RHENIUM AND IRIDIUM

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Abstract

Rhenium is used together with the metal iridium in a number of metallurgical applications. Iridium has been used as coating for rhenium rocket thrusters and as an oxidation-resistant coating in a number of other applications. The high strength of rhenium at elevated temperature is combined with the oxidation resistance and high-melting point of iridium. The use of the two metals together is advantageous due to the absence of any stable intermetallic compounds. Both rhenium and iridium alloying additions improve the ductility of tungsten. The high solubility of rhenium in iridium is also taken advantage of to produce iridium-based alloys for structural applications. The uses of rhenium in conjunction with iridium are discussed.

DISCLAIMER

Introduction

Iridium is included as one of six platinum group metals. It is characterized by its excellent corrosion resistance, good oxidation resistance, and high melting point of 2447°C, which is 670°C above that of platinum. Iridium is produced primarily as a by-product of platinum production. The price of the iridium metal powder is currently about $2 per gram. Annual usage world wide is about 1800 kg (ref. 1). A major use for iridium is in coatings for electrodes used in chlor-alkali production plants. One of the more common uses of bulk iridium is in crucibles for crystal growth of oxide materials such as yttrium aluminum garnet, ruby, and sapphire, which have melting temperatures up to 2000°C. Iridium also finds use in aircraft spark plugs, electrical contacts, high-temperature thermocouples, certain vacuum tube filaments, some ceramic fiber extrusion dies, and as an alloying addition in some platinum alloys. Iridium alloys are used for fuel cladding for radioisotope thermoelectric generators used for space power (2).

Rhenium is one of the less common refractory metals. It has good strength and ductility at elevated temperature but poor oxidation resistance. It is used as an alloying element in tungsten and molybdenum alloys to improve ductility and is also used as an alloying element in high-temperature thermocouples for nonoxidizing environments.

The physical metallurgy and properties of iridium are reviewed. The properties of iridium are shown to complement those of rhenium, leading to use of the two metals together in a number of applications. The two metals also share some similar properties so that in some instances they can substitute for one another.

Properties of Iridium

Environmental Resistance of Iridium

Iridium has good resistance to oxidation in air or oxygen. Iridium has low solubility for oxygen and, at temperatures of 1100°C and below, forms a stable stoichiometric IrO_2 solid (3). The predominant gas species is IrO_3, although IrO and IrO_2 gases can also be formed. The oxidation rates are sensitive to partial and total gas pressures and can be affected by gas flow rates over the surface. Mass loss measurements are linear with time. The rate of metal recession determined from weight-loss measurements in oxygen and air are shown in Figure 1 for pressures from 1000 to 10^{-4} mbar and temperatures of 1675, 1965, 2210, and 2260°C (ref. 4).
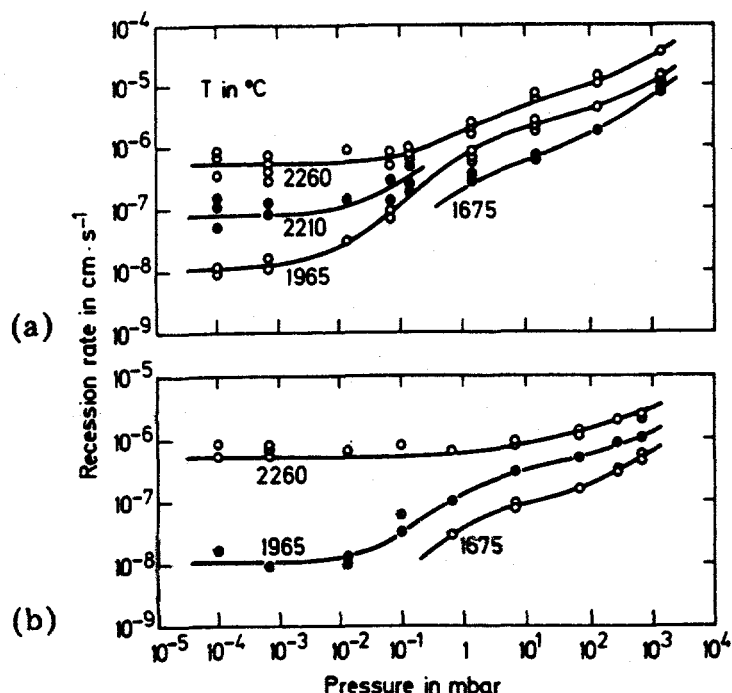
Figure 1 - The effect of gas pressure on the rate of weight loss of iridium due to oxidation both in (a) oxygen and (b) air at temperatures from 1675 to 2260°C (from ref. 4).

Improvement in the oxidation resistance can be achieved through alloying of iridium. Alloys with hafnium and tantalum additions decrease weight gains in tests in air at 1925°C, but are susceptible to internal oxidation. Surface recession is 25 μm/h for pure iridium as compared to 3 μm/hr for an Ir-16.2% Hf-7.5% Ta alloy, which forms a continuous hafnium-oxide scale. If the depth of penetration from internal oxidation is considered, metal loss of the alloy is 25% lower than that of the pure metal in short time tests (5). Alloying of iridium with aluminum to produce iridium aluminide has recently been developed using the chemical vapor deposition (CVD) process. Oxidation resistance is two orders of magnitude better than that of pure iridium at 1600°C but is equivalent to pure iridium at 2000°C (ref. 6). The melting point of IrAl is 2120 ± 20°C and the Ir-IrAl eutectic temperature is 2060°C (ref. 7).

Mechanical Properties of Iridium

Iridium has good high-temperature strength and creep properties. The tensile strength at temperatures up to 1700°C is intermediate between that of molybdenum and tungsten. The stress rupture properties are superior to that of molybdenum at 1100°C (ref. 8) Tensile

strength of iridium at temperatures of 1000 to 2000°C is shown in Table I (ref. 9). Tensile properties of an Ir-0.3% W-0.006% Th alloy are shown in Figure 2 for the temperature range of 600 to 1100°C (ref. 10).

Table I Ultimate Tensile Strength of Iridium at
Elevated Temperature (from ref. 10)

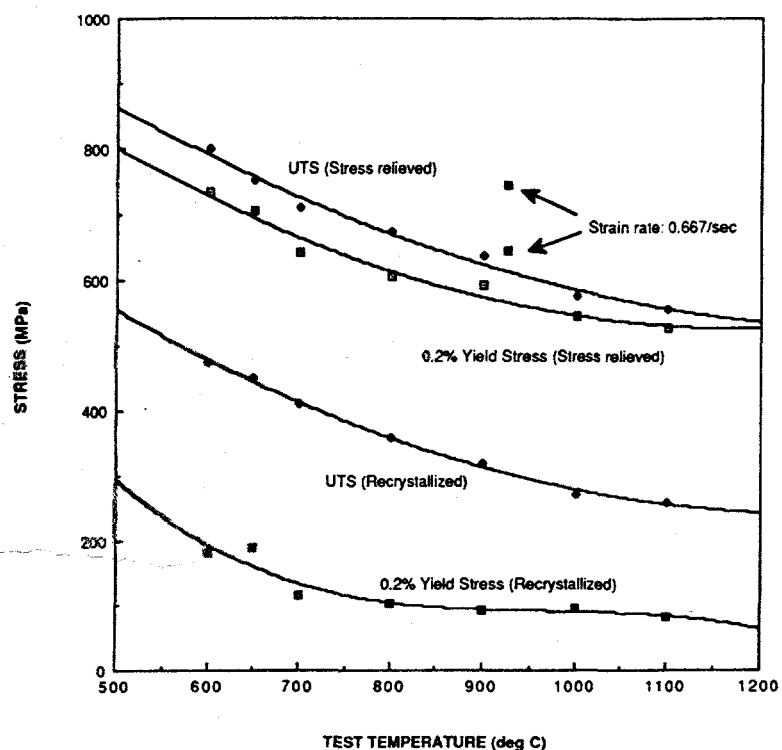| Temperature (°C)	Ultimate Tensile Strength (MPa)
1000	280
1200	165
1400	85
1600	60
1800	45
2000	35

Figure 2 - Tensile properties of an Ir-0.3% W-0.006% Th alloy in the temperature range of 600 to 1100°C (from ref. 10).

Although iridium has a face-centered cubic (FCC) structure, its mechanical behavior is similar to many body-centered-cubic metals, in that it shows a ductile-to-brittle transition. Iridium exhibits cleavage fracture in tensile tests over a large range of temperatures, although frequently after significant tensile elongation. The cleavage is inherent to the material and not caused by impurities (11). Intergranular fracture is also a failure mode under some conditions. An iridium alloy, Ir-3% Re-2% Ru, exhibits intergranular fracture in tensile tests above 1250°C. Transgranular fracture of both this alloy and pure iridium at low temperature has been associated with carbon impurities (12). Grain size is important in controlling intergranular cracking of iridium (13). The tendency for grain-boundary fracture can be decreased and ductility of iridium increased by additions of thorium at levels of 200 ppm or less (14,15). A similar effect is also seen with cerium additions (16).

Microstructures of Iridium

Pure iridium can recrystallize at temperatures as low as 800°C. The recrystallization temperature for alloys can be considerably higher. The Ir-0.3% W-0.006% Th alloy has a recrystallization temperature of about 1200°C. Grain growth is also affected by composition (17). Grain boundary segregation in iridium alloys occurs for a number of elements. Thorium and the rare earth metals (cerium, yttrium, and lutetium) are known to segregate to grain boundaries, with grain-boundary concentrations of several percent in materials with bulk contents of less than 40 ppm (ref. 18). Tungsten does not strongly segregate to grain boundaries (19).

Iridium-Rhenium Phase Diagrams

The hexagonal, close-packed rhenium dissolves up to 45 wt % Ir, and the FCC iridium dissolves up to about 40 wt % Re, as shown in Figure 3. No intermetallic phases are formed (20). Rhenium is unique among the refractory metals (Nb, Mo, Ta, W, and Re) in that it does not form intermetallic phases with the platinum group metals (Ru, Rh, Pd, Pt, Ir, and Os). The only exception is the palladium-tungsten system (21). The lattice parameters, c and a, for rhenium-rich iridium-rhenium alloys have been measured (22). The c/a ratio decreases from 1.612 for pure rhenium to 1.588 for Re-40 at. % Ir.

Neither iridium nor rhenium form stable carbides. The solubility of carbon in iridium is 0.2% at the eutectic temperature of 2295°C. The solubility of carbon in rhenium is 0.8% at the eutectic temperature of 2486°C (ref. 23). The solubility of carbon in both metals for the temperature range of 820 to 1256°C is shown in Figure 4. The solubility of carbon in
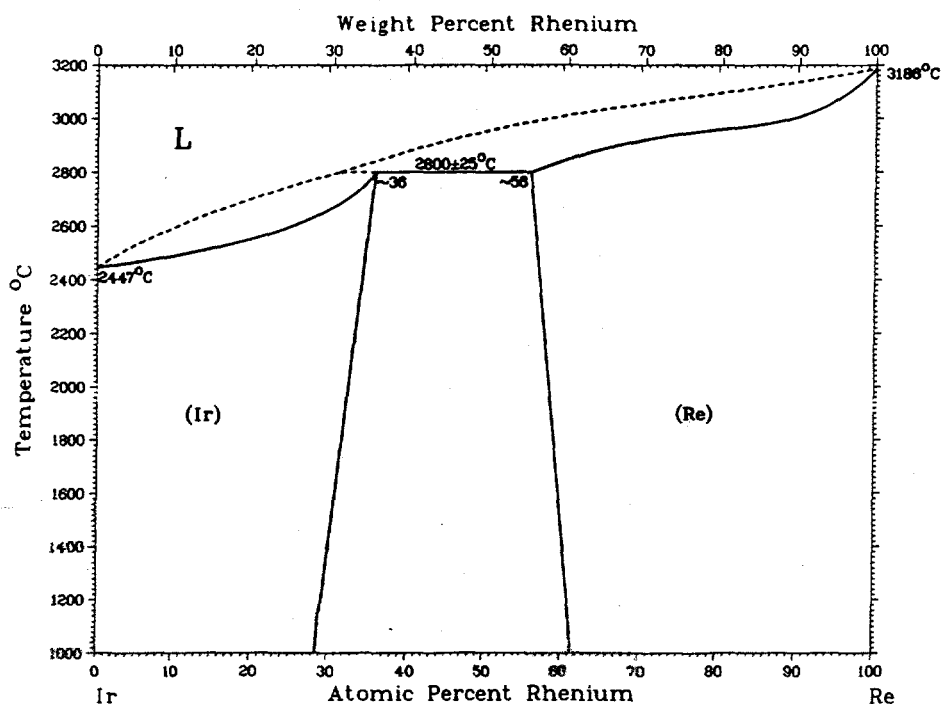
Figure 3 - The Ir-Re binary phase diagram shows substantial mutual solubility of the two metals and the absence of intermetallic compounds (from ref. 21).
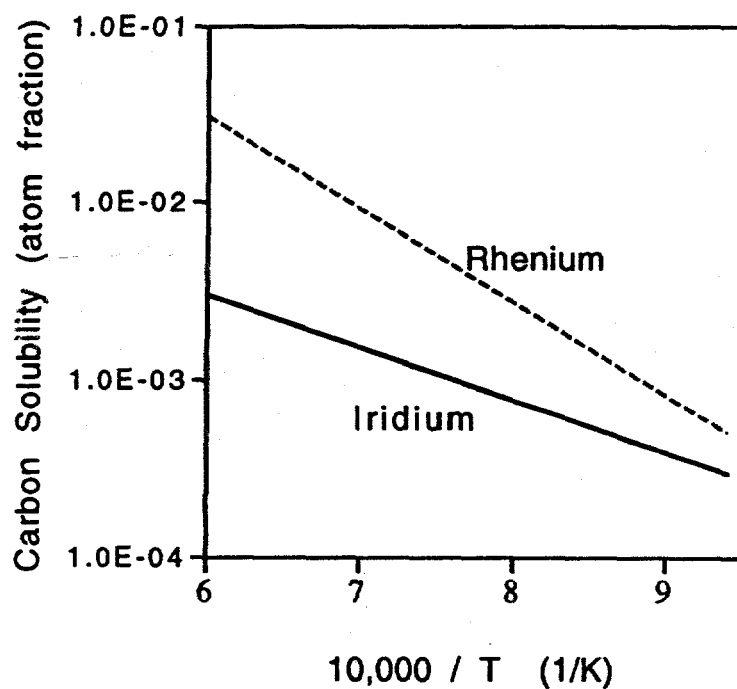

Figure 4 - The solubility of carbon in both iridium and rhenium for the temperature range of 820 to 1256°C (after ref. 24).

rhenium increases from 70 to 1200 ppm, and the solubility of carbon in iridium increases from 15 to 150 ppm over this range of temperatures (24). In contrast to pure carbon, metal carbides are generally not stable in contact with iridium. Both TiC and HfC react with iridium to form intermetallic compounds or alloys and regions of graphite (25).

The W-Re-Ir ternary phase diagram is of particular interest due to the prevalence of W-Re alloys and the use of iridium as a coating for high temperature oxidizing environments. An isothermal section of the tungsten-rich portion of this ternary system at 1500°C is shown in Figure 5. The solubility of iridium in tungsten-rhenium alloys decreases with increased rhenium content for the range of 0 to 40% Re. Iridium stabilizes the sigma phase over large portions of the ternary phase diagram (26). With regard to the use of iridium as a coating, the phase diagram indicates that while no intermetallic compounds will form with iridium coating of rhenium, all of the tungsten-rich tungsten-rhenium alloys will form intermetallic reaction layers at elevated temperature.
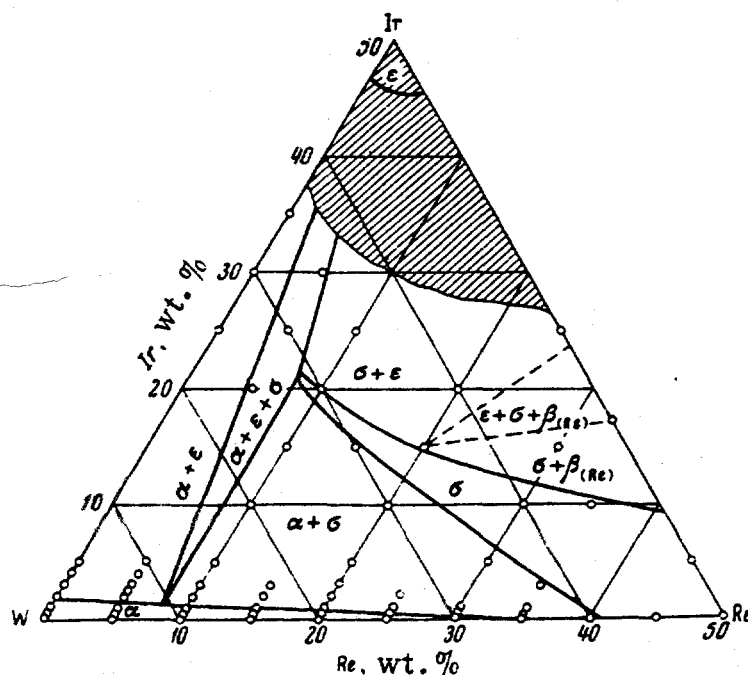

Figure 5 - The isothermal section of the tungsten-rich portion W-Re-Ir ternary phase diagram at 1500°C (from ref. 26).

Comparison of Iridium and Rhenium In Solid Solution Softening of Tungsten

The effect of rhenium as an alloying addition to tungsten and molybdenum to produce both solid solution softening and enhanced tensile ductility is well known. It has been shown

that iridium produces the same effect in tungsten as does rhenium, but at much lower levels of alloying (27). The microhardness, yield strength, and ultimate tensile strength show minima at 0.4% Ir. The tensile ductility of the W-Ir alloys are shown in Figure 6. At room temperature, the alloys all fracture by transgranular cleavage. The elevated-temperature strength of tungsten is increased by additions of iridium (28). The yield strength of the W-0.4% Ir alloy is about the same as the W-3.6% Re alloy at 1327°C and is greater than that of the W-3.6% Re alloy at higher temperatures. The yield strengths do not approach those of the W-26% Re alloy (29).
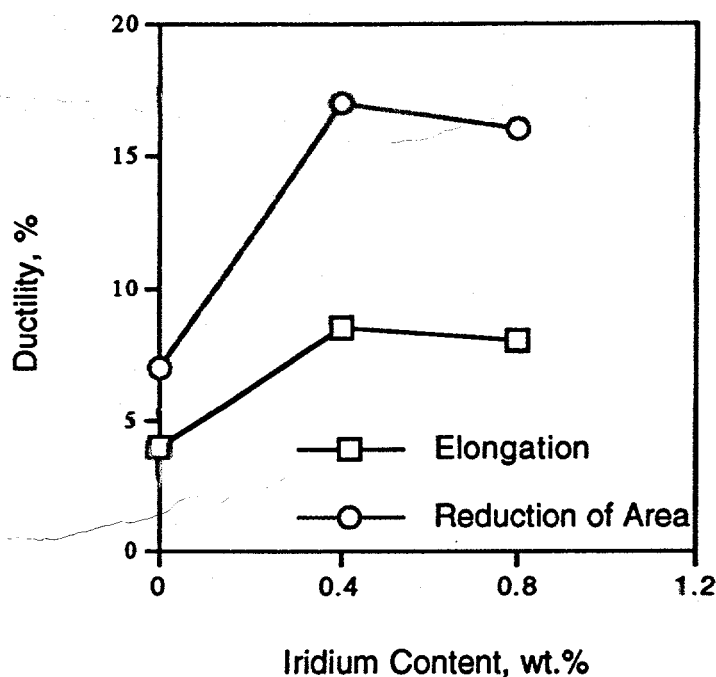
Figure 6 - The effect of iridium content on the room temperature tensile ductility of the W-Ir alloys (from ref. 27).

As a practical matter, tungsten-rhenium alloys are most commonly fabricated by powder metallurgy for economic reasons. While there is considerable powder metallurgy technology for W-Re, there is little for W-Ir system (30). The effect of iridium on the sintering behavior of tungsten is complex. The addition of 1% Ir increased sintered density at 2000°C from 16.1 to 16.7 g/cc with an increase in hardness and compressive strength (31). In the temperature range of 1050 to 1200°C, iridium additions of 0.25 to 4% decrease the sintering rate, as compared to pure tungsten (32).

Rhenium provides solid solution strengthening and improved creep resistance to iridium. Creep curves for Ir-5% Re tested 9.8 MPa at temperatures of 1600 and 1700°C are shown in Figure 7. This alloy is intended for use in crucibles for growth of gadolinium-gallium-garnet crystals (33). The alloy is less reactive with molten crystal material than Ir-W alloys. Further, rhenium alloy additions to iridium do not depress the melting point, whereas tungsten additions depress the melting point by about 7°C for each 1% addition.
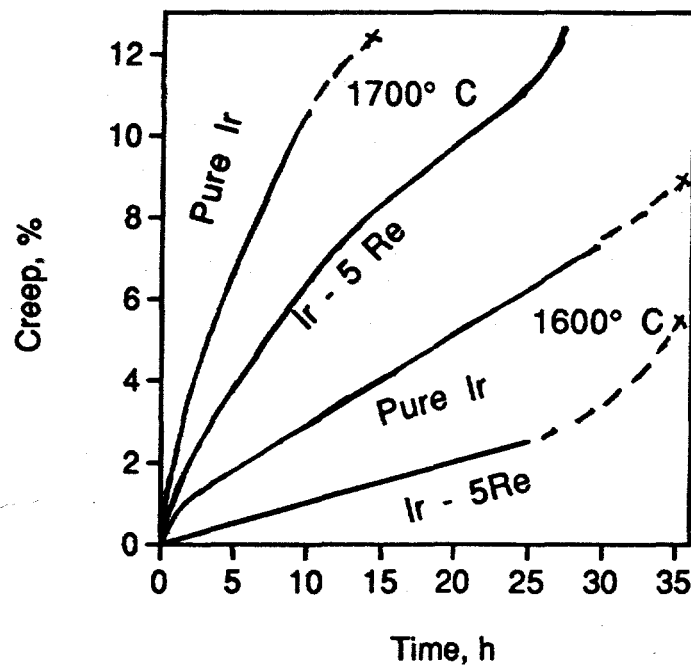
Figure 7 - Creep curves at 1600 and 1700°C for pure iridium and Ir-5% Re alloy tested 9.8 MPa (2 in. gauge length, from ref. 33).

Rhenium also increases the tensile properties of iridium. The tensile properties at 1370°C of iridium with binary alloying additions of 0.65% Hf, 10% Ru, 1.92% W, or 1.98% Re are listed in Table II (ref. 34). The yield and tensile strengths from the rhenium addition are not as high as those with a similar tungsten addition, although the tensile elongation is higher for the rhenium-containing alloy. The tensile elongation of this alloy is also higher than that of the pure iridium. Weight losses from oxidation in air at 1000°C for 200 h for the alloys were similar to that for pure iridium. At temperatures of 870 and 770°C, oxidation rates of the alloys were lower than pure iridium.

Table II Tensile Properties of Iridium Alloys at 1370°C (from ref. 34)

Alloy (wt %)	Yield Stress (MPa)	Tensile Strength (MPa)	Elongation (%)
Iridium	50	160	50
Ir-0.65% Hf	100	425	50
Ir-1.92% W	115	310	42
Ir-1.98% Re	85	205	55
Ir-10% Ru	85	260	43

A study of the effect of iridium coating on the work function of rhenium mass spectrometer elements shows that the work function increases with increased iridium coverage (35). The addition of iridium to W-Re alloy coatings of impregnated tungsten cathodes has similarly been shown to increase the work function. The same study shows that the diffusion of iridium in the 40% Re-40% Ir-20% W alloy is significantly lower than that of rhenium (36).

Iridium Coating of Rhenium

The use of iridium as an oxidation-resistant coating for rhenium rockets has been developed over the past 15 years (37). Iridium can be deposited by CVD onto a molybdenum mandrel followed by deposition of rhenium also by CVD and chemical dissolution of the molybdenum mandrel. The high strength of rhenium is combined with oxidation resistance of the iridium coating. No intermetallic compounds are formed, so that ductility of the coating remains even after exposure at the very high operating temperatures of up to 2200°C. This serves to minimize spallation of the coating and increase resistance to thermal shock. In some applications coating of the iridium with oxides, such as HfO_2 and ZrO_2, or composites of these oxides with iridium shows improved oxidation resistance at high temperatures (38). A carbon-carbon composite structure has been tested which permits the use of a thin internal-coated rhenium liner to achieve significant cost and weight reductions (39). An alternative method for fabrication of iridium coated rhenium employs an electrochemical deposition of iridium onto a rhenium structure produced by powder metallurgy (40).

Diffusion in iridium-coated rhenium produced by CVD has been studied for the temperature range of 1400 to 1900°C in vacuum (41). The material was produced by CVD coating a

layer of iridium 50 µm thick at a rate of about 20 µm/h onto a molybdenum mandrel. The 2-mm-thick rhenium layer was then deposited at about 40 µm/h. As deposited, the interface exhibited 2 to 3 µm of intermetallic layer identified as IrMo and Ir3Mo. This is formed by interdiffusion of the iridium and molybdenum during deposition of the rhenium layer at a temperature stated to be about 1200°C. The growth of iridium-molybdenum intermetallic layers in the temperature range of 1200 to 1500°C has been characterized (42). These intermetallics form over this entire temperature range and are not removed by normal acid cleaning procedures. The thickness of the intermetallic layer formed on the CVD iridium coating is less than would be predicted for 50 h at 1200°C. The intermetallic layer remained after the molybdenum mandrel was chemically removed, and this layer could be removed electrochemically, if desired.

The diffusion of rhenium through the CVD iridium is shown to be controlled primarily by grain boundary diffusion, although there is also some diffusion from the grain boundary to the interior of iridium grains. It has been proposed that the diffusion of rhenium into the iridium would lead to an elevated rhenium content at the free surface and consequent failure of the coating. In practice, coating life has substantially exceeded that predicted by this diffusion-related failure mechanism (43). The more appropriate model for transport of rhenium may be diffusion through iridium grain boundaries and subsequent oxidation to the volatile Re_2O_7 oxide. This permits a steady state to be reached with low levels of rhenium dissolved in the iridium in the vicinity of the free surface and a finite rate of transport and loss of rhenium. Such a mechanism in some ways analogous to the grain boundary diffusion of thorium and subsequent external oxidation to ThO_2 observed in the Ir-0.3% W-0.006% Th alloy when heated in low pressure oxygen (44). In the case of the ThO_2, patches of oxide appear on the surface of the iridium, while in the case of rhenium, the oxide violatilizes. This model would predict a rate of iridium oxidation essentially unaffected by the underlying rhenium substrate and a finite rate of rhenium consumption by diffusion through the iridium coating.

Summary

Iridium and rhenium have some similarities in their properties. Both metals have high density, high melting points, and good elevated temperature strength. Both elements present some challenges in their fabrication, and both elements can be used as alloying agents in tungsten to improve the low temperature ductility and high temperature strength. Although iridium does form volatile oxides when heated in air at temperatures above 1200°C, nevertheless, it has good resistance to oxidation combined with high melting

temperature, which makes it attractive in a number of applications. For the same reasons, iridium has found use as a coating for rhenium in high temperature oxidizing environments. The absence of intermetallic formation in the iridium-rhenium system permits the coating to remain ductile during use and, thus, minimize spallation and damage from thermal shock. Rhenium is also used as an alloying addition in some iridium alloys to improve strength.

Acknowledgements

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