

# Phase Equilibria in the Platinum-Molybdenum System

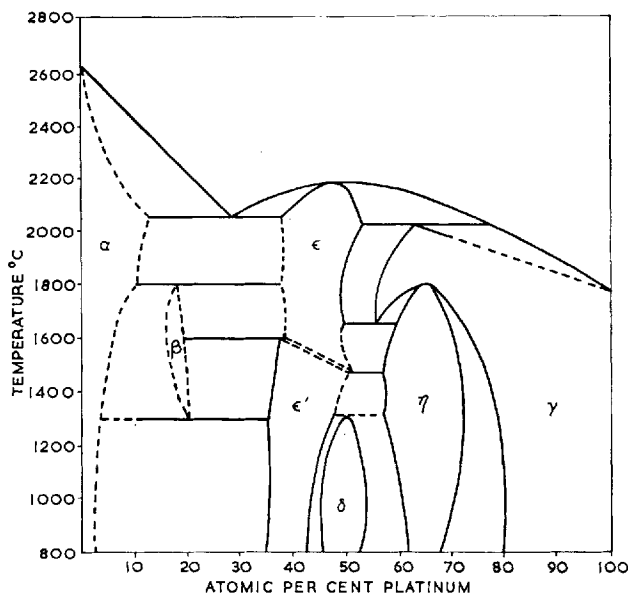
## SIGNIFICANCE IN THE GLASS INDUSTRY

The practical significance of the high temperature phase relationships in the platinum-molybdenum binary system has been discussed in two recent articles in this journal, (1), (2), which described the way in which platinum-clad molybdenum glass handling equipment can fail at temperatures above 1300°C by creep of the protective sheath if high temperature intermetallics are allowed to form on its inner surface. The interpretation of the interfacial diffusion zone microstructures observed during these investigations was made more difficult by the lack of sound information on the binary system between the two metals, and it is pleasing to note, therefore, that a thorough investigation recently carried out by H. Ocken and J. H. N. Van Vucht in the Philips Research Laboratories at Eindhoven (3) has resulted in the presentation of a phase diagram for the platinum-molybdenum system which serves to bring into perspective the many partial

investigations which have previously been made.

Seven single-phase regions are shown in the new diagram, which was determined by conventional metallurgical techniques using arc-melted alloy buttons. The molybdenum-rich  $A_{15}$  phase, whose formation is thought to be largely responsible for the high interfacial strains developed in the platinum claddings of molybdenum glass stirrers, is shown to form via a peritectoid reaction between the b.c.c. Mo solid solution and a disordered form of the hexagonal intermediate phase, originally observed by Raub (4), at approximately 1800°C, and to decompose eutectoidally at approximately 1300°C, forming a duplex mixture of the terminal molybdenum-rich solid solution and the ordered hexagonal phase.

It must surely be more than a coincidence that the decomposition temperature of this phase corresponds closely with what is



*The new phase diagram for the platinum-molybdenum binary system put forward by H. Ocken and J. H. N. Van Vucht*

regarded as the maximum long-term operating temperature of a conventional platinum-clad molybdenum component in the glass industry.

The investigators at Philips paid particular attention to the formation and properties of this molybdenum-rich compound. An alloy containing 28 atomic per cent platinum was shown to be superconducting. The highest superconductive transition temperature for this eutectic composition, 5.6°K, was observed after annealing the alloy at 1800°C.

Other significant features of the diagram include a proposed orthorhombic phase of equiatomic composition, stable at temperatures below 1300°C, and an extensive solubility of platinum in molybdenum. The latter finding is of interest in that it was originally predicted on theoretical grounds by means of the Engel-Brewer correlation (5), and was

confirmed experimentally some time later (1).

At the platinum-rich end of the system, the new diagram indicates the existence of a second orthorhombic phase, of approximate composition Mo Pt<sub>2</sub>. This structure appears to be an ordered form of the terminal face-centred cubic platinum solid solution, and occupies the position formerly ascribed to the tetragonally distorted phase denoted  $\alpha_1$  by Raub (4).

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### References

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- 2 A. S. Darling and G. L. Selman, *Platinum Metals Rev.*, 1968, **12**, (3), 92
- 3 H. Ocken and J. H. N. Van Vucht, *J. Less-Common Metals*, 1968, **15**, (2), 193
- 4 E. Raub, *Z. Metallk.*, 1954, **45**, 23
- 5 W. Hume-Rothery, *Progress in Materials Science*, 1967, **13**, (5), 231

## Phosphine Complexes of Rhodium and Ruthenium as Homogeneous Catalysts

### HYDROFORMYLATION OF OLEFINS

One of the most rapidly advancing areas of physical-inorganic chemistry is undoubtedly the application of phosphine complexes of the platinum metals as homogeneous catalysts for hydrogenation and hydroformylation of olefins. In a paper presented at the recent symposium on "New Olefin Reactions" at the University of Manchester Institute of Science and Technology, Professor Geoffrey Wilkinson of Imperial College described recent new work in this field: the reactions he discussed are characterised by a degree of specificity not commonly encountered in other catalytic processes.

Perhaps his most startling disclosure was that concerning the rhodium complex *trans*-RhH(CO)(PPh<sub>3</sub>)<sub>2</sub> which catalyses the hydroformylation of olefins under ambient conditions. With the widely used cobalt catalyst CoH(CO)<sub>4</sub> temperatures of about 100°C and pressures in excess of 100 atmospheres have to be used. When  $\alpha$ -olefins are hydroformylated with the rhodium catalyst, the ratio of straight- to branch-chain aldehyde is

about 20, which is much higher than found with the cobalt catalyst. The reaction is believed to involve the five-coordinate RhH(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as an intermediate.

Professor Wilkinson also reported a new, extremely active homogeneous catalyst for olefin hydrogenation: this is the ruthenium complex RuClH(PPh<sub>3</sub>)<sub>3</sub>, also a five-coordinate species. This complex is even more active than the rhodium complex RhCl(PPh<sub>3</sub>)<sub>3</sub> but it is selective for  $\alpha$ -olefins, as internal olefins are reduced more slowly by a factor of about a thousand. This specificity is explained by the steric effects of the bulky triphenylphosphine groups. Unfortunately, solutions of the ruthenium complex are very sensitive to air and tend to lose activity during use.

These disclosures give further proof of the power of homogeneous catalysis as a technique for organic reactions, although many difficult technical problems will need to be overcome before reactions such as those described find commercial application.

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