, which is refined by multiple EB drip melting to produce reactor grade Nb. This is used to manufacture coolant tubes of Zr-2.5Nb alloy for heavy water nuclear reactors.

Recently M/s MIDHANI, Hyderabad, has produced sheets of C-103 (Nb-10Hf-1Ti) alloy for satellite applications, starting from imported sheets of high purity raw material. Two EBM furnaces of 150 and 300 kW have been recently established at MIDHANI to develop alloys based on refractory metals. BARC, Mumbai, is actively pursuing development of Nb-1Zr-0.1C alloy for nuclear applications. DMRL is involved in developing an Nb-based (Nb–W–Zr) alloy for aerospace applications.

DMRL has pioneered the development and application of tungsten for penetrator applications. An industrial plant (Ordnance factory) is in operation at HAPP, Trichy, producing W-based penetrators based on the DMRL technology. C-Met, Hyderabad, has perfected the technology of producing high purity tantalum for capacitor applications.

12.6 Summary

Future high temperature materials will depend on developments in refractory metals and alloys in view of their high melting temperatures and good high temperature mechanical properties. Refractory metals, with their unique properties, can perform in situations where no other materials can meet the required properties. The future developments in this area include developing alloys with the desired combinations of strength, ductility, and oxidation resistance. Niobium is particularly attractive for aerospace applications because of its lower density among refractory metals, which is comparable to that of nickel-base superalloys.

An effort has been made in this chapter to discuss the important features of refractory metals and their alloys in general, and niobium and niobium-based alloys in particular.

References

1. Stephen JJ (1990) Recent advances in high-temperature niobium alloys. JOM 42(8):22–23
2. Wittenauer J (1990) Refractory metals 1990: old challenges, new opportunities. JOM 42(8):07–10
3. Lambert JB (1990) Refractory metals and alloys. In: ASM handbook volume 2: properties and selection: nonferrous alloys and special-purpose materials. ASM International, Materials Park, OH, USA, pp 557–585
4. Frank RG (1968) Recent advances on columbium alloys. In: Machlin I, Begley RT, Weisert ED (eds) Refractory metal alloys metallurgy and technology. Plenum Press, New York, USA, pp 325–372
5. Cornie JA (1971) Development of precipitation strengthened columbium base alloys. AFML technical report AFML-TR-71-51, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Dayton, OH, USA
6. Roche TK, Graham DL (1970) Development of oxidation-resistant high strength columbium alloys. AFML technical report AFML-TR-69-344, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Dayton, OH, USA
7. Craigwojcik C (1991) High temperature niobium alloys. In: Stephens JJ, Ahmad I (eds) High temperature niobium alloys. The Minerals, Metals & Materials Society (TMS), Warrendale, PA, USA, pp 1–12
8. Sankar MV, Satya Prasad VV, Baligidad RG, Alam MdZ, Das DK, Gokhale AA (2015) Microstructure, oxidation resistance and tensile properties of silicide coated Nb-alloy C-103. Mater Sci Eng, A 645:339–346
9. Eckert J (1997) Refractory metals. In: Habashi F (ed) Handbook of extractive metallurgy, vol III'. Wiley-VCH, Weinheim, Germany, pp 1403–1416
10. Wojcik CC (1998) High temperature niobium alloys. Adv Mater Processes 154(6):27–30
11. Katsutoshi O, Kim YH (1992) Electron beam melting and refining of niobium. ISIJ Int 32(5):650–655
12. Choudhary A, Hengsberger E (1992) Electron beam melting and refining of metals and alloys. ISIJ Int 32(5):673–681
13. Loomis BA, Greber B (1970) The yield-stress of niobium and niobium-oxygen solid solutions. Scr Metall 4(11):921–924
14. Sankar M, Baligidad RG, Gokhale AA (2013) Effect of oxygen on microstructure and mechanical properties of niobium. Mater Sci Eng, A 569:132–136
15. Buckman RW (2000) New applications for tantalum and tantalum alloys. JOM 52(3):40–41
16. Mendiratta MG, Lewandowski JJ, Dimiduk DM (1991) Strength and ductile-phase toughening in the two-phase Nb/Nb_5Si_3 alloys. Metall Trans A 22A:1573–1581
17. Mendirattaa MG, Dimiduk DM (1993) Strength and toughness of a Nb/Nb5Si3 composite. Metall Trans A 24A(2):501–504
18. Bewlay BP, Jackson MR, Lipsitt HA (1996) The balance of mechanical and environmental properties of a multielement niobium-niobium silicide-based in-situ composite. Metall Mater Trans A 27A(12):3801–3808
19. Bewlay BP, Jackson MR, Subramanian PR (1999) Processing of high-temperature refractory metal silicide in-situ composites. JOM 51(4):32–36
20. Kashyap C, Tiwary CS, Chattopadhyay K (2013) Microstructural and mechanical behaviour study of suction cast Nb-Si binary alloys. Mater Sci Eng, A 583:188–198

21. Subramanian PR, Mendiratta MG, Dimiduk DM, Stucke MA (1997) Advanced intermetallic alloys—beyond gamma titanium aluminides. Mater Sci Eng, A 239–240:1–13
22. Bewlay BP, Jackson MR, Gigliotti MFX (2002) Niobium silicide high temperature in situ composites, Chap 26. In: Westbrook JH, Fleischer RL (eds) Intermetallic compounds—principles and practice—Volume 3: progress, 3rd edn. Wiley, Hoboken, NJ, USA, pp 541–560
23. Shields JA (1992) Molybdenum and its alloys. Adv Mater Processes 142(3):28–36
24. Wittenaurer JP, Nieh TG, Wadsworth J (1992) Tungsten and its alloys. Adv Mater Processes 142(3):28–37
25. Carlen JC, Bryskin BD (1994) Rhenium—a unique rare metal. Mater Manuf Processes 9(6):1087–1104
26. Sherman AJ, Tuffias RH, Kaplan RB (1991) The properties and applications of rhenium produced by CVD. JOM 7(7):20–23
27. Bryskin BD (1992) Rhenium and its alloys. Adv Mater Processes 142(3):22–27
28. Reed RC (2008) The superalloys: fundamentals and applications. Cambridge University Press, New York, NJ, USA, pp 170–187