

Properties of Binary Rhodium Alloys

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Rhodium has a higher melting point, greater specific strength and better oxidation resistance than most of the refractory and platinum group metals but, to date, neither rhodium nor its alloys have found wide application as structural materials. During a recent study of rhodium alloys a vast amount of data was collected, and a selection of this information is recorded here. An investigation of the mechanical properties of some of these alloys indicates that a number of them could be useful for specific applications that take place under arduous conditions.

Crucibles made of rhodium have found limited use, specifically during the growth of calcium tungstate (CaWO_4) and barium metatitanate (BaTiO_3) single crystals, being selected for this application because rhodium maintains its shape better than zirconia grain stabilised (ZGS) platinum alloys at the operating temperature range of 1610 to 1650°C (1). Additionally a number of rhodium alloys have been considered as structural materials for use in the glass industry, but they did not find practical application because rhodium dissolved from the fabricated product and discoloured the glass. Now, however, advances in metal melting technology have made it possible to produce a large number of new rhodium alloys, the development and properties of which are summarised here.

At the start of this investigation a survey of published information revealed that most elements have a solid solubility of 2 to 15 atomic per cent in rhodium, as shown by their phase diagrams, but only limited information about the mechanical properties of rhodium alloys was discovered (2-7). For this reason a series of dilute rhodium alloys was prepared by argon arc melting pure elements. These alloys are listed in Table I. The concentration of the additional elements was 1 weight per cent, which for most alloys is below the solid solubility limit and thus prevents precipitation of a second phase. The cast alloys were then fabricated into sheets, and their stress rupture

properties determined at loadings of 110 to 345 bar, at temperatures of 1200, 1300 and 1400°C. As a result of an initial study, further alloys were then prepared to enable the effect of the concentration of refractory group metals and indium upon the creep life of these rhodium alloys to be determined.

As-cast hardness values for binary rhodium alloys containing 1 weight per cent of the alloying element are given in Table I. Most elements produced a small hardness increase of 20 to 70 Hv, compared to the figure for pure rhodium. However, the addition of boron, selenium or cerium resulted in a significant increase in hardness, to 665, 446 and 304 Hv, respectively; but of these only the cerium alloy was workable. Later the amount of the alloying element was reduced to 0.5 weight per cent for the hafnium, gadolinium and dysprosium alloys, and to 0.1 weight per cent for boron-, sulphur- and phosphorus-containing rhodium alloys, because higher concentrations made the alloys unworkable.

The addition of 0.5 weight per cent hafnium and 1 weight per cent tungsten, rhenium, platinum or ruthenium improved the cold formability of annealed hot-rolled rhodium sheet, as shown by the cupping test results given in Table II.

The principal mode of oxidation of rhodium alloys at temperatures of 1200 and 1400°C was by grain boundary diffusion and internal oxidation. Alloys which contained hafnium, niobium

Table III											
Contact Angle between Crown Glass and Binary Alloys of Rhodium Containing 1 Weight Per Cent of the Second Element											
contact angle in degrees											
Colour of Liquid Crown Glass after Compatibility Testing at 1200°C											
Mg									Al		
v. light brown								60	clear		
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu		
v. light brown	47 v. light green	52 v. light green	55 clear	clear	45 clear	clear	58 blue	55 brown	62 clear		
	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag		
	v. light blue	52 light green	47 clear	v. light brown		73 clear	33 light brown	57 v. light green	57 clear		
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au		
	v. light green	62 clear	v. light green	v. light green	53 v. light green	56 clear	67 clear	62 v. light brown	38 clear		
	Ce	Pr	Nd		Sm		Gd	Tb	Dy		
	light blue	clear	v. light green		v. light brown		v. light green	v. light brown	v. light green	Er	Lu
										v. light brown	clear

v. light = very pale (colour)

or zirconium developed the most protective oxide layer. The surface of the hafnium-containing alloy revealed slight pitting, and the oxide layer which had formed after 281 hours at temperature was only 0.002mm thick, compared with 0.1 to 0.3mm for the other refractory group metals. Initial calculations based on thickness measurements made of the oxide layers formed at 1200°C on alloys containing refractory group metals revealed that the rate of oxidation was controlled by the diffusion of the alloying element. The protective oxide layer which formed on zirconium alloys made them very difficult to weld during fabrication trials. Most of the alloys revealed an increased weight as the alloying element was converted into oxide.

Glass compatibility tests showed that several of the alloys listed in Table III did not colour liquid crown glass at 1200°C. Apparently the dissolution of rhodium into the liquid glass had been prevented by either the alloying element or by the formation of a protective oxide layer which prevented colouration of the liquid glass. The only alloy which did not display a substantially increased contact angle with this glass was 1 weight per cent gold-rhodium.

At both 1200 and 1400°C, the effect of most alloying elements was to increase the stress rupture life compared to that of rhodium, at a loading of 345 bar (Table IV). The alloys with the longest creep lives at 1200°C were those containing scandium, zirconium, holmium and lutetium, and at 1400°C niobium and tantalum. The creep resistance of these rhodium alloys was less than that of ZGS 10 per cent rhodium-platinum; the elongation to fracture for the rhodium alloys was a minimum of 3.9 per cent at 1200°C, and 6.6 per cent at 1400°C, compared with 0.1 per cent for ZGS 10 per cent rhodium-platinum at both these test temperatures. During creep testing rhodium alloys became very brittle due to grain boundary cavitation. This embrittlement may limit the usefulness of these rhodium alloys, as they would not be suitable for use in highly stressed components.

The effect of the concentration of refractory

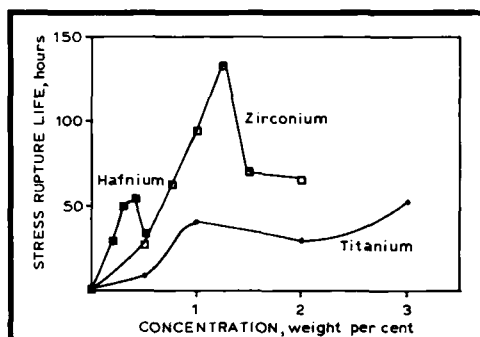


Fig. 1 The stress rupture life of rhodium alloys, at a temperature of 1200°C and a loading of 345 bar, varies with the concentration of Group IVB alloying elements

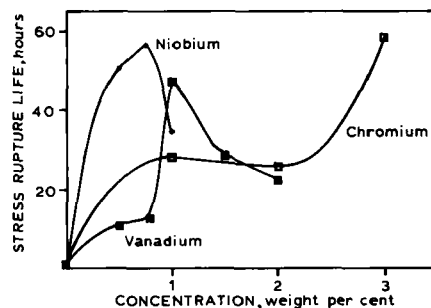


Fig. 2 The stress rupture life of rhodium alloys at 1200°C and 345 bar varies with the concentration of the Group VB elements and chromium

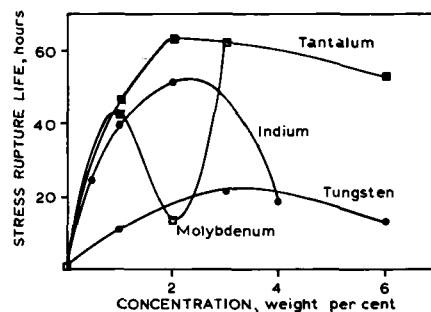
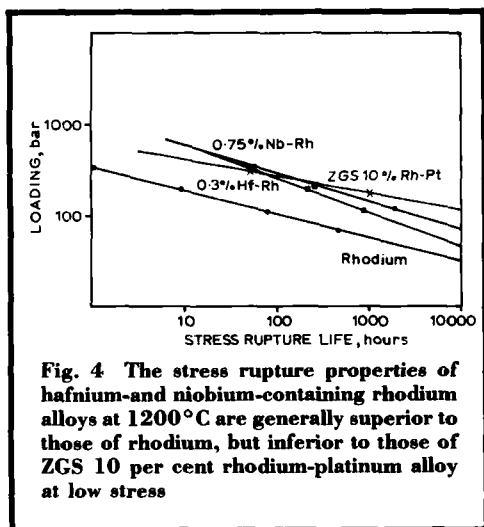


Fig. 3 Variations in the stress rupture life of rhodium alloyed with Group VIB elements, tantalum and indium, at 1200°C and 345 bar. The latter alloy achieves a maximum life at about 2 weight per cent indium

group metals and indium on creep life at 1200°C and a loading of 345 bar is shown in Figures 1 to 3. As the concentration of hafnium,



zirconium, niobium, vanadium and indium was increased, a maximum stress rupture life was reached for each alloy. These maxima may have been produced by the optimum dispersion of oxide particle size and distribution. At higher concentrations the stress rupture life decreased as the oxide particle size distribution exceeded the optimum, and promoted large particles at the grain boundaries which acted as crack initiators. The alloys containing titanium, chromium and molybdenum revealed an initial peak in the stress rupture life, and then a higher secondary peak; this effect may have been caused by the precipitation of a second metallic phase. The maximum creep life of alloys containing tungsten and tantalum was less affected by concentration and may have been caused by solid solution hardening. Small additions of 0.1 per cent boron or 0.1 per cent carbon to rhodium increased the creep life from 0.6 hours to 13.3 hours and 25.1 hours, respectively, at 1200°C and a loading of 345 bar. At 1400°C, the maximum creep life of alloys containing titanium, zirconium, vanadium and molybdenum occurred with higher concentrations of the alloying elements, this data being collected in Table V.

At applied stress values of 110 and 207 bar the rhodium alloys are weaker than ZGS 10 per cent rhodium-platinum, at 1200°C, as is shown

in Figure 4. At the relatively low stress of 110 bar, the most effective alloy addition was 0.1 weight per cent silicon, this alloy having a creep life of 2147.6 hours (Table VI). The premature failure of rhodium alloys at these low stress values was due to oxygen diffusion. This caused oxidation of the alloying elements, and the resultant large oxide particles acted as crack initiators; in addition the oxygen caused cavitation to occur at grain boundary triple points.

The effect of temperature upon the mechanical properties of a 0.75 per cent niobium-rhodium alloy is shown in Figure 5. Both proof stress and tensile strength decreased rapidly at 900°C, with the onset of recovery. Nevertheless this alloy was twice as strong as a cobalt based alloy from which most spinner baskets used for the manufacture of continuous fibres are generally made, and had a strength to weight ratio of 1.22 bar/g compared with 1.05 bar/g for the cobalt based alloy.

Discussion

If the Lewis acid base stabilisation theory is applied for oxides (8), it can be used to explain the improvement in stress rupture lives of dilute solutions of the transition metals zirconium, hafnium and niobium binary alloys. This shows that the improvement in the creep strength of binary rhodium alloys with refractory group metals can be explained by examining the binding energy of AB compounds

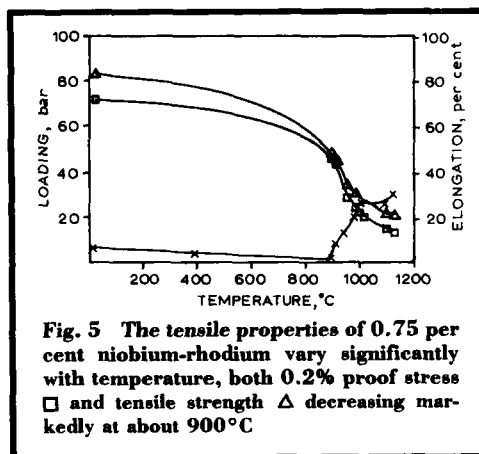


Table V
Effect of Composition on the Stress Rupture Properties of Rhodium Alloys,
at a loading of 345 bar

Alloying element	Test temperature, °C	Concentration of the alloying element, weight per cent														
		0.0	0.1	0.2	0.3	0.4	0.5	0.75	0.8	1.0	1.25	1.5	2.0	3.0	6.0	
Time to failure, hours																
Boron	1200 1400		13.3 0.8													
Carbon	1200 1400		25.1 0.3						0.2							
Chromium	1200 1400								28.0 2.1				25.5 1.2	58.6 3.4		
Hafnium	1200 1300 1400		28.8 10.2 3.7	49.8 9.4 3.9	53.9 5.3	34.1 8.5 1.4										
Indium	1200 1400					24.9 2.1			40.0 3.1				51.8 4.4			
Molybdenum	1200 1400								42.7 2.8				13.7 3.5	62.6 10.2		
Niobium	1200 1300 1400					50.6 35.7 6.3	56.2 16.6 9.1		34.5 12.8 7.8							
Phosphorus	1200 1400		0.6 1.4													
Silicon	1200 1400		0.5 0.9						0.05							
Sulphur	1200 1400		1.3 1.4													
Tantalum	1200 1400								46.5 6.2				63.2 9.2			52.7 4.1
Titanium	1200 1400					8.4 0.6			40.9 3.8				29.3 6.3	52.7 3.1		
Tungsten	1200 1400								11.1 0.3					21.7 1.6	13.2 0.8	
Vanadium	1200 1400					11.0 0.5		12.7 1.5	47.2 5.7				28.6 4.1	22.5 4.4		
Zirconium	1200 1400					27.9 2.0	62.3 5.4		94.4 4.1	133.4 5.0			68.1 5.4			
Pure Rhodium	1200 1300 1400	0.6 0.28 0.03														

Table VI
Variations in the Stress Rupture Properties of Binary Alloys of Rhodium
with Composition, Temperature and Loading

		Test Temperature, °C	Loading, bar					
			110		207		345	
Composition, weight per cent			S.R.L., hours	Elongation, per cent	S.R.L., hours	Elongation, per cent	S.R.L., hours	Elongation, per cent
1.0 Carbon		1200	5.6	2.6			0.2	1.3
0.5 Gadolinium		1200	502.1	2.6	117.7	6.5	45.7	5.2
0.3 Hafnium		1200	869.5	6.6	211.3	6.6	49.8	5.2
		1300					9.4	3.9
		1400	86.5	6.6	22.9	6.6	3.9	7.9
1.0 Holmium		1200	1092.4	3.9			99.8	3.9
0.5 Indium		1200	837.5	3.9			24.9	3.9
1.0 Indium		1200	1751.0	3.9			40.0	5.2
0.75 Niobium		1000					426.6	14.1
		1200	1919.6	5.2	254.0	3.9	56.2	7.9
		1300					16.6	6.6
		1400			32.5	5.2	9.1	7.9
0.1 Silicon		1200	2147.6	2.6			0.5	3.9
1.0 Silicon		1200	5.65	1.3			0.05	1.3
1.0 Strontium		1200	1444.2*	2.6			4.1	2.6
		1300	460.5	3.9				
		1400	444.3	6.5			62.1	7.8
1.0 Tin		1200	1060.0	3.9			37.2	2.6
1.0 Tungsten		1200	435.7	2.6			11.1	5.2
		1400	131.8	5.2			0.3	
2.0 Zirconium		1200	677.4	2.6	189.0		66.1	
		1300	206.8	7.8			25.6	
		1400			14.8		5.4	
		1500	13.1	2.6				

S.R.L. = stress rupture life

between these metals. Group III and IV elements such as scandium and zirconium produced the largest binding energy with rhodium, and they also produced the longest stress rupture lives.

The stress rupture results show that at high loadings some rhodium alloys are superior to

ZGS 10 per cent rhodium-platinum, but at lower loadings failure occurs more rapidly because of inherent grain boundary weakness. At high loadings the creep life is dependent upon the particle size distribution and the grain size. Alloys which internally oxidised rapidly, such as scandium-rhodium, and which had a

very small grain size and a fine oxide particle size distribution, produced the longest creep life. At lower stresses creep failure was dependent upon the strength of the grain boundaries and upon microslip and diffusion. Under these conditions the rhodium alloys failed more quickly than ZGS 10 per cent rhodium-platinum, due to rapid diffusion of oxygen which caused internal oxidation and produced large oxide particles which acted as crack initiators. These oxides also prevented grain boundary sliding and microslip and recovery which would have prevented cavitation at the triple points. Failure occurred rapidly in alloys which contained elements that form volatile oxides, such as tungsten, carbon and sulphur, or which develop a non-protective oxide layer. These volatile oxides either promoted void formation or failed to prevent oxygen diffusing to existing voids at the grain boundaries. It is thought that the improvement in the creep life

caused by the addition of indium may have increased the grain boundary cohesion.

Conclusions

This study has shown that it is now possible to manufacture many binary rhodium alloys, some of which have properties that may be useful commercially. For example, it is possible to make a rhodium alloy which will not colour glass, and which can be fabricated into products with an acceptable creep life. At high stress several of these rhodium alloys have a creep life superior to that of ZGS 10 per cent rhodium-platinum.

In addition, on certain rhodium alloys it is possible to produce a protective oxide layer which prevents the metal loss normally associated with the platinum group metals.

A similar account of work on ternary and other complex rhodium alloys will appear in a subsequent issue of this journal.

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Tribological Properties of Thin Platinum Coatings

It is known that the sliding wear behaviour of hard metals can be improved by coating one or both of the contacting surfaces with a thin layer of a soft metal, but this advantage can be lost by, for example, the formation of oxide or corrosion products. Therefore platinum with an annealed hardness of 48Hv and notable environmental stability would appear to be a suitable material for tribological applications, and the results of an investigation carried out at the National Institute for Materials Research, C.S.I.R., Pretoria, support this assumption ("The Use of Platinum in Thin Tribological Coatings", A. Wells and D. J. de Wet, *Wear*, 1988, 127, (3), 269-281).

Their wear tests were carried out using a ball-on-flat rig; however the applied load was higher than that normally used for such tribological

experiments. Alumina or steel spheres were used, the latter in both the uncoated condition and after sputter ion plating with platinum. The flat steel specimens were in the uncoated condition, or coated with platinum by sputtering, or by deposition from fused salt or aqueous electrolytes.

Both lubricated and dry surfaces were investigated in air at room temperature, and representative results are presented. Alumina sliders rapidly eroded thin platinum coatings, however on sliding steel surfaces the use of platinum reduced the coefficient of friction and the wear damage, and it is concluded that when the topography of the surface provides sinks for wear debris and reservoirs for lubricants, the use of thin platinum coatings on steel can provide excellent sliding properties.