

Ternary and Complex Rhodium Alloys

AN INVESTIGATION OF MECHANICAL PROPERTIES

By J. R. Handley

Johnson Matthey, Materials Technology Division

A previous study on binary alloys of rhodium has shown that the addition of small quantities of suitable alloying elements produce useful commercial alloys (1). It was found that certain binary alloys did not colour liquid glass, had an acceptable creep life and could be fabricated into products used in the production of glass fibre. At high loading and high temperatures, some binary rhodium alloys had a superior creep life to zirconia grain stabilised (ZGS) 10 per cent rhodium-platinum. Binary alloys which contain hafnium, zirconium and niobium form a protective surface oxide layer which prevents metal loss by the evaporation that is normally associated with the platinum group metals.

This investigation of rhodium alloys was carried out to see if the useful properties of binary alloys could be enhanced by the addition of further alloying elements, and if the creep life could be improved by the addition of grain boundary strengthening elements, such as carbon, or by the formation of a gamma prime precipitate or an oxidation-resistant oxide spinel.

The concentration of the alloying elements used in this study was generally 1 weight per cent, which for most alloys is below the solid solubility limit, thus preventing precipitation of a second intermetallic phase. The alloys were argon arc melted and fabricated into sheets, and their stress rupture properties were determined at loadings of 110 to 345 bar at temperatures of 1200, 1300, 1400 and 1500°C.

The addition of a further alloying element to the binary alloys only produced a small increase of up to 50 Hv in the as-cast hardness of the ternary alloys, as shown in Table I. In the previous paper it was shown that the binary alloys containing scandium, holmium, zirconium and lutetium had the longest stress rupture lives of

127, 99, 94 and 73 hours, respectively, at a loading of 345 bar and at a temperature of 1200°C; but the rare earth alloys had poor workability (1). The addition of tantalum or rhenium to these alloys improved their workability. The addition of tantalum and rhenium to binary alloys of the other refractory group metals, and certain other elements, improved their cold formability, as shown in Table II.

The principal mode of oxidation in the binary alloys was by grain boundary diffusion and internal oxidation. The addition of a spinel oxide former, such as chromium, was made to improve the oxidation resistance of these alloys. At the lower temperature of 1200°C chromium did improve the oxidation resistance of binary alloys. This improvement was similar to that found in stainless steels and nickel superalloys. At the higher temperature of 1400°C, chromium no longer formed a protective oxide spinel. The oxidation resistance of the more complex alloys was similar to that found in the binary alloys where the addition of a strong oxide former prevented rhodium evaporation. Most of the alloys revealed a weight gain after oxidation, as a result of the alloying element being converted to an oxide, Table III. The most resistant oxide layers formed upon the ternary alloys containing tantalum or niobium.

Glass compatibility tests carried out on binary alloys revealed that the addition of a strong oxide former, such as chromium or hafnium, prevented rhodium from colouring liquid glass. The effect of small additions of these elements to those binary alloys which mildly coloured glass was to prevent them from colouring liquid glass (Table III). The addition of a third or fourth element to most of the binary alloys did not reduce the contact angle of liquid glass. Only two of the

Table I
The As-Cast Hardness of Ternary Rhodium Alloys Containing 1 Weight
Per Cent Each of the Second and Third Elements, Compared to the
Basic Binary Alloy
 hardness values, Hv

Element	Binary	Cr	Hf*	Nb	Mo	V	Ta	Ti	Zr
Al	176						168		
Ag	98			137			114		
Au	128						115		
Ca	152						153		
Co	130						130		
Cr	117	117	163	209	152	128	163	143	206
Dy*	158						164		
Er	174	169		161	181		194		
Fe	117						118		
Gd*	157						160		
Hf*	179	163	179	159	142	154	172	150	149
Ho	156	158	177	168	161	197	173		
Ir	94			127			110		
La	151						164		
Lu	162		166	165			170		
Mg	108						143		
Mn	134						150		
Mo	121	152	142	132	121	145	151	128	187
Nb	131	209	159	131	132	141	279	145	161
Nd	160						159		
Ni	134			145			143		
Os	111			136			104		
Pd	109			133			131		
Pt	110			119			109		
Re	102		135	123			136		
Ru	98			125			120		
Sc	189	167	199	185	176		189	205	
Sm	156						161		
Ta	126	163	172	279	151	138	126		172
Tb	168						142		
Ti	118	143	150	145	128	128		118	216
Tm	167						169		
V	164	128	154	141	145	164	138	128	193
W	116	129		121	145	121	170	122	164
Y	187						189		
Yb	146						181		
Zr	151	206	149	161	187	193	172	216	151

*0.5 wt.% dysprosium and gadolinium; 0.3 wt.% hafnium

more complex alloys, lutetium-tantalum-rhodium and hafnium-rhenium-scandium-rhodium, reduced the contact angle of liquid glass to below the 33° angle that occurs with rhodium to 20° and 27°, respectively.

In the previous study it was shown that binary alloys formed by the addition of refractory group

metals, rare earth metals and indium produced the longest stress rupture lives. Therefore a series of ternary alloys was made to determine the effect of additions of 0.75 weight per cent niobium and 1 weight per cent tantalum to binary alloys, and the results are given in Tables IV and V. These results show that the most significant

Table II
Cuping Tests of Rhodium Alloys Containing 1 Weight
Per Cent Each of the Second and Third Elements, Compared to the
Basic Binary Alloy

Erichsen number of turns of a 25 mm diameter disc, depth in 0.01mm per turn

Element	Binary	Cr	Hf*	Nb	Mo	V	Ta	Ti	Zr
Al	11						41		
Ag	41						57		
Au	45						54		
Ca	34						29		
Co	47						54		
Cr	29	29	33	36	50	37	59	40	
Er	28	29		32	29		19		
Fe	46						57		
Hf*	47	33	55	47	38	29	100+	32	54
Ho	33	18	22	29	21	34	28		
Ir	49			60			55		
Lu	33		29	24			30		
Mn	39						48		
Mo	41	50	38	40	41	26	38	34	19
Nb*	38	36	47	38	40	48	75+	43	40
Nd	19						31		
Ni	52			33			55		
Os	36			50			51		
Pd	45			48			57		
Pt	56			53			61		
Re	54		102	59			64		
Ru	53			42			54		
Sc	8	20	29	26	18		26	14	
Sm	19						25		
Ta	43	59	100+	75+	38	54	43	56	46
Tb	29						39		
Ti	30	40	32	43			56	38	28
Tm	26						32		
V	30	37	29	48	26	30	54		29
W	71		100+	48			31	34	27
Y	21						31		
Yb	35						29		
Zr	42		54	40	19	29	46	28	42

*0.3 wt.% hafnium, *0.75 wt.% niobium

improvement in creep life occurred in those alloys which contained either another refractory group metal, a rare earth metal, indium or another platinum group metal. The addition of 1 weight per cent of osmium or iridium to a 0.75 per cent niobium-rhodium alloy increased the stress rupture life from 56 to 105 hours. The effect of osmium concentration on the 0.75 per cent niobium-rhodium alloy is seen in Table VI, which shows the optimum osmium

content to be 1 per cent. The ternary alloys of niobium-rhodium and tantalum-rhodium which had the longest creep life were zirconium-niobium-rhodium, molybdenum-niobium-rhodium and tungsten-tantalum-rhodium of 156, 151 and 106 hours, respectively, at 345 bar and 1200°C.

Therefore a further series of ternary alloys including refractory group metals was made to determine which combination would produce

Table III								
Glass Compactibility Tests and Oxidation of Complex Alloys of Rhodium								
Alloying elements	Glass test					Oxidation		
	Contact angle, degrees		Colour			Weight loss or weight gain, mg/cm h		
						at 1200°C	at 1400°C	
Ag-Ta			v.v.l. brown			-16.2		
Al-Ta			clear			0.0	6.0	
Au-Ta			v.v.l. green			-18.7		
Cr-Ta	64		clear			1.8		
Cr-Mo	68		clear			-4.7		
Co-Ta			d. blue			8.1		
Co-Ta-W			d. blue			20.2		
Er-Ta	46		l. brown			6.6		
Fe-Ta			v.v.l. brown			-3.0		
Hf-Cr	47		v.l. brown			-4.6		
Hf-Cr-Mo			clear			13.1		
Hf-Lu	45		brown			12.6		
Hf-Re	54		l. brown			9.4	17.5	
Hf-Sc	49		l. brown			0.5		
Hf-Ta	62		clear			16.2	60.0	
Hf-Ti			clear			2.5		
Hf-V			clear			4.6		
Hf-W	50		clear			7.6	15.7	
Hf-Re-Mo						2.5		
Hf-Re-Sc	27					-5.6		
Hf-Re-Ta	58		clear			5.6		
Hf-Ta-W	46		clear			1.3		
Hf-Cr-Mo-Ta	51		clear			11.1	17.4	
Ho-Ta			l. brown			5.0		
Lu-Ta	20		clear			5.6		
Mn-Ta			clear			-2.4		
Mo-Ta	81		l. blue			-2.5		
Nb-Cr	47		l. blue			6.1		
Nb-Cr-Mo			l. blue			6.1		
Nb-Lu			l. brown			4.0		
Nb-Mo			blue			-1.0		
Nb-Ni			d. brown			0.0		
Nb-Ni-Ti			l. brown			18.2		
Nb-Re-Sc	68		v.v.l. brown			2.5		
Nb-Sc	34		l. brown			20.7		
Nb-Ta	55		clear			11.0	16.6	
Nb-Ta-Ir	38		clear			6.8	6.1	
Nb-Ti			v.v.l. brown			-3.0		
Nb-V			l. blue			1.0		
Pd-Ta			brown			5.6		
Pt-Ta	47		v.l. brown					
Re-Ta	64		v.l. brown			-4.4		
Ru-Ta						-6.4		
Sc-Ta	57		clear			1.8		
Ta-W			clear			3.1		
Ta-Zr	57		clear			12.3	39.2	
V-Ta	68		clear			0.0		
Y-Ta	56		v.l. brown			6.1		
Zr-B			clear			-7.5	-125.0	
Element	Cr	Hf	Nb	Pt	Re	Sc	V	Ta
Contact angle, °		62	47	62	53	47	55	
Glass colour	cl	cl	cl	v.l.br	v.l.gr	v.l.gr	v.l.bl	v.l.gr

v.l. very light, v.v.l. very very light, d. dark, l. light, cl clear, br brown, gr green, bl blue

Table IV
Stress Rupture Lives of Ternary Alloys of Rhodium-0.75 wt.%, Niobium Containing 1 Weight Per Cent of the Third Element at a Loading of 345 bar and at Temperatures of 1200°C (upper) and 1400°C (lower)
 time to failure, hours

Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
	103.3 9.5	23.8 2.9	23.7 4.2	39.4 5.8				50.7 2.1				39.8 3.4		
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
50.2 9.5		156.5 7.3	56.2 9.1	151.9 12.6		54.8 3.7	56.2 9.1	22.9 4.6	12.0 4.9		100 10.4			
Ba	La	Hf*	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
92.9 7.2		64.2 8.8	98.6 13.0	76.2 6.3	20.3 0.6	104.6 10.0	105.6 6.9	48.8 6.9				38.1 5.5		
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
										30.1 3.7	31.0 2.4			85.5 11.2

Table V
Stress Rupture Lives of Ternary Alloys of Rhodium Containing 1 Weight Per Cent Tantalum and 1 Weight Per Cent of the Third Element at a Loading of 345 bar and at Temperatures of 1200°C (upper) and 1400°C (lower)
 time to failure, hours

Mg											Al	Si	P	S
18.5 2.4											19.7 1.8			
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
27.5	97.5 6.8	35.9 3.9	100 6.5	35.9 1.9	20.9 5.1	35.9 1.5	27.4 2.1	32.0 2.6	17.1 4.7					
Sr	Y	Zr	Nb*	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
	37.8 3.7	37.5 1.4	98.6 13.0	57.5 7.1		22.6 9.3	46.5 6.2	24.0 1.6	26.5 3.6			93.6		
Ba	La	Hf*	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
		82.9 17.2	46.5 6.2	106.6 7.5	55.5 6.7	34.8 0.7	24.3 4.3	20.9 2.2	9.0 0.7					
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			27.9 0.2		13.0			42.6 0.8		32.5 2.3	123.8 5.6	15.4 6.5	1.1 0.05	40.2

*0.3 wt.% hafnium, 0.75 wt.% niobium

the longest creep life, and the results are seen in Table VII. This shows that some of the strongest alloys are produced from combinations of elements on the same line of the Periodic Table (zirconium/niobium/molybdenum and hafnium/tantalum/tungsten). Two of these alloys, 0.75 per cent niobium-1 per cent zirconium and 0.75 per cent niobium-1 per cent molybdenum, had a longer stress rupture life than a cobalt-based superalloy at a loading of 345 bar and at a temperature of 1200°C.

The effect of the addition of a refractory group metal on the stress rupture properties of the

binary alloys of scandium, holmium, erbium and lutetium is seen in Table VIII. This shows that most refractory group metals reduced the stress rupture life of these rare earth-containing alloys. However, the addition of hafnium to lutetium-rhodium, chromium to scandium-rhodium and tantalum to erbium-rhodium, increased the stress rupture life compared to that of the binary alloys, while only chromium improved the formability. The effect of the addition of osmium, iridium and rhenium upon the stress rupture properties of ternary alloys is given in Table IX. Of these elements, the addition of osmium and rhenium

Alloying elements, weight per cent	Temperature, °C	Element	Concentration, weight per cent			
			C	Os		
1% Cr 1% V	1200 1400	C	0.0	0.01		
			32.4 1.7	27.7 1.2		
0.75% Nb 1% Ag	1200 1400	C	0.0	0.01		
			12.0 4.9	48.2 9.2		
0.75% Nb 1% Er	1200 1400	C	0.0	0.01		
			31.0 2.4	29.6		
0.75% Nb 1% Os	1200 1400	C	0.0	0.01		
			104.6 10.0	35.6 4.7		
1% Ti 1% Cr	1200 1400	C	0.0	0.01		
			34.2 1.7	29.2 4.0		
1% Ti 1% Mo	1200 1400	C	0.0	0.01		
			43.5 6.0	33.8 4.8		
1% Ti 1% Zr	1200	C	0.0	0.02		
			83.4	27.9		
0.75% Nb	1200 1400	Os	0.0	0.5	1.0	2.0
			56.2 16.6	46.0 10.6	104.6 10.0	21.0 2.0

Table VII
Stress Rupture Properties of Ternary Alloys of Rhodium and the Refractory Group Metals at a Loading of 345 bar

Element, weight per cent	Temperature, °C	Time to failure, hours								
		1% Ti	1% Zr	0.3% Hf	1% V	0.75% Nb	1% Ta	1% Cr	1% Mo	1% W
1% Ti	1200	40.9	83.4	27.5	39.8	23.5	35.9	34.2	43.5	5.7
	1400	3.8	9.6	6.5	4.7	2.9	3.9	1.7	6.0	2.4
1% Zr	1200	83.4	94.4	58.7	52.2	153.5	37.5	46.9	55.9	34.9
	1400	9.6	4.1	4.6	5.8	7.3	1.4	2.4	4.5	4.3
0.3% Hf	1200	27.5	58.7	49.8	53.8	62.4	82.9	50.7	75.6	48.5
	1400	6.5	4.6	3.9	10.5	8.8	17.2	2.1	6.6	3.8
1% V	1200	39.8	52.2	53.8	47.2	23.7	100.0	32.6	28.0	10.5
	1400	4.7	5.8	10.5	5.7	4.2	6.5	3.6	4.2	1.1
0.75% Nb	1200	23.5	153.5	62.4	23.7	56.2	98.6	39.4	151.9	76.2
	1400	2.9	7.3	8.8	4.2	9.1	13.0	5.8	12.6	6.3
1% Ta	1200	35.9	37.5	82.9	100.0	98.6	46.5	35.5	57.1	106.6
	1400	3.9	1.4	17.2	6.5	13.0	6.2	1.9	7.1	7.5
1% Cr	1200	34.2	46.9	50.7	32.6	39.4	35.9	28.0	75.5	10.2
	1400	1.7	2.4	2.1	3.6	5.8	1.9	2.1	2.1	0.2
1% Mo	1200	43.5	55.9	75.6	28.0	151.9	57.1	75.5	42.7	18.3
	1400	6.0	4.5	6.6	4.2	12.6	7.1	2.1	2.8	0.1
1% W	1200	5.7	34.9	48.5	10.5	76.2	106.6	10.2	18.3	11.1
	1400	2.4	4.3	3.8	1.1	6.3	7.5	0.2	0.1	0.3

produced the most significant improvements in the stress rupture life of these ternary alloys.

The effects of the addition of non-metallic elements carbon, boron, phosphorus, sulphur and silicon on the creep lives of 0.75 per cent niobium-rhodium and 1 per cent zirconium-rhodium alloys are seen in Table X. This shows that even at low concentrations these elements can substantially reduce the stress rupture life achieved by the binary rhodium alloys. A similar result produced by small additions of carbon to other ternary alloys is given in Table VI. Very low concentrations of carbon in alloys which contain a strong carbide forming element, such as

niobium, improved the stress rupture life; but at higher concentrations the stress rupture life was decreased.

The effect of loading upon the creep life of complex alloys is seen in Table XI. The addition of 0.75 per cent niobium to 0.1 per cent silicon-rhodium alloy at a loading of 110 bar at 1200°C reduced the stress rupture life from 2147 to 2045 hours. Most of the alloy additions to the binary niobium-rhodium alloys substantially reduced the stress rupture life, at the loading of 110 bar at 1200°C, from 1919 hours. Only one alloy, the 0.3 per cent hafnium-1 per cent zirconium-rhodium, produced a significant

increase in the stress rupture life compared with that of the binary rhodium alloys containing hafnium or zirconium, at a loading of 110 bar and a temperature of 1200°C. Lives were increased from 869 and 677 hours to 1565 hours, respectively. The stress rupture results show that at high loadings the addition of a third element improves the creep life, but at lower loadings a further alloy addition makes no significant improvement. This lack of improvement in creep properties is due to the fact that the alloy addition does not prevent the oxygen diffusion which produces large oxide particles, which then act as crack initiators.

It was found that the ternary alloy 0.75 per cent niobium-1 per cent of tantalum-rhodium could be used as a welding rod for rhodium alloys. Stress rupture results obtained from welded rhodium alloys of niobium-tantalum, hafnium-vanadium and hafnium-titanium at 110 bar and a temperature of 1200°C gave lives of 792, 1919 and 869 hours, respectively. This ternary alloy was used to weld fabricated rhodium spinner baskets.

Some alloys were made which contained a gamma prime precipitate, of either Ni, Ti or Nb, Ti, in order to determine their effect upon stress rupture properties. The results revealed that at 345 bar and a temperature of 1200°C, the gamma prime precipitates produced only a small increase in the stress rupture life of 51 hours for 3 per cent nickel-titanium-rhodium and 48 hours for 3 per cent niobium-titanium-rhodium, when compared to the values of 21, 34, and 41 hours for the binary alloys of nickel-rhodium, niobium-rhodium and titanium-rhodium, respectively.

Other possible hardening ternary alloys were investigated. The addition of cobalt to a tungsten-rhodium alloy increased the stress rupture life from 11 to 85 hours, at a loading of 345 bar and at 1200°C. The addition of gallium and indium, which are used to harden platinum, reduced the stress rupture life of indium-rhodium from 40 to 16 hours, at 345 bar and 1200°C.

The formation of an oxide spinel used to protect the low alloy steels of chromium, and molybdenum, together with the strong oxide

Table VIII
Stress Rupture Properties of Ternary Alloys of Rhodium with Rare Earths and Refractory Metals at a Loading of 345 bar

Element, weight per cent	Temperature, °C	Time to failure, hours												
		1% Sc	1% Ho	1% Er	1% Lu	1% Ti	1% Zr	0.3% Hf	1% V	0.75% Nb	1% Ta	1% Cr	1% Mo	1% W
1.0% Sc	1200	127.5				93.8		66.1			97.5	136.8	72.0	
	1400	5.2				4.1		5.3			6.8	2.7	9.3	
1.0% Ho	1200		99.8					15.2	24.8	30.1	32.5	11.7	17.0	
	1400		2.6					6.1	1.1	3.7	2.3	1.4	1.0	
1.0% Er	1200			52.9						31.0	123.8	43.6	16.2	
	1400			4.35						2.4	5.6	1.9	1.4	
1.0% Lu	1200				72.9			165.5		85.5	40.2			
	1400				1.5			0.6		11.8				

Table IX
Stress Rupture Lives of Complex Alloys of Rhodium at a Loading of 345 bar

Stress rupture lives, hours										
Ternary Alloy				Complex Alloy						
Alloying elements		Temperature, °C		Alloying elements			Temperature, °C			
		1200	1400				1200	1400		
Cr	Ho	11.7	1.4	Cr	Ho	Os	31.1	1.7		
Cr	Sc	136.8	2.7	Cr	Sc	Os	48.0			
Cr	Sc	136.8	2.7	Cr	Sc	Re	1.4	2.4		
Co	Ta	27.4	2.1	Co	Ta	W	85.1	4.4		
Er	Mo	16.2	1.3	Er	Mo	Re	22.9	1.8		
Hf	Ho	15.2	6.1	Hf	Ho	Re	46.3			
Hf	Ti	27.5	6.5	Hf	Ti	Ir	92.0			
Hf	Ti	27.5	6.5	Hf	Ti	Os	26.3	7.3		
Hf	Nb	62.4	8.8	Hf	Nb	Os	137.6	7.0		
Hf	Mo	75.6	6.6	Hf	Mo	Re	99.9	21.2		
Hf	V	53.8	10.5	Hf	V	Os	32.2	3.8		
Hf	Zr	58.7	4.6	Hf	Zr	Os	135.8	5.8		
Hf	Sc	66.1	5.2	Hf	Sc	Re	87.7			
Hf	Ta	82.9	17.2	Hf	Ta	Re	163.7	5.0		
Hf	Ta	82.9	17.2	Hf	Ta	W	50.7	4.2		
Ho	Mo	17.0	1.0	Ho	Mo	Re	39.2	1.1		
Ni	Ta	32.0	2.6	Ni*	Ti	Ta	51.4	3.0		
Nb	Cr	39.4	5.8	Nb	Cr	Os	22.0	4.3		
Nb	Ta	79.5	8.0	Nb	Ta	Ir	92.4	16.2		
Nb	Ti	23.5	2.9	Nb	Ni	Ti	15.0	3.1		
Nb	Lu	85.5	11.8	Nb	Lu	Os	40.6	4.8		
Nb	V	23.7	4.2	Nb	V	Os	43.7	5.4		
Mo	Zr	55.7	4.5	Mo	Zr	Os	88.2	4.2		
Mo	Sc	72.0	9.3	Mo	Sc	Re	89.2	4.5		
Mo	V	28.0	4.2	Mo	V	Re	2.7	1.9		
Sc	Ti	93.8	4.1	Sc	Ti	Os	111.0			
Y	Ta	37.8	3.7	Y	Ta	Ir	61.1			
Hf	Cr	Mo	18.1	1.1	Hf	Cr	Mo	Ta	156.4	5.9

All alloy additions contain 1 wt. % of element, except 0.3 wt. % hafnium, *3 wt. % nickel-1 wt. % titanium and 0.75 wt. % niobium

formers, hafnium and tantalum, produced one of the longest lives of 156 hours, when tested at a loading of 345 bars and at 1200°C.

Discussion

Studies of nickel and cobalt superalloys have shown that the presence of low levels of non-metallic elements can significantly reduce the

stress rupture lives of these alloys (2). The present investigation has shown that small additions of boron, carbon, phosphorus, sulphur and silicon to a 0.75 weight per cent niobium-rhodium alloy all reduce the stress rupture life of the binary alloy, see Figure 1. This effect was also found in a 1 weight per cent zirconium-rhodium alloy, and in other ternary alloys. At

very low levels of carbon, alloys which form very stable carbides, such as niobium, revealed an increased stress rupture life at 345 bar and at 1200°C. This improvement in stress rupture life may be due to the formation of fine particles of NbC which increased the grain boundary cohe-

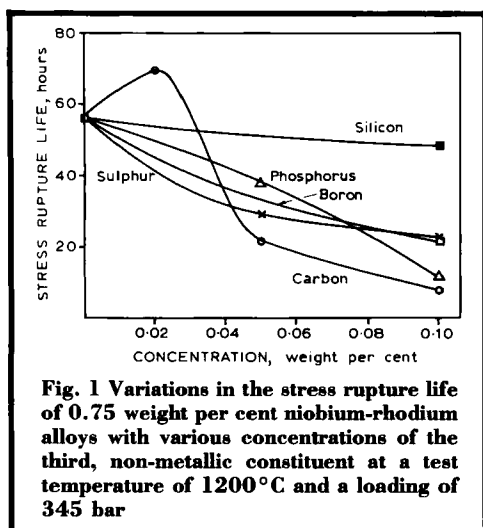
sion. A similar improvement is found in the stress rupture properties of nickel superalloys with low carbon content. Studies of nickel superalloys have shown that the carbon increases the grain boundary adhesion, but at higher concentrations of carbon it forms large carbides at the grain

Table X
Effect of Non-metallic Element Concentration on the Stress Rupture Properties of Binary Rhodium Alloys at a Loading of 345 bar

Element	Temperature, °C	Alloying element	Concentration of non-metallic element, weight per cent				
			Stress rupture life, hours				
0.75% Nb	1200 1400	B	0.0	0.02	0.05	0.1	
			56.2 9.1			21.2 0.8	
	1200 1400	C	0.0	0.02	0.05	0.1	
			56.2 9.1	69.3 6.3	21.5 4.3	7.9 1.0	
	1200 1400	P	0.0	0.02	0.05	0.1	
			56.2 9.1		38.0 4.8	11.6 2.1	
	1200 1400	S	0.0	0.02	0.05	0.1	
			56.2 9.1		29.0 3.2	22.6 2.8	
	1200 1400	Si	0.0	0.02	0.05	0.1	
			56.2 9.1			48.3 5.0	
	1% Zr	1200 1400	B	0.0			0.1
				94.4 4.1			39.9 5.4
1200 1400		C	0.0	0.01			
			94.4 4.1	47.1 6.3			
1200 1400		Si	0.0			0.1	
			94.4 4.1			61.4 3.8	

Loading, bar	Table XI Stress Rupture Properties of Rhodium Alloys at Loadings of 110, 207 and 345 bar											
	110						345					
	Time to failure, hours						207					
Alloying elements Temperature, °C	SRL	Elongation, per cent	Bend angle, degrees	SRL	Elongation, per cent	Bend angle, degrees	SRL	Elongation, per cent	Bend angle, degrees	SRL	Elongation, per cent	Bend angle, degrees
1% Er 0.75% Nb 1200	896.2	5.2	30							31.0	7.8	5
1% Cr 1% V 1200	462.4	6.5	20							32.6	7.8	130
0.3% Hf 1% Zr 1200	1565.5	5.2	25							58.7	6.5	30
1300	242.3	6.5	45									
0.3% Hf 1% Mo 1% Re 1200	665.1	2.6	15							99.9	3.9	80
1400	44.6	5.2	85							21.2	9.2	50
1500	18.1	2.6	65									
0.75% Nb 1% Cr 1400	66.3	1.3	35							5.8	6.6	80
0.75% Nb 2.0% Os 1200	514.9	5.2	90							25.1	5.2	155
0.75% Nb 1% Mo 1400	276.4	1.3	20							12.6	9.2	110
0.75% Nb 0.1% Si 1200	2045.0	3.9	25							48.3	6.3	110
0.75% Nb 1% Sc 1200	86.4	3.9	30							5.2	9.2	30
0.75% Nb 1% Ta 1200	787.6	9.2	5									
1300	661.0	7.9	50	188.6	11.8	45				79.5	11.8	105
1400	291.8	3.9	50	168.6	10.5	55				24.6	13.1	45
1500	103.0	6.6	70	54.6	6.6	100				8.0	11.8	140
1% Mo 1% Ti 1200	901.8	6.5	45							43.5	2.6	100
1% V 1% Zr 1200	829.4	3.9	35							52.2	2.6	40
1% V 1% Zr 0.01% C 1200	444.3	6.5	10							62.1	7.8	20

Bend Test around a 5mm radius



boundaries which act as crack initiators promoting premature failure. In addition, at high temperature these elements are readily oxidised to volatile gases which form voids, which then cause rapid failure.

The results of this investigation show that additions of non-metallic elements have a deleterious effect upon the high temperature properties of rhodium, and this effect may occur in other platinum group metals or alloys. The use of electron beam melting makes it possible to produce alloys with a lower non-metallic content than can be achieved by conventional melting techniques. The use of such equipment for melting platinum group metals and their alloys for high temperature applications will reduce the concentration level of non-metallic elements, and hence may improve their high temperature properties.

The superior stress rupture lives of binary and ternary rhodium alloys which contain additions of one or more refractory group metals can be explained by the Lewis acid based stabilisation theory. If this theory is applied to the formation of oxides (3) in rhodium alloys and those rhodium alloys which contain other platinum group metals, it can explain the improvement in the stress rupture properties of dilute solutions of refractory group metals in binary and ternary alloys. It shows that the improvement in creep

strength of ternary alloys of refractory group metals is produced by the large binding energies of the AB compounds between these metals. Metals from Groups III and IV, such as scandium and zirconium, produce the largest binding energies with rhodium, and also in ternary alloys containing these elements. The effect of the addition of a second platinum group metal, such as iridium or osmium, is to promote the formation of even more stable AB compounds, such as IrHf_3 and ZrIr_3 . Also the theory predicts extremely strong bonding of osmium with hafnium, niobium and zirconium; and in those ternary and quaternary alloys of rhodium which contain combinations of two or more of these refractory group metals with osmium some of the longest lives at 345 bar at 1200°C occurred.

At high loadings the creep properties of certain rhodium alloys are superior to those of ZGS platinum, ZGS 10 per cent rhodium-platinum, nickel and cobalt superalloys. At loadings of 345 bar the principle mode of failure is by slip, which is easily made more difficult by internal oxidation of refractory group metals to a fine dispersion of oxides. At a lower loading of 110 bar failure is initiated by grain boundary sliding and cavitation. Under these conditions the easy diffusion of oxygen along the grain boundaries of rhodium alloys promotes the formation of large oxide particles. These large oxides prevent dynamic recovery and act as crack initiators promoting rapid failure of the alloys. Under conditions of low stress this investigation could not find any rhodium alloys which had longer stress rupture lives than ZGS platinum or nickel and cobalt superalloys.

Conclusions

The addition of one or more elements to binary alloys of rhodium can improve the properties of the binary alloys. The formation of a stable protective oxide coat can prevent liquid glass from being coloured. The inherent grain boundary weakness of rhodium will limit its usefulness as a high temperature material. The presence of small additions of non-metallic elements significantly reduced the stress rupture life of rhodium alloys. The longest creep lives in

rhodium based alloys were obtained from alloys containing mixtures of either refractory group metals, or rare earths and refractory group metal, or refractory group metal with the addition of osmium or iridium.

A Review of Cathodically Modified Alloys

The beneficial effects conferred on base metals and their alloys by small additions of the platinum group metals have been reported here frequently. In recent issues, for example, the literature on the enhancement of corrosion resistance in stainless steels has been reviewed (1, 2); and that on amorphous chromium alloys (3) and surface-implanted titanium alloys has also been reported (4).

The platinum group metals enhance the corrosion resistance of such alloys in corrosive media by modifying the cathodic reaction, and this has led to the description "cathodically modified alloys".

Now, an extensive review of the literature on base metals cathodically modified with noble metals has been published (5). This report surveys the literature on chromium, stainless steels and titanium. The author claims that it is the first comprehensive review of the subject which, he considers, has been neglected as a topic in recent years—the only active groups being Professor Tomashov's team in the U.S.S.R. Academy of Sciences, Moscow and Dr. Higginson and his co-workers at Mintek.

Several studies have been made on the effect of small additions of platinum group metals to chromium in both oxidising and reducing acids. In reducing conditions, platinum group metal modified alloys self passivate easily and their corrosion resistance is several orders of magnitude higher than that of pure chromium. The effectiveness of the platinum group metals is as follows: platinum>palladium>iridium>ruthenium>osmium. During the period of active dissolution that precedes the onset of passivation, an enrichment of the platinum group metals occurs at the alloy surface.

The work carried out on stainless steels in reducing acids shows that platinum group metal additions are more beneficial to ferritic steels than to austenitic steels, and that their effect is enhanced with increasing chromium content of the steel. When molybdenum is also present, there is a synergistic effect with the platinum group metal addition.

More economic use of the platinum group metals through surface alloying, rather than by

References

- 1 J. R. Handley, *Platinum Metals Rev.*, 1989, **33**, (2), 64
- 2 J. J. deBarbadillo, *Trans. AIME*, 1983, **14A**, 329
- 3 J. K. Gibson, L. Brewer and K. A. Gingerich, *Trans. AIME*, 1984, **15A**, 2075

bulk alloying, favourably influences the commercial viability of cathodically alloyed steels.

In contrast, the alloying of titanium with platinum group metals has been shown to be beneficial in both oxidising and reducing media. Palladium has been the most studied addition, and the research has led to the development of the widely used commercial titanium-0.2 per cent palladium alloy which is particularly suited to service in reducing conditions. Surface alloying by, for example, ion-implantation with palladium or platinum is also effective in conferring enhanced corrosion resistance as well as certain mechanical properties, such as fatigue. C.W.C.

References

- 1 I. R. McGill, *Platinum Metals Rev.*, 1990, **34**, (2), 85
- 2 I. R. McGill, *ibid.*, 1990, **34**, (3), 144
- 3 C.W.C., *Platinum Metals Rev.*, 1990, **34**, (2), 84
- 4 [Anon.] *Platinum Metals Rev.*, 1990, **34**, (2), 97
- 5 J. H. Potgieter, Report M397, Mintek, Randberg, January 1990, 13pp, ISBN 0-86999-876-5

Oxidation-Resistant Alloys

Tungsten and molybdenum possess high melting points and good mechanical strengths at elevated temperatures, but even at moderate temperatures both oxidise rapidly. Previous studies have shown that tungsten-chromium-palladium alloys have remarkable oxidation resistance when heated in air, and different mechanisms have been proposed to explain the advantageous action of the palladium.

A recent investigation of the oxidation mechanism and of the characteristics of this alloy system, and of some quaternary alloys produced by substituting large amounts of molybdenum for some of the tungsten, has now been reported (D.-B. Lee and G. Simkovich, *J. Less-Common Met.*, 1990, **163**, (1), 51-62).

Between 1000 and 1250°C, the oxidation resistance of the alloys increases with temperature, the molybdenum-containing alloys being the more resistant. The palladium enhances the formation of a protective chromic oxide scale, acts as a reservoir for chromium, facilitates the outward movement of chromium and prevents oxygen diffusing inwards.