

Electron Configuration and Crystal Structure of Platinum Metal Alloys

INTERMEDIATE PHASE FORMATION INTERPRETED IN TERMS OF THE ENGEL-BREWER CORRELATION

By A. S. Darling, Ph.D., A.M.I.Mech.E.

Research Laboratories, Johnson Matthey & Co Limited

The platinum metals react with some of their closer neighbours in the Periodic Table to produce intermediate phases of high stability. While this behaviour tends to confirm some of the predictions made by protagonists of the Engel-Brewer theory of alloying, the general validity of this theory is still a matter of vigorous controversy. In this article some of the conflicting opinions that have been advanced are reviewed and discussed.

Correlations between the electron configuration and crystal structures of the metallic elements and their alloys were first proposed by Engel in 1949 (1, 2), and since that time Brewer has enlarged and refined the original conception and has used it to predict constitutional relationships in a wide range of alloys (3, 4, 5). Recent comments by Hume-Rothery (6, 7) have stimulated a great deal of discussion; the Engel-Brewer theory has been brought to the attention of a wide range of metallurgical opinion and is no longer a matter of purely academic interest.

The basic point of contention is whether a hypothesis, suggested originally by the valency and crystal structure sequence exhibited by sodium, magnesium and aluminium, can with justification be used to interpret the behaviour of the transition metals and their alloys. Since the elements to the right of ruthenium and osmium in the second

and third long periods do not use all their valency electrons for bonding, differing interpretations of their alloying behaviour have figured prominently in the papers referred to above. Before exploring the implications of the theory so far as the platinum metals are concerned, its general background and scope deserve a little attention.

Genesis of the Theory

The integral electron concentration theory first advanced by Engel was in fact an extension and generalisation of some of Hume-Rothery's ideas on electron compounds (8, 9). When considering intermediate phases containing iron, cobalt or nickel, Hume-Rothery was able to correlate crystal structure and electron atom ratios only by assuming that the transition element contributed no electrons to the crystal structure. Engel, however, concluded that the *d* electrons of the transition element participated in the bonding of these intermediate phases, thus explaining their high melting points. The Engel-Brewer theory now states that all unpaired electrons participate in crystal bonding, but that the *d* electrons have no effect upon the type of crystal symmetry adopted, which is determined solely by the number of *s* and *p* electrons.

Thus the 1, 2 and 3 valency electrons of sodium, magnesium and aluminium explain why these elements crystallise respectively in the b.c.c., h.c.p. and f.c.c. systems of symmetry. The b.c.c. lattice is apparently stable from 1 to 1.75 electrons/atom, the

h.c.p. lattice from 1.8 to 2.2, while the f.c.c. lattice extends from 2.25 to more than three electrons per atom (10).

To thermodynamic aspects of the Engel-Brewer correlation Professor Hume-Rothery has so far devoted little attention. This part of the theory is of great interest as it provides a strong link between the electronic approach and metallurgical thermo-chemistry. When for example the electron/atom concentration suggests hexagonal and body centred structures of comparable total energy, the theory predicts that the b.c.c. structure will be the stable high temperature form, as the h.c.p. structure, having a lower co-ordination would make a larger contribution to the high temperature entropy.

Transition Metal Compounds

The theory indicates that combinations of the transition elements from the left and right of the Periodic Table should produce compounds of high stability. Metals from Rb to Tc and Cs to Re use all their valency electrons for bonding while the platinum metals do not. A mixture of these two types of atom promotes, therefore, a flow of electrons from the element with an excess to that with vacant orbitals. Thus when Zr and Ir are alloyed the Ir donates electrons to the Zr. The stability of the compound $Zr Ir_3$ thus formed is according to Brewer (5) attributable to the fact that 31 electrons contribute to the bonding process compared to the 25 bonding electrons of the uncombined atoms.

For a given base metal the number of electrons transferred on combination should increase as the atomic weight of the platinum metal increases. This explains, in a qualitative way, the high stability of $Zr Pt_3$ compared to $Zr Ir_3$. Brewer has attempted (5) to verify the prediction in a more specific manner by heating zirconium carbide with Pt, Ir and Os. In all instances the carbide dissociated, graphite was liberated and the zirconium formed an intermetallic compound with the platinum metal.

These platinum metal compounds must

therefore be more stable than zirconium carbide. Experiments of this sort reported by Raub (11) several years ago used in general lower concentrations of carbide, and in most instances the base metal was taken into solid solution by platinum.

Zirconium carbide, although one of the most stable known, has a lower free energy of formation than the refractory oxides. Bronger and Klemm (12) showed in 1962 that zirconium oxide can be effectively reduced by hydrogen in the presence of platinum, and this has been cited by Brewer in support of his general predictions. Aluminium oxide was also reduced however, and the solubility of aluminium in platinum is high. The activity of aluminium in this dilute solid solution must therefore have been very low.

Bronger also reported the reduction of yttrium and lanthanum oxides with hydrogen in the presence of platinum with the formation of the compounds $Pt_5 Y$ and $Pt_5 La$. All the lanthanides between lanthanum and thulium have since (13) been reduced in a similar manner. In this series of experiments dry ammonia was employed as a reductant. Complete reductions were achieved at $1200^\circ C$ for all elements with the exception of samarium and europium which required temperatures between 1350 and $1500^\circ C$.

Some Inconsistencies

It is reported (14) that hafnium and platinum, when heated together, react with explosive violence. This finding, and the other results reported above, leave no doubt that the compounds between platinum and those base metal transition elements which form refractory oxides are of quite extraordinary stability.

For practising metallurgists, however, many baffling inconsistencies remain. Platinum and palladium can, for example, be safely melted under hydrogen in zirconia crucibles. Slight contamination of the platinum metal undoubtedly occurs under such conditions, although it is a minor effect and usually associated with silicious attack. Refractory oxide dispersants

in a solid platinum matrix are, however, notoriously unstable, and this appears to suggest a high affinity of solid platinum for the refractory metal.

Differences in geometry could also be involved in these apparent anomalies as platinum, when held molten against a refractory wall, might prevent complete removal of gaseous reaction products such as water vapour.

The experimental results and interpretations given in this recent group of papers will undoubtedly lead to a great deal of further work, and should moreover encourage detailed constitutional studies on platinum metal alloys.

References

1 N. Engel, Metals as Electron Concentration Phases, *Kem. Maanedstbl*, 1949, 30, 53

2 N. Engel, Alloys as Electron Concentration Phases, *Ibid.*, 97, 105, 113
 3 L. Brewer, Paper in "Electronic Structure and Alloy Chemistry of the Transition Elements", Ed. P. A. Beck, Interscience New York, 1963
 4 L. Brewer, "Predictions of High Temperature Phase Diagrams". UCRL 10701, Univ. California, 1963
 5 L. Brewer, *Acta Metall.*, 1967, 15, 553
 6 W. Hume-Rothery, *Ibid.*, 1965, 13, 1039
 7 W. Hume-Rothery, *Ibid.*, 1967, 15, 567
 8 W. Hume-Rothery "The Structure of Metals and Alloys". Monograph and Report Series No. 1, Inst. Metals, London, 1936
 9 W. Hume-Rothery, "Atomic Theory for Students of Metallurgy". Monograph and Report Series No. 3, Inst. of Metals, London, 1948
 10 N. Engel, *Acta Metall.*, 1967, 15, 565
 11 E. Raub and G. Falkenburg *Z. Metallkunde*, 1964, 55, 186
 12 W. Bronger and W. Klemm, *Z. anorg. allgem. Chem.*, 1962, 319, 58
 13 W. Bronger, *J. less-common Metals*, 1967, 12, 63
 14 J. Margrove, note to (5)

Brazing Graphite to Metals

A NEW PALLADIUM-BASE BRAZING ALLOY FOR NUCLEAR ENERGY APPLICATIONS

The development of advanced molten-salt reactors posed a problem of making mechanically strong and pressure-tight joints between graphite and refractory metals and alloys for service in contact with fused fluorides at elevated temperatures. According to a report recently released from Oak Ridge National Laboratory (USAEC Report ORNL-3970, 1966), a satisfactory solution to this problem was found in brazing with a new palladium-base brazing alloy.

The new material, melting below 1250°C, is based on the well-known 60 per cent Pd-40 per cent Ni brazing alloy to which 5 per cent chromium was added at the expense of nickel. Palladium was chosen as the basis of the new alloy because of its relatively low thermal neutron cross section (eight barns) and its good resistance to the corrosive action of molten salts; chromium, which is one of the carbide forming elements, was added to make the alloy capable of wetting graphite.

As was to be expected, the 60 Pd-35Ni-5 Cr alloy exhibited good wetting properties on graphite, molybdenum and tungsten. Lap joints made with this alloy between graphite and molybdenum parts in a vacuum furnace at 1250°C were defect-free not only in the

as-brazed condition but also after thermal cycling tests (ten cycles between 700°C and room temperature). A 1000 hours test in a molten LiF-B₂F₂-ZrF₄-ThF₄-UF₄ mixture at 700°C produced only a slight surface roughening of the brazing alloy.

Surprisingly, no cracking - which often occurs in graphite-metal brazed joints due to differential thermal expansion/contraction of the metallic and non-metallic parts - was observed in this case. This was attributed to the fact that the thermal expansion coefficient of molybdenum is only slightly larger than that of graphite. It is claimed, in fact, that by using molybdenum inserts, or so-called 'transition' pieces, crack-free joints can be made with the Pd-Ni-Cr alloy between graphite and metals with high thermal expansion coefficients.

Although the new alloy was developed as a special purpose material, there is no doubt that palladium-base alloys of this kind would prove useful in general engineering applications in which a high strength and good resistance to corrosion and oxidation at both room and elevated temperatures are important considerations.

M.H.S.