

Alloys of Platinum and Tungsten

FURTHER INVESTIGATION OF THE ALLOYING BEHAVIOUR COULD HELP TO IDENTIFY ADDITIONAL APPLICATIONS

By A. G. Knapton

Group Research Centre, Johnson Matthey & Co Limited

The availability of a complete and accurate phase diagram is an essential requirement if a full understanding of the properties, and hence the potential applications, of an alloy system is to be gained. Although the general nature of the tungsten-platinum constitutional diagram has been known for many years, it is now apparent that intermediate phases which are not incorporated in the published phase diagrams may exist, and evidence to support this is presented.

It might be expected that the combination of the highest melting point metal with one of the most oxidation resistant would result in materials with particularly useful technological properties, but few applications have in fact been found for alloys of tungsten with platinum. One such application is the composition containing 4 weight per cent tungsten and a small amount of thoria which is used with advantage as the sparking plug electrode in internal combustion engines where high reliability and a long life are required (1). This material has good erosion resistance and good electron emission properties and finds application in helicopter and light aircraft engines.

The alloys in wire form are used to a limited extent as electrical resistance materials. For example 8 weight per cent tungsten in platinum is included as Regalohm 62 in the Johnson Matthey Metals Limited range of resistance wires, and similar compositions may be employed in high temperature strain gauges (2). At the other end of the alloy system, small additions of platinum to the tungsten targets of X-ray tubes are claimed to result in exceptionally long lives (3). The additions inhibit roughening of the targets even after prolonged operation.

In the past, tungsten-platinum alloys have also been applied in wear resistant situations,

such as nib tips for fountain pens or for gramophone needles (4). Tungsten-platinum alloys also featured as electrical contact materials (5), but do not appear to be used currently for this.

Perhaps due to the limited range of uses of the alloys, the constitution of the tungsten-platinum system has received very little attention, compared for example with the closely related molybdenum-platinum alloys. Interest in the latter stems largely from the requirements of the glass industry, where stirrers, electrodes and mandrels used in glass melting are frequently fabricated from platinum-clad molybdenum components. In such applications the life of the platinum sheath is largely dictated by the interdiffusion of molybdenum and platinum, which may be limited to a considerable degree by interposing a suitable barrier layer. It was during the course of studies of the use of tungsten as a possible barrier that information was obtained on the formation of intermediate phases in the tungsten-platinum system. This paper describes the evidence accumulated for the existence of these phases during this investigation, and reviews other published information on the alloying behaviour of the metals.

The general nature of the tungsten-platinum liquidus and solidus relationships were first

determined many years ago (6) and are shown in the upper part of Figure 1. At the higher temperatures, the phase diagram is of the simple peritectic type with the peritectic at about 2460°C. The solid solubility of tungsten in platinum is high, with a maximum of about 60 atomic per cent tungsten*, while the limit of the solubility of platinum in tungsten was placed at about 4 per cent. The form of the diagram and the absence of intermediate phases from the melt has been abundantly confirmed by subsequent investigations (7 to 10), but more accurate determinations of solubility and temperature data are obviously required.

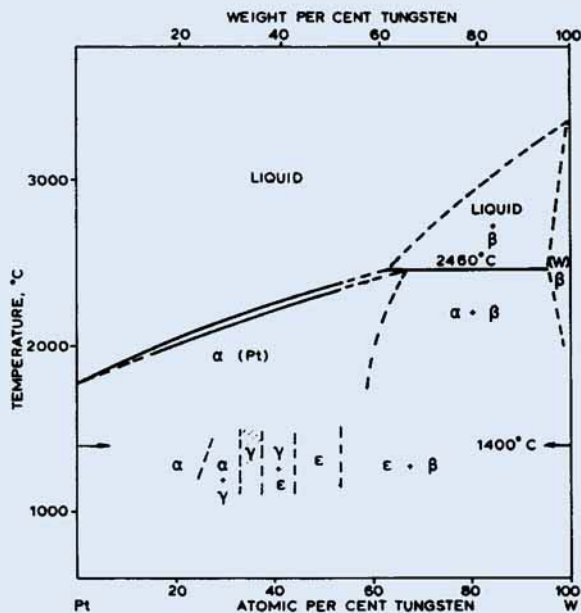
Although it had been suggested from hardness or other anomalies that additional phases were present at lower temperatures in the platinum-tungsten system (6), the first direct evidence for these appears to be from the diffusion measurements of Rapperport, Merses and Smith (11). The data available are reproduced in Table I and showed the presence of two new phases (γ) near 35 per cent tungsten and (ϵ) at 45 to 50 per cent, but no further details of these phases have been published.

Sinha in a study of ordered AB_3 phases detected an intermetallic compound, WPt_2 with the orthorhombic $MoPt_2$ structure in an alloy annealed at 900°C (12).

Other more recent studies by Luo (9) and by Khan and Raub (10) have concentrated on the anomalous behaviour of the face-centred cubic platinum solid solutions, and largely ignore the possible intervention of intermediate phases. Lattice spacings reported by these two authors are shown plotted in Figure 2. Luo found that the values passed through a minimum at 18 per cent tungsten followed by the increase that would be expected from Goldschmidt atomic diameter considerations. Data from Khan and Raub on the other hand show a relatively flat minimum, with considerably lower values especially at the higher tungsten contents. The discrepancy in these results undoubtedly arises from the difference in sample preparation. Rapidly quenched alloys were used by Luo, whereas Khan and Raub gave a relatively short annealing treatment of 4 hours at 1000°C. Consequently, it is probable that the latter alloys are not truly representative of the platinum

*All percentages in this paper are atomic per cent unless otherwise stated.

Fig. 1 Partial phase diagram of the tungsten-platinum system. The form of the upper part of the diagram and the liquid/solid relationships are well established. At lower temperatures intermediate phases exist, but the reactions leading to their formation from the platinum base solid solution still remain to be elucidated



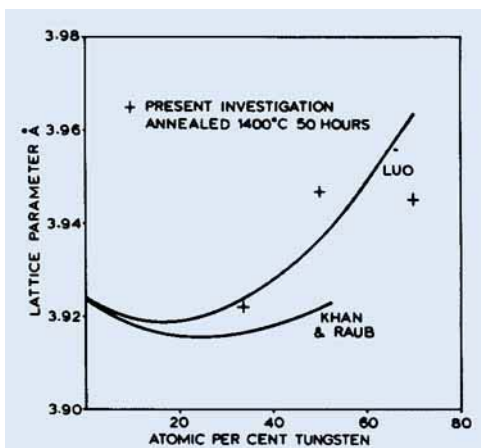


Fig. 2 Lattice spacing measurements on face-centred cubic platinum solid solution alloys. Considerable discrepancies are present between the results of Luo (9) and those of Khan and Raub (10). The higher values of Luo are in agreement with the observations in the present work

solid solution and that some precipitation of a second phase has occurred in the 25 to 50 per cent tungsten range. The results of Luo must, therefore, be considered as more accurate in this instance. Superconducting transition temperatures and magnetic susceptibility measurements have been used by these authors to confirm that the anomalous minimum in the lattice parameters has its origin in electronic

structure changes in the alloys. As far as the constitution of the alloys is concerned, the information given by these investigators is a further demonstration of the extensive solubility of tungsten in platinum.

Diffusion Study

During a limited study of the interdiffusion of platinum and tungsten at the Johnson Matthey Research Laboratories, a number of observations were made pertinent to the alloying behaviour of the metal. A diffusion couple comprising a high purity tungsten rod encased in a tightly fitting platinum tube was annealed for 256 hours at 1400°C. A cross-section of this couple was examined by electron probe micro analysis, and the tungsten trace taken with $W\text{L}\alpha$ radiation is shown in Figure 3. Three distinct zones can be recognised in this trace, corresponding to (i) the limit of solid solubility, 25 per cent of tungsten in platinum at 1400°C, (ii) a comparatively wide band (15 microns) of intermediate phase (γ) at 33 to 37 per cent tungsten, (iii) a narrower band (5 microns) of a phase (ϵ) occurring over the composition range 45 to 52 per cent tungsten.

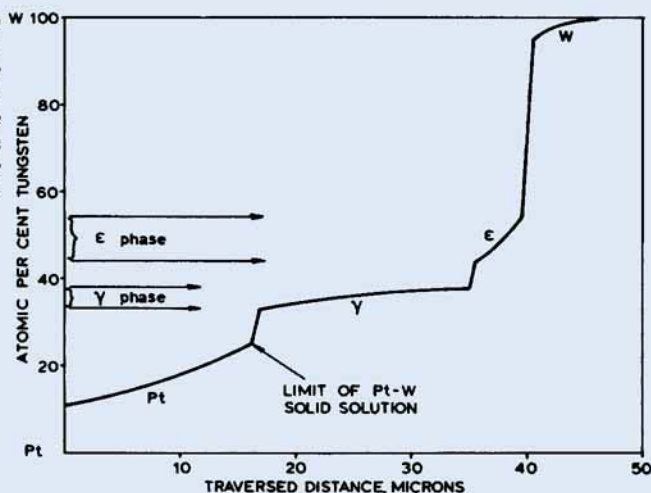
These results will be seen to be substantially in agreement with those of Rappoport and co-workers and the nomenclature γ and ϵ used by these authors has been adopted here.

The findings of this diffusion study have

Table I
Diffusion Data on Tungsten-Platinum from Rappoport, Merses & Smith (11)

Composition Atomic per cent platinum	Phase	A cm^2/s	Q Kcal/mol	Temperature, °C
2	(β)	3.1×10^{-2}	139	} 1300-1743
50 } 55 }	(γ)	{ 4.7×10^{-3} 3.3×10^{-3}	83.6 82.1	
65	(ϵ)	4.4×10^{-2}	92.0	1473-1743
77 } 80 } 85 }	(α)	{ 1.8×10^{-2} 1.2×10^{-2} 1.3×10^{-2}	78.0 75.4 74.2	} 1300-1743 1300-1700

Fig. 3 Electron probe micro analysis scan of a tungsten-platinum diffusion couple annealed 1400°C, 256 hours, showing the considerable solubility of tungsten in platinum in the solid state and the formation of two intermediate phases ϵ and γ



been included in the phase diagram shown in Figure 1, which illustrates that these phases are formed at some temperature below the solidus from the platinum-base solid solution. Such a study has not of course resulted in any detailed information on the precise mode of formation of these structures from the solid solution, but by analogy with the molybdenum-platinum system, the phase relationships in this region of the diagram may prove to be complex (13, 14).

Alloy Investigations

Additional confirmatory evidence for the presence of these phases coupled with crystal structure data were obtained from a study of three selected alloy compositions namely platinum with 35, 50 and 70 per cent tungsten respectively. Alloys were prepared by thoroughly mixing appropriate quantities of high purity platinum and tungsten powders, and pressing the mixture into compacts. The compacts were further treated by sintering at 1400°C, or by arc melting, to effect alloying. Melted samples were also given prolonged anneals at 1400°C to allow precipitation of the intermediate phases in these alloys. The resultant compositions were examined by X-ray diffraction and electron probe micro analysis and the results are given in Tables II and III.

From the diffraction data it is apparent that the γ phase detected near 35 per cent in the diffusion couple is a tetragonally deformed version of the face-centred cubic platinum structure. This phase appears in a number of samples shown in Table II, and typically has lattice parameters $a = 3.896\text{\AA}$, $c = 3.933\text{\AA}$, $c/a = 1.010$. In this respect it is very similar to the $\beta(\text{Pt}_3\text{Mo})$ phase described by Rooksby and Lewis (15) in the molybdenum-platinum system. A similar analogy can be drawn between the hexagonal close-packed phase ($a = 2.80\text{\AA}$, $c = 4.50\text{\AA}$, $c/a = 1.61$) and the corresponding $\delta\text{Pt}_3\text{Mo}_2$ phase.

The lattice spacings of the platinum solid solution show a substantial increase with additions of tungsten from $a = 3.923\text{\AA}$ for the pure metal to $a = 3.947\text{\AA}$ for the 50 per cent tungsten alloy. The values obtained have been plotted in Figure 2 and tend to confirm the results of Luo rather than the lower figures given by Khan and Raub.

A number of anomalies are present among the data presented in Table II and in view of these it cannot be claimed that complete equilibrium has been achieved during the heat treatments at 1400°C.

Electron probe micro analysis was carried out on samples in the arc melted condition and

Table II
X-ray Diffraction Data on Tungsten-Platinum Alloys

Composition	Alloy treatment at 1400°C	Phases present	Lattice Constants		
			a(Å)	c(Å)	c/a
Platinum 35 per cent tungsten	Sintered 50 hours	Tetragonal (γ)	3.896	3.943	1.012
		Cubic b.c.	3.165	—	—
	Sintered 268 hours	Tetragonal (γ)	3.895	3.943	1.012
		Cubic b.c.	3.166	—	—
Melted 50 hours	Cubic f.c.	3.922	—	—	
Melted 218 hours	Tetragonal (γ)	3.896	3.933	1.010	
Platinum 50 per cent tungsten	Sintered 50 hours	Tetragonal (γ)	3.915	3.946	1.008
		Hexagonal (ϵ)	2.796	4.493	1.607
		Cubic b.c.	3.166	—	—
	Sintered 268 hours	Tetragonal (γ)	3.903	3.940	1.009
Melted 50 hours	Cubic b.c.	3.165	—	—	
	Cubic f.c.	3.947	—	—	
Melted 218 hours	Tetragonal (γ)	3.911	3.940	1.007	
Platinum 70 per cent tungsten	Sintered 50 hours	Tetragonal (γ)	3.934	3.935	~
		Hexagonal (ϵ)	2.793	4.507	1.614
		Cubic b.c.	3.166	—	—
	Sintered 268 hours	Cubic f.c.	3.934	—	—
		Hexagonal (ϵ)	2.80	4.50	1.61
		Cubic b.c.	3.168	—	—
Melted 50 hours	Cubic f.c.	3.945	—	—	
	Hexagonal (ϵ)	2.79	4.50	1.61	
Cubic b.c.	3.170	—	—		

Table III
**Electron Probe Micro Analysis Results on Melted and
Annealed Tungsten-Platinum Alloys**

Composition	Arc melted		Melted+annealed at 1400°C for 50 hrs	
	Platinum per cent	Tungsten per cent	Platinum per cent	Tungsten per cent
35 per cent tungsten	71.7	28.3 (min)	67	33.0 (min)
	63.2	36.8 (max)	63.6	36.4 (max)
50 per cent tungsten	53.2	46.8 (min)	62.0	38.0*
	48.6	51.4 (max)	46.5	53.5
70 per cent tungsten	40.0	60.0	41.7	58.3†
	8.3	91.7	36	64
			8.3	91.7

Suggests that γ formation was occurring on 1400°C annealing. †X-ray diffraction shows the ϵ phase, Pt and W base solid solutions in this alloy.

after annealing at 1400°C for 50 hours with the results shown in Table III. The melted samples confirmed the peritectic form of the diagram, the 35 and 50 per cent tungsten alloys consisting of cored solid solutions with the maximum and minimum composition variations as shown. The 70 per cent tungsten alloy was duplex, the primary tungsten solid solution phase containing 8.3 per cent platinum in a matrix composition of 40 per cent.

After the 50 hour anneal, partial homogenisation of the cored structure had occurred in the 35 per cent tungsten alloy. Some precipitation of the γ phase was suggested by the probe results on the 50 per cent alloy, but the proportion of this phase present was insufficient to be detectable by X-ray diffraction. Three distinct areas could be distinguished in the 70 per cent tungsten alloy after annealing. The tungsten-base primary phase was accompanied by a fine eutectoid-like structure analysing at 64 per cent tungsten in a single phase matrix of 58.3 per cent. This is obviously a non-equilibrium structure and cannot be interpreted with certainty from the data available. During this study no evidence was obtained for the existence of the orthorhombic WPt_2 phase described by Sinha (12). As the heat treatment temperature used by this author was 900°C compared with 1400°C in the present investigation, this may be indicative of further solid state reactions occurring at low temperatures in the system.

Conclusions

It has now been firmly established that at least two intermediate phases are present in the tungsten-platinum system which have not been incorporated in the published phase diagrams. Evidence obtained from diffusion studies, arc melted or sintered samples are compatible with the formation of a tetragonal phase (γ) near 35 per cent tungsten and a hexagonal phase (ϵ) near 50 per cent tungsten, both phases being stable at 1400°C. Electron probe micro analyses and X-ray diffraction have been used to determine composition and lattice spacing data for these phases. Analogous structures have been

reported by earlier workers in the molybdenum-platinum system.

There is a high probability that further developments of advanced power sources, such as thermonuclear fusion, magnetohydrodynamic systems or thermoelectric generators, will make increasing demands for materials capable of withstanding extremes of temperature. In such applications the importance of refractory metal alloys or clad structures cannot be overemphasised, and a full understanding of these relies heavily on proper constitutional diagram information. In this context it is perhaps curious that certain of the more exotic platinum group metal systems, for example osmium-tungsten or iridium-tungsten, have been the subject of reasonably complete studies, whereas tungsten-platinum has been largely neglected. Further phase diagram studies are obviously well overdue on what must surely be something of a Cinderella among platinum alloy systems.

References

- 1 *British Patent* 578,956; 1946
- 2 A. P. Adakhovskiy, N. S. Agushevich and E. Yu. Nekhendzi, *Tr. Inst. Fiz. Met. Ural. Nauchn. Tsentra Akad. Nauk SSSR*, 1971, **28**, 184
- 3 *British Patent* 1,243,279; 1971
- 4 C. J. Smithells, "Tungsten", Chapman and Hall, London, 1936, p. 225
- 5 G. Windred, "Electrical Contacts", Macmillan and Co. Ltd., London, 1940, p. 350
- 6 M. Hansen and K. Anderko, "The Constitution of Binary Alloys", McGraw Hill Book Co, New York, 1958, p. 1146
- 7 P. Greenfield and P. A. Beck, *Trans. AIME*, 1956, **206**, 265
- 8 A. G. Knapton, *J. Inst. Met.*, 1958-59, **28**, 87
- 9 H. L. Luo, *J. Less-Common Met.*, 1968, **15**, (3), 299
- 10 H. R. Khan and C. J. Raub, *Metall. (Berlin)*, 1972, **26**, (12), 1222
- 11 E. J. Rapperport, V. Merses and M. F. Smith, U.S. Rep. ML-TDR-64-61, March 1964 (Quoted in C. J. Smithells, "Metals Reference Book", Butterworths, London, 1976)
- 12 A. K. Sinha, *Trans. Metall. Soc. AIME*, 1969, **245**, (2), 237
- 13 G. L. Selman, *Platinum Metals Rev.*, 1967, **11**, (4), 132
- 14 G. L. Selman, *Platinum Metals Rev.*, 1968, **12**, (4), 134
- 15 H. P. Rooksby and B. Lewis, *J. Less-Common Met.*, 1964, **6**, (6), 451