

enhanced by the presence of the platinum metals. Palladium and platinum tend, in general, to be more effective in promoting such reactions than ruthenium or rhodium.

Most of the reactions start in the temperature range 700 to 800°C, although reduction temperatures as low as 600°C have been observed. The driving force for these reactions is the high affinity of the platinum metals for the metal of the refractory oxide. This affinity results in the formation of intermetallic compounds or stable solid solutions, whose partial molar free energies of formation might be as high as -100 kcal per mol at 1000°C (the Pd/Pt-Mg systems).

The results of this experimental study are of value not only in helping to prevent damage to industrial platinum apparatus. They also suggest that metals could be brazed to refractory oxides with the aid of a platinum-containing brazing alloy, under suitably reducing conditions. Useful information on the thermodynamic behaviour of platinum metal alloys has also been obtained.

Acknowledgement

The authors wish to thank the A.I.F. (Arbeitsgemeinschaft Industrieller Forschungsvereinigungen e.V.) for supporting these investigations.

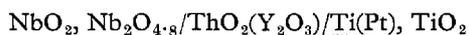
References

- 1 A. R. Powell, *Platinum Metals Rev.*, 1958, **2**, (3), 95
- 2 C. B. Alcock, *Platinum Metals Rev.*, 1961, **5**, (4), 134
- 3 A. S. Darling, G. L. Selman and R. Rushforth, *Platinum Metals Rev.*, 1970, **14**, (2), 54 and *Platinum Metals Rev.*, 1971, **15**, (1), 13
- 4 W. Gorski, *Z. Anorg. Allgem. Chem.*, 1968, **358**, (3/4), 163
- 5 E. Raub and W. Plate, *Z. Metallkunde*, 1957, **48**, (10), 529
- 6 W. Bronger and W. Klemm, *Z. Anorg. Allgem. Chem.*, 1962, **319**, (1/2), 58
- 7 W. Bronger, *J. Less-Common Metals*, 1967, **12**, (1), 63
- 8 H. Schulz, K. Ritapal, W. Bronger and W. Klemm, *Z. Anorg. Allgem. Chem.*, 1968, **357**, (4/6), 299
- 9 H. R. Khan and Ch. J. Raub, *J. Less-Common Metals*, 1971, **25**, (4), 441
- 10 E. Raub and G. Falkenburg, *Metall*, 1973, **27**, 669 and *Z. Metallkunde*, 1964, **55**, (4), 190
- 11 L. Brewer, *Acta Metall.*, 1967, **15**, (3), 553
- 12 E. Röschel and Ch. J. Raub to be published
- 13 D. Ott and Ch. J. Raub to be published

High Temperature Thermodynamic Properties of Platinum-Titanium Alloys

Many of the enigmas of the interaction of platinum metal with other substances, in particular refractory oxides, are yielding to the systematic application of thermodynamic analysis, guided in no small measure by the Engel-Brewer predictions made over the past few years. Among the latest contributions to this field is the work recently reported by P. J. Meschter and W. L. Worrell (*Metall. Trans. A*, 1976, **7**, (2), 299-305) who describe high temperature thermodynamic measurements on platinum-titanium alloys.

The study concentrated on platinum-rich alloys containing 2 to 25 atomic per cent titanium and over the temperature range 1150 to 1400K. The thermodynamic information was obtained from e.m.f. measurements, using a solid ionic conductor as the electrolyte in a cell of the type:



The e.m.f. data were used to derive the

integral molar free energies, enthalpies and entropies for the range of platinum-titanium compositions studied, and also the partial molar quantities for platinum and titanium in the alloys. The activity of titanium in platinum was shown to be extremely low, that for the 20 per cent titanium alloy at 1300K being, $a_{\text{Ti}} = 2.6 \times 10^{-12}$. In accordance with Brewer's predictions, the standard free energies of formation of the intermetallic compounds also proved to be highly negative $\Delta G_f^\circ(\text{TiPt}_8) = -73.8$, and $\Delta G_f^\circ(\text{TiPt}_3) = -71.3$ kcal/g atom Ti at 1300K.

A tentative phase diagram is presented for the 0 to 25 atomic per cent titanium region of the system, based on the e.m.f. and X-ray data. It is proposed that TiPt_8 forms peritectoidally from TiPt_3 and Pt at $1350 \pm 20\text{K}$.

The authors have made similar thermodynamic studies of the related systems, Pt-Zr and Pt-Hf, and expect to present these in a future publication.

A. G. K.