

Solubility Relationships in the Ruthenium-Platinum System

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Ruthenium hardens platinum very effectively and the dilute solid solutions thus obtained are strong, ductile, and remarkably resistant to corrosion. In view of their wide application in electrical technology and in the manufacture of jewellery it is surprising that little has hitherto been published on the true nature of these valuable noble metal alloys. Until very recently the widths of the primary solid solutions at each end of the diagram were very uncertain. Whereas early Russian workers had suggested that platinum would dissolve at least 70 atomic per cent (1) and probably 79 atomic per cent (2) of ruthenium,

more recent investigations at the Battelle Memorial Institute (3) indicated that the solid solubility of ruthenium in platinum was only about 32 atomic per cent.

Practical experience within the Johnson Matthey Research Laboratories supported the view that the solubility of ruthenium in platinum was very high indeed. Although difficulty was experienced in working alloys containing more than about 30 atomic per cent of ruthenium this was invariably found to be associated with internal and grain boundary oxidation effects, which occurred whenever these alloys were heated in air to

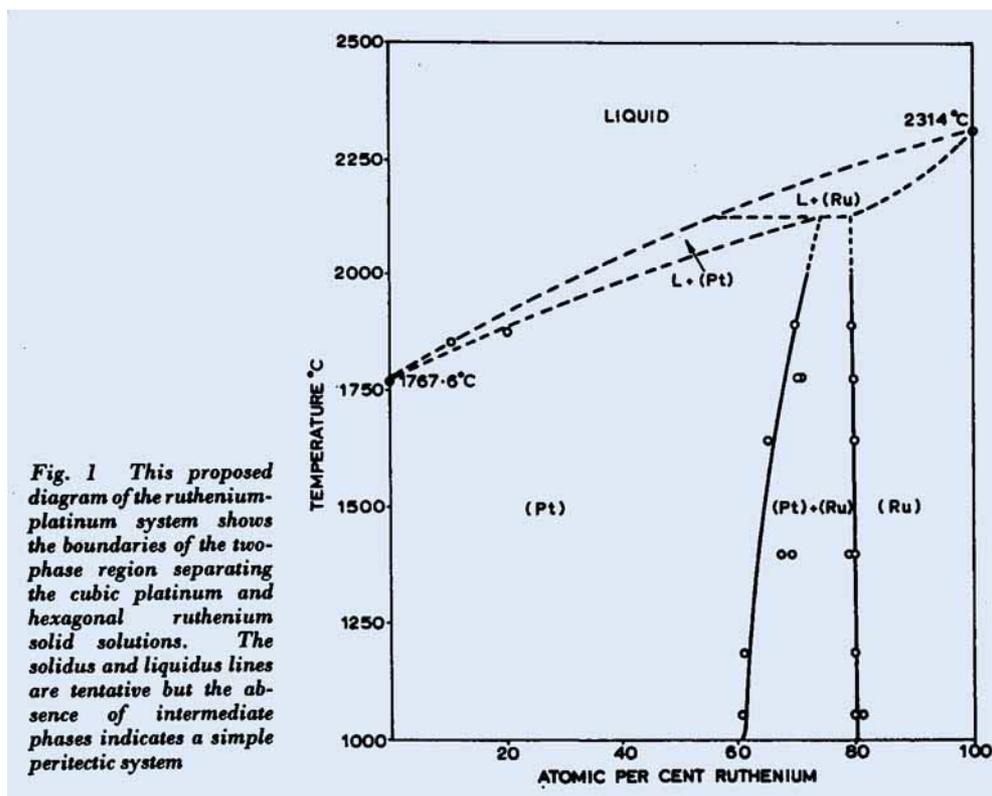
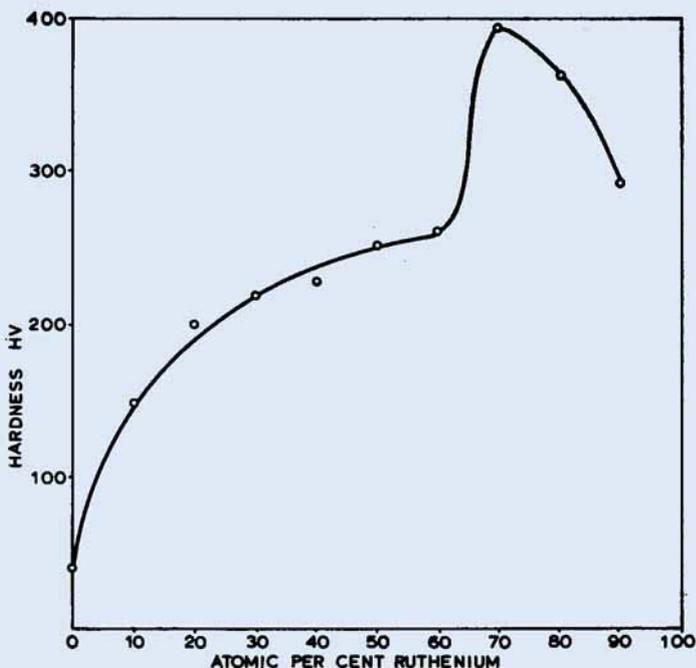


Fig. 2 The hardness of ruthenium-palladium alloys quenched from 1800°C. This curve shows a gently ascending line typical of normal solution hardening followed by a peak associated with precipitation across the whole width of the duplex region



temperatures much in excess of 900°C. No evidence of a ruthenium-rich phase was found even in alloys containing 40 and 50 atomic per cent of ruthenium, and it has now been established that platinum at 1000°C will dissolve approximately 62 atomic per cent of ruthenium. This solubility increases to 70 atomic per cent at 1900°C.

The boundaries of the two-phase region separating the cubic platinum and hexagonal ruthenium solid solutions are shown in Fig. 1. The solidus and liquidus lines in this diagram are purely tentative, but in view of the complete absence of intermediate phases in these alloys it seems evident that the system is, as indicated, of the simple peritectic type.

The experimental points defining the limits of the solubility of platinum in ruthenium were obtained without difficulty by micro-probe analysis, and showed little inconsistency. The solubility of platinum in ruthenium increases with temperature very slowly indeed and little precipitation from these solutions occurred on quenching. The solubility of ruthenium in platinum, however,

increases fairly rapidly with increasing temperature, and it was found that the high temperature structure of the saturated platinum solutions could not be fully retained by quenching. Considerable precipitation occurred, and this influenced the composition of the retained phases and reflected itself in the high hardness of the quenched duplex alloys. In the hardness curve shown in Fig. 2 a gently ascending line typical of normal solution hardening is followed by a well-defined hardness peak associated with precipitation across the whole duplex region.

Metallography provided supporting evidence for the phase boundaries shown in Fig. 1. Thus, the microstructure of the quenched 70 atomic per cent ruthenium alloy shown in Fig. 3 displays a volumetric distribution of the two phases commensurate with the position of this alloy within the two-phase area. The 80 atomic per cent alloy shown in Fig. 4 contains only a small proportion of the platinum-rich phase, thus confirming that the alloy is just within the duplex boundary at 1000°C.

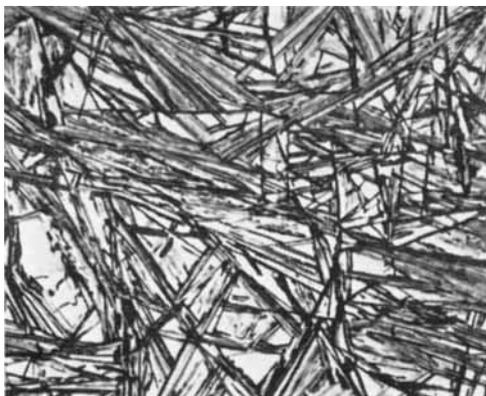


Fig. 3 The microstructure of quenched 70 at.% ruthenium-platinum alloy displays a volumetric distribution of the two phases commensurate with the position of this alloy within the two-phase area

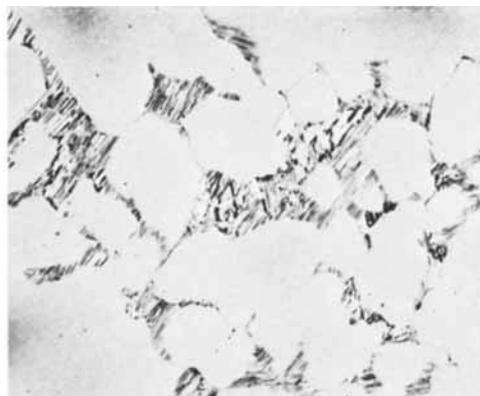


Fig. 4 The microstructure of 80 at.% ruthenium-platinum. This alloy contains only a small proportion of the platinum-rich phase, thus confirming that it is just within the duplex boundary at 1000°C

Acknowledgements are due to Mr J. H. F. Notton for the micro-probe analysis.

1 N. V. Ageev and V. G. Kuznetsov, *Izv. Akad. Nauk S.S.S.R. (Khim.)*, 1937, 753-755

2 V. A. Nemilov and A. A. Rudnitskii, *Izv. Akad. Nauk S.S.S.R. (Khim.)*, 1937, 33-40

3 R. I. Jaffee et al., AIME Metallurgical Soc. Conferences, Vol. II, Refractory Metals and Alloys, 383-463 (especially 418-420), Interscience Publishers Inc., New York, 1961

The Electrodeposition of Osmium

Of all the platinum group of metals osmium has the highest melting point and hardness, and it is chemically very resistant although oxidised in air above 400°C. These properties make it potentially useful in the form of an electrodeposited coating where the atmosphere is not oxidising, as for example in reed relays, and in the last few years efforts have been made to develop a suitable electrolyte for this purpose.

A number of workers have reported unsatisfactory results with hexachloroosmate solutions, while other electrolytes that have been tried include molten cyanides, which gave granular deposits and were unstable, and alkaline electrolytes prepared from OsO_4 and sulphuric acid. The latter showed some promise, but now further and more successful results with hexachloroosmate baths have been reported by J. M. Notley of International Nickel in a paper presented to the annual conference of the Institute of Metal Finishing held in May 1972. (*Trans. Inst. Metal Finish.*, 1972, 50, (2), 58).

The advancement described in the paper is the stabilisation of the electrolyte by addition of (i) potassium chloride to suppress hydrolysis of the hexachloroosmate to osmium

dioxide, and (ii) of potassium bisulphate to buffer the pH at ~ 1.5 . Any dioxide that is precipitated is redissolved by chlorine generated at the anode. If the bath is being operated at too low a current density to produce chlorine then a short burst at high current density is usually sufficient to redissolve the dioxide.

The osmium is deposited at 1 to 4 A/dm² at 70°C with a current efficiency of 20 to 30 per cent, and plating rates up to 4 $\mu\text{m}/\text{h}$. The deposits are bright and although cracked at thicknesses greater than 1.5 μm may be obtained up to 10 μm thick.

Very careful control of the electrolyte at pH 1.0 to 1.5 is necessary to prevent precipitation of OsO_2 on to the cathode.

Details are given of the synthesis of the plating salt, K_2OsCl_6 , and of the preparation and analysis of the bath. The kinetics of the decomposition of the electrolyte were investigated and the results were used to adjust the composition to obtain a stable system. The effects of current density and temperature on plating rate and efficiency were determined for a bath using ammonium hexachloroosmate and a sulphamic acid/ammonium sulphamate buffer. C. W. B.