

The Platinum Metals and Their Alloys

A REVIEW OF THEIR ELECTRONIC STRUCTURE AND CONSTITUTION

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In this paper the electronic structures of the elements of Group VIII of the Periodic Table are outlined, and the difference between the platinum metals and other metals in the group is emphasised. The constitution of the alloys of the platinum metals with silver and gold is then discussed, and an interpretation is offered. The alloying behaviour of the platinum metals with a number of transition metals is interpreted in terms of some recently established electron concentration principles.

The platinum metals lie in Group VIII of the Periodic Table and their properties and alloying characteristics can be understood only by considering the Group as a whole, namely:

Fe - Co - Ni
Ru - Rh - Pd
Os - Ir - Pt

In each transition series a group of 8 electrons expands into one of 18 by the building up of a sub-group of ten *d* electrons. In the solid metals the sharp energy states of the free atoms broaden out into energy bands, and the outer or bonding electrons are in hybridised *s p d* states. There is general agreement that, on passing along the second and third transition series, the number of bonding electrons per atom increases from 1 to 6 on passing from Group IA (Rb,Cs) to Group VIA (Mo,W). The physicists are not agreed on

what happens in the later elements of the transition series. The supporters of the so-called "collective electron theories" regard all the outer electrons in, say, platinum as taking part in the cohesive process, and the undoubted fall in the strength of cohesion on passing from (Ru,Os)→(Rh,Ir)→(Pd,Pt) is ascribed to an increasing proportion of the repulsive part of the wave-function. Those who follow the general viewpoint of Pauling consider that on proceeding from Group VIA→VIIA . . . , the additional electrons enter atomic *d* orbitals which are not involved in the metallic bonding process. In the original Pauling hypothesis* it is considered that in all three transition series, from Group VIA to VIIIC the valency (i.e. the number of bonding electrons per atom) in the metallic state is 5.78. The number of atomic *d* electrons is thus 0.22, 1.22 . . . 4.22 on passing from Group VIA→VIIA . . . VIIIC. These numbers were deduced from the saturation magnetic moments of the metals of the first transition series, and Pauling regarded all three transition series as having similar sequences of electronic configuration in the solid metals. This, however, is not in agreement with the physical properties, or with the alloy chemistry of the later transition elements. In the first transition series, the strength of cohesion increases steadily on passing from K→Ca→Sc→Ti→V, after

*In the 1960 edition of *The Nature of the Chemical Bond*, Pauling regarded the constant valency of the later transition element as being 6 in contrast to the value 5.78 referred to above. Neutron scattering work has shown this later view to be untenable, and the early Pauling view is now the more probable.

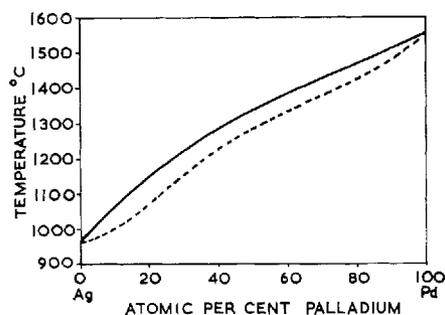
Fig. 1 The system Ag-Pd. This is the simplest kind of equilibrium diagram when a continuous solid solution is formed

which the behaviour is erratic—Mn has abnormally weak cohesion, while Fe, Co and Ni resemble one another very closely. In the second and third transition series, strength of cohesion increases steadily on passing from Group IA→VIA, remains high in Groups VIIA and VIIIA, and then falls rapidly on passing from Group VIIIA→B→C.

Many lines of work confirm this difference between the metals of the first and of the second and third long periods. It seems probable, therefore, that the details of the Pauling scheme are wrong, although the idea of atomic *d* electrons may well be correct. If this is accepted, the most probable valency scheme for the elements at the ends of the second and third transition series is that the valency is 6 for Mo and W, remains at about this value on passing to (Tc,Re) and (Ru,Os) and then falls to, perhaps, 2-3-4 in Pd and Pt. In contrast to this, in the first long period the valency rises to 5 on passing from K→V, remains at about this value in Cr, falls on passing to Mn, and then remains roughly constant at 2 to 3 in Fe, Ni and Co. There is thus a clear distinction between the characteristics of the platinum metals on the one hand, and of iron, nickel and cobalt on the other.

This difference is in the same direction as that between the predominant valencies in the chemistry of these elements. It is well established that, for the later transition elements, the predominant valencies in any one group increase on passing from the first→second→third transition series. Thus iron and cobalt show predominant valencies

Fig. 2 The system Au-Pt. A continuous solid solution is formed at high temperatures. At low temperatures, a miscibility gap appears and Au and Pt do not mix so readily as Ag and Pd

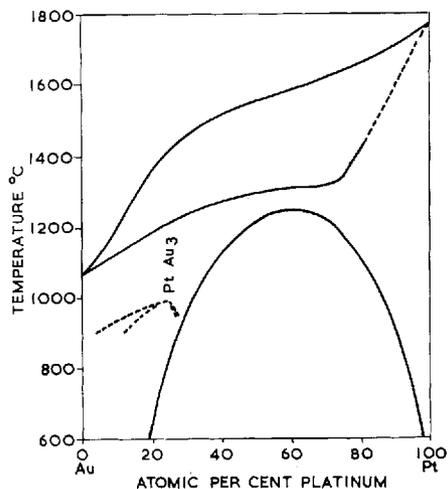


of 2 and 3, whereas Os and Ir have several higher valency states. Since the valency is a measure of the number of electrons which can be perturbed sufficiently to take part in chemical combination, it is natural that the chemical valencies should run parallel to the number of electrons taking part in the metallic bonding process.

At the ends of the second and third long periods, the sequence of crystal structures is:

Groups V, VI Nb, Ta, Mo, W b.c. cubic	Groups VII, VIIIA Tc, Re, Ru, Os c.p. hexagonal
Groups VIIIB, VIIIC Rh, Pd, Ir, Pt f.c. cubic	Group IB Ag, Au f.c. cubic

In these transition metals of Groups V, VI, VII and VIIIA, the bonding forces are very strong, and the electrons are in hybrid *s p d* states, the proportion of *d* function diminish-



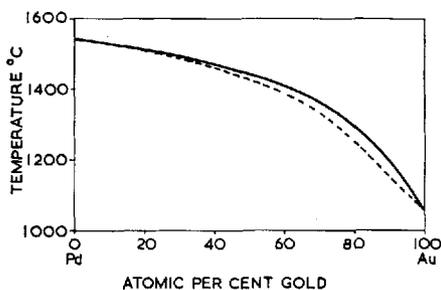


Fig. 3 The system Au-Pd. This equilibrium diagram resembles that for Ag-Pd

ing rapidly on passing through Group VIII. It is possible that in the body-centred cubic structures of Groups V and VI, and in the very stable close-packed hexagonal structures of Groups VII and VIIIA, the bonding forces are much more directional in nature than is usually imagined. The face-centred cubic structures become more stable on passing from (Rh,Ir)→(Pd,Pt)→(Ag,Au), and the proportion of *s* function in the bonding hybrids increases in this order.

Alloys with Silver and Gold

The exact nature of the cohesion in silver and gold is uncertain, and they are probably best regarded as univalent metals in which one *s* electron per atom pulls the "hard" ions into contact, and then the cohesion is increased by a Van der Waals type of attraction between the outermost electrons of the ions. That is to say, the outer electrons of adjacent ions move in sympathy or harmony with one another and so reduce the energy,

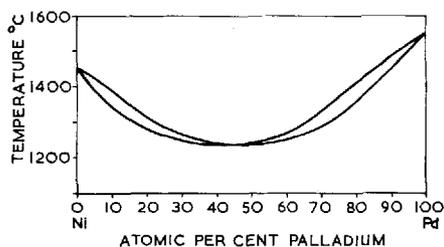


Fig. 5 The system Ni-Pd. The marked minimum in the liquidus curve is to be noted

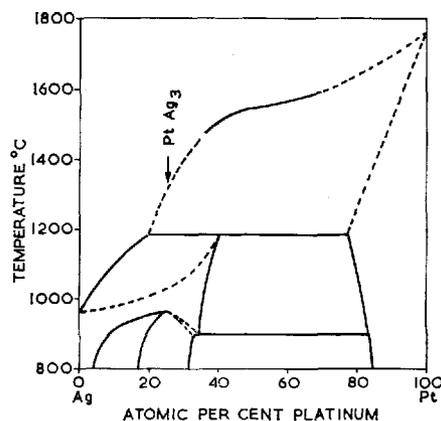


Fig. 4 The suggested equilibrium diagram for the system Ag-Pt. This resembles that for Au-Pt except that a continuous solid solution is not formed at high temperatures

but without any electron sharing or bonding. The equilibrium diagrams suggest that Pd and Pt can provide electrons with the *s* characteristics required by Ag and Au, and that when acting as solutes, Ag and Au can adjust themselves to the lattices of Pd and Pt respectively. The equilibrium diagrams (Figs. 1 and 2) suggest that this adjustment is more difficult in Au-Pt than in Ag-Pd. This is curious in view of the fact that the (*5d*)¹⁰ sub-group of Au is less stable and more easily polarisable than the (*4d*)¹⁰ sub-group of Ag. The difference between the Ag-Pd and Au-Pt diagrams appears to lie in the difference between Pd and Pt, rather than in that be-

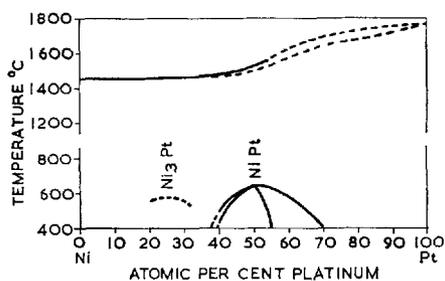


Fig. 6 The suggested equilibrium diagram for the system Ni-Pt. Although the diagram is incomplete it is clear that, in contrast to Ni-Pd, the liquidus curve does not show a pronounced minimum

tween Ag and Au because, as can be seen from Figs. 3 and 4, Au and Pd are freely miscible (like Ag and Pd) whereas Ag and Pt are not. The difference between the phase diagram relations for Au-Pt and Ag-Pt agree with the greater polarisability of the Au ($5d$)¹⁰ ion. The difference between the Ag-Pd and Au-Pt diagrams must be ascribed to some other factor, and this may be the higher valency of Pt compared with Pd, as a result of which it is more difficult for a univalent metal to give the high proportion of d function required by Pt.

On passing back from Rh-Pd and Ir-Pt we find that Ag and Au are almost immiscible with Rh and Ir respectively, and it seems that in these last two metals the proportion of d function is so high that the Group IB element cannot give electrons with the characteristics needed for mixing of the two kinds of atom. If we are correct in regarding Ir and Pt as possessing higher valencies and hence electrons with higher proportions of d function, the difference between Ag-Pt and Au-Pd falls into line with the difference between Ag-Pd and Au-Pt on the one hand, and Ag-Rh and Au-Ir on the other.

If we then consider Ag-Ir and Au-Rh we see that the ($4d$)¹⁰ sub-group in Ag is more stable than the ($5d$)¹⁰ sub-group in Au, while Ir has a higher valency than Rh. Consequently we can understand why Ag and Ir are almost immiscible, whilst Au and Rh form slight solid solutions.

Alloys with Iron, Cobalt and Nickel

The above comments refer to alloys of the Pt-group metals with the essentially univalent metals Cu, Ag and Au which find it difficult to provide electrons with a sufficiently high proportion of d function. When we consider alloys of Pd and Pt with transition metals of the first long period, we find effects clearly related to the more easily polarisable electron cloud of the Pt ion or core compared with that of Pd. Figs. 5 and 6 show the equilibrium diagram of the systems Ni-Pd and Ni-Pt, in which the atomic diameters of Pd (2.75Å) and

Pt (2.77Å) are so nearly equal that size factor effects are similar in the two systems. In the Ni-Pd system there is a marked minimum in the solidus and liquidus curves which indicates that there is appreciable strain in the solid solution lattice. In contrast to this, the Ni-Pt liquidus and solidus show little or no sign* of a minimum, and the curves rise from the melting point of Ni to that of Pt. Analogous effects are found on comparing the equilibrium diagrams of the systems of Co-Pd and Co-Pt, and also the systems Fe-Pd and Fe-Pt.

In general, we expect Pt atoms to undergo deformation more easily than Pd atoms but, if our views are correct, it has also to be considered that Pt has the higher valency and the higher proportion of d function in its electrons.

Alloys with Aluminium

If we consider the elements of Group VIII in the three transition series we find that those of the second and third transition series are more electronegative than those of the first. The Pauling electronegativity values are:

Fe - Co - Ni	1.8	1.8	1.8
Ru - Rh - Pd	2.2	2.2	2.2
Os - Ir - Pt	2.2	2.2	2.2

The elements of Group VIIIc have a tendency to absorb electrons into their d shells so as to complete the (nd)¹⁰ sub-group. This tendency is greater in Pd and Ni than in Pt. The absorption of electrons into the d shell means that, if Ni or Pd contribute electrons to a metallic structure, they also absorb electrons and so act as elements of zero valency or at any rate of very low valency. This effect is distinct from the simple electronegativity effect. Thus the electronegativities of (Fe, Co and Ni) are all about 1.8, and those of (Ru, Rh and Pd) about 2.2, but the tendency for Fe or Ru to complete their d shells is much less than for Ni or Pd.

*The curves are not known very accurately but the absence of an appreciable minimum is established.

It is well known that, in the alloys of copper and silver, there is a tendency for body-centred cubic structures to occur at an electron:atom ratio of $3/2$. If one element is of zero-valency and the second element is 3-valent, the electron concentration of $3/2$ corresponds to the equiatomic ratio, e.g. Al-Pd (3 electrons for Al, 0 for Pd:2 atoms). Now

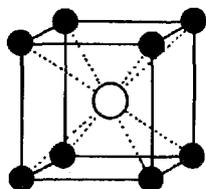
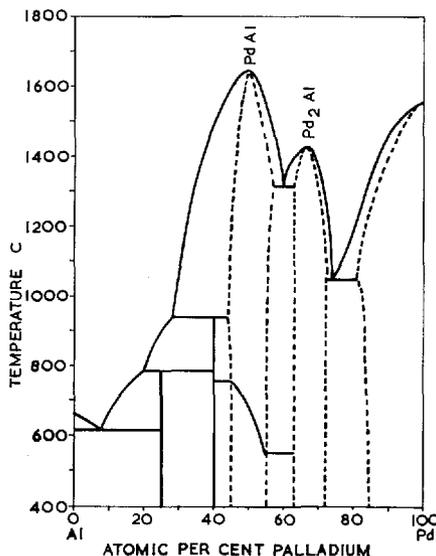


Fig. 7 The CsCl structure. Each atom is surrounded by eight of the opposite kind

this equiatomic ratio permits the formation of an ordered body-centred cubic structure with the CsCl structure of Fig. 7. In this, each atom is surrounded by 8 of the opposite kind, so that the structure is very suitable for combinations of electropositive and electronegative elements. It is for this reason that the system Al-Pd contains the very stable equiatomic ordered b.c. cubic phase shown in Fig. 8. The phase is stabilised because the tendency of the Pd atoms to complete their



$3d$ shells enables the superlattice factor to reinforce that of the electron atom ratio. In the system Al-Pt there is no corresponding body-centred cubic phase at the equiatomic composition, and this agrees with the smaller tendency of the Pt atoms to complete their d shells.

In its equiatomic alloy with aluminium, palladium is acting as a zero-valent element, but this is not always so. In the case of alloys of nickel with B sub-group elements, systematic examination of the equilibrium diagrams suggests clearly that the valency of nickel is variable not only in different systems but at different compositions in a given system (e.g. Ni-Zn, and Ni-Al). In the system Be-Pd there is an equiatomic compound of fixed composition and a melting point of 1465°C .

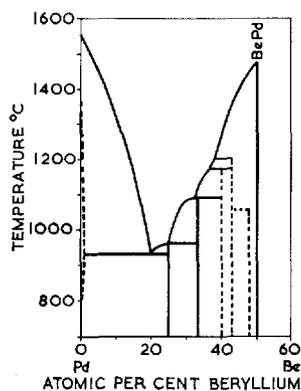


Fig. 9 The system Pd-Be

This has the CsCl type of ordered b.c. cubic structure. It might be looked on as a simple example of a high electrochemical factor producing the CsCl structure in which each atom has eight neighbours of the opposite kind.

If Pd were univalent, BePd would correspond to an electron atom ratio of $3/2$, and electron concentration effects might stabilise the b.c. cubic structure but, on the whole, the

Fig. 8 The system Al-Pd. The marked stability of the equiatomic phase is to be noted. This has the CsCl structure

Fig. 10 In this figure the phase boundaries of solid solutions in the close-packed hexagonal metals Ru, Re and Os, and of the intermediate close-packed hexagonal or ϵ -phases, are shown as functions of the temperature and the average group number (AGN) for the alloy. The diagram shows that the close-packed hexagonal phases are confined to a fairly definite range of AGN values

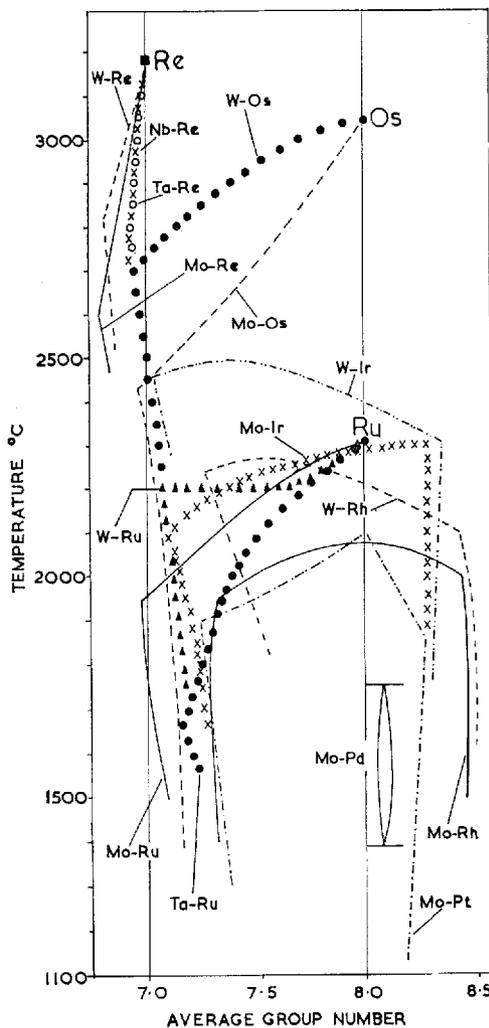
form of the equilibrium diagram (Fig. 9) does not suggest this. It is to be noted that the melting point of BePd (1465°C) is distinctly lower than that of AlPd (1645°C) where the equilibrium diagram undoubtedly resembles that of Al-Ni and filling of the d shell is occurring.

Group Number Principles

We may now consider the alloys of the palladium and platinum groups of metals with some of the preceding transition elements. Here the recent developments of alloy chemistry have shown the existence of the following types of structure:

b.c.c. σ χ c.p.h. f.c.c.

If we draw the equilibrium diagrams with the transition metal (of Groups V to VIII) of lower atomic number on the left-hand side, we find that, on proceeding from left to right, the phases appear in the above order. In any one binary system one or more of the above phases is always absent, but for the remaining phases the above order is retained. Since the valencies of transition metals are in dispute, it is convenient to refer to the Average Group Number (AGN) of an alloy, rather than to its electron concentration. For this purpose, Group Numbers of 8, 9 and 10 are allotted to the elements of Groups VIIIA, VIIIB and VIIIC respectively. Thus, an equiatomic alloy of Rh and Pd has an AGN value of 9.5, and equilibrium diagrams can be drawn in terms of AGN values. We thus find that, to a rough approximation, the above phases occur over characteristic ranges of AGN values. Fig. 10 shows the composition limit (in AGN values) of the solid solutions of various



elements in Ru, Re and Os and of the intermediate close-packed hexagonal phases which are formed in systems such as Mo-Rh. The tendency for these phases to be restricted to a definite range of AGN values is very striking. If all the electrons outside the rare-gas shell are counted, the AGN value is the same as the electron concentration, and it is clear that, in these alloys, we have the same kind of effect that is formed in connection with the well-known electron compounds of the β -brass or γ -brass types.

Just as the limits of the terminal Cu-rich and Ag-rich solid solutions in alloys with the B sub-group element occur at a roughly

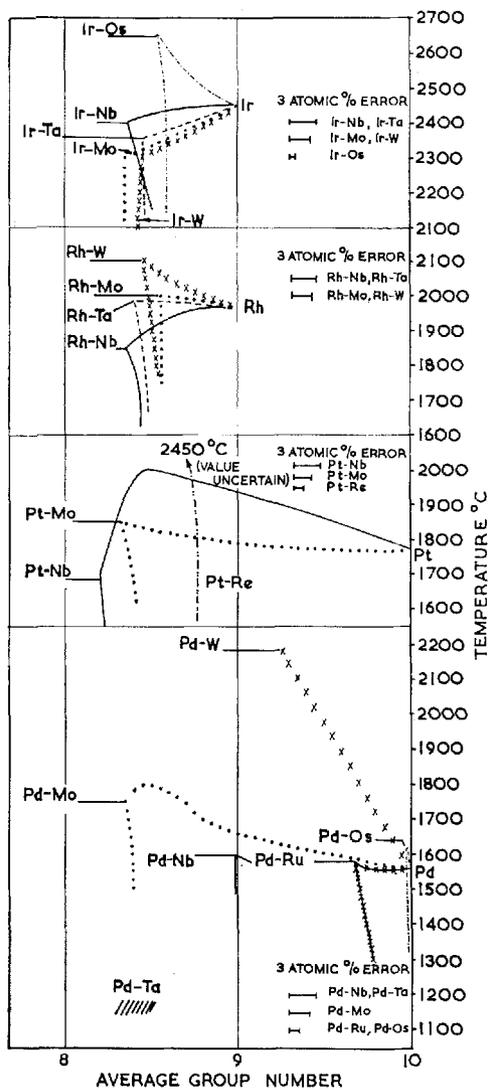


Fig. 11 In this figure the limits of terminal solid solutions in the face-centred cubic metals Ir, Rh, Pt and Pd are shown as functions of the temperature and the AGN values of the alloys concerned

correspond to the electron concentration principles of the Cu-Zn and Cu-Ga types of system.

These principles apply to the alloys of the later transition elements of the second and third long periods, irrespective of whether the two elements are from the same (e.g. Mo-Ru) or different (e.g. Mo-Ir) periods. They do not apply to alloys of elements from the first long period with those of the later periods because the size factors are here considerable. In alloys of the first transition series among themselves (e.g. Cr-Co), there is no longer a clear-cut relation between AGN values and the composition stability limits of the different structures, and AGN relations are seen only occasionally.

For elements from the second and third transition series, the AGN kinds of relation are found for elements separated by 2, 3 or 4 places in the Periodic Table. In some cases the tendency to complete the $(nd)^{10}$ sub-group introduces complications. Thus, Mo is freely soluble in Pd, and the solubility limit obeys the AGN principle referred to above. But, at the other side of the Mo-Pd equilibrium diagram, only about 8 atomic per cent Pd dissolve in molybdenum, and the solid solubility limit is at a lower AGN value than those for the solid solutions of Ru and Rh which obey an AGN principle. Here it seems that in Pd, electrons have entered atomic $4d$ orbitals to such an extent that the Pd atom cannot give electrons with the high proportion of d function required by Mo, because, once an orbital has become atomic, it is no longer available for bonding. There is, however, no corresponding restriction on the entry of Mo atoms into the Pd lattice, and so the wide solid solution can be understood.

constant electron concentration, so the face-centred cubic solid solutions in Pd, Pt and Rh formed by preceding transition metals tend to extend backwards to a characteristic AGN value which is about 8.4. This is shown in Fig. 11, and although there are exceptions, the general tendency is clear.

Until recently it was thought that electron concentration principles were confined to alloys with the B sub-group metals, but the work of the last 10 to 15 years has established the existence of the above AGN principles for the transition metal alloys, which clearly