Intermetallic Compounds of the Platinum Group Metals

SELECTED MATERIALS AND THEIR PROPERTIES

By I. R. McGill

Group Research Centre, Johnson Matthey & Co Limited

Many of the platinum group inter-metallic compounds possess unique properties which may occur in most interesting combinations. This paper draws attention to a number of these and briefly describes some applications for them. It suggests that further study is required before a full appreciation can be made of their perhaps considerable potential for use in hostile environments.

The search for new high temperature materials has gained increasing impetus over the last ten years. Greater demands are being placed on existing materials as the environmental conditions under which they must operate become increasingly severe. In particular the trend towards optimising performance and efficiency in modern gas turbines requires the development of high strength materials with structural stability and corrosion resistance at temperatures in excess of 1000°C. With few exceptions the desire for higher creep rupture strength linked to better corrosion resistance cannot be economically fulfilled by the use of any single material. Greater emphasis has therefore been placed on the development of protective coating systems which are compatible with new generation high strength materials and offer suitable corrosion protection at operating temperatures. Already the platinum group metals, and in particular the platinum aluminides, have contributed towards advances in coating technology.

The demand for high purity single crystals of mixed refractory oxides is rapidly increasing. Consequently, the choice of suitable non-reactive container materials becomes more selective. At temperatures around 2000°C iridium and rhodium are obvious choices, although are more often used under an atmosphere of nitrogen to minimise precious metal loss. In terms of thermodynamic stability and resistance to environmental attack, a number of the platinum group intermetallics offer exciting alternatives to the present range of crucible materials.

From an extensive survey by Paine et al [1] in 1960 covering 798 binary metal systems, only 95 were shown to either contain or expected to contain intermetallic compounds with high temperature ranges of stability. Only two systems containing platinum group metals were studied with respect to high temperature oxidation resistance, namely beryllium–platinum and beryllium-palladium. As a result of the unexpected volume expansion of the intermetallics during isothermal oxidation tests, experimental work on these systems was discontinued. It was unfortunate that other precious metal intermetallics were not considered. The following text gives some insight into the current and potential uses of intermetallics of the precious metals and is based on theoretical prediction supported by a selection of published experimental data.

The extraodinary stability of intermetallic compounds formed by combination of the

platinum group metals with elements from the left of the $3d$, $4d$ and $5d$ transition series has been satisfactorily explained by the Engel-Brewer approach to metallic bonding. It would be appropriate, therefore, to summarise briefly the basis and implications of the Engel-Brewer correlation before considering a selection of published data on the stability and high temperature properties of a number of platinum group intermetallics.

A Basis For Prediction

In general the high melting points of intermediate phases in binary alloys of the transition elements can be explained on the basis of availability of unpaired s, p and d bonding electrons. Although s and p electrons do contribute to bonding their concentration and ratio have more influence on long range order and crystal symmetry. The d electrons, in transition metal alloys are, however, directly responsible for the degree of metallic bonding and as such their distribution affects bonding capacity. Elements to the left of and including rhenium and technetium in the $4d$ and $5d$ transition series make use of all their valence electrons for bonding as their electron configurations are not limited by the Pauli exclusion principle. Optimisation of d electron bonding is obtained for elements with the d^5 configuration and is clearly reflected by the melting points of Group VI elements, molybdenum and tungsten. The effect of resonance coupling of unpaired d electrons on atomic bond strength is reflected by a lowering of melting point of the elements from ruthenium to palladium and osmium to platinum. Similarly, the general effectiveness of d electron bonding increases from the first to third transition series. The d electrons, therefore, ultimately dictate thermodynamic stability and in this sense are of more concern to the metallurgist as a means of predicting the degree of transition metal interaction and the potential existence of high temperature materials in a number of selected alloy systems.

The genesis of such a prediction must,

therefore, be based on attaining the right combination of transition elements such that d orbital overlap can be maximised. This condition can be fulfilled by the interaction of suitable electron-deficient and electron-rich elements. The position of the platinum group metals in the $4d$ and $5d$ transition series is most appropriate as their electron configuration and in particular d orbital structure make them primary source electron donors. The choice of electron acceptor can therefore be made from the transition elements of Groups V to III.

A simple illustration of the Engel-Brewer concept can be made by comparing the melting or decomposition temperatures of the compounds AIr_3, where A is a transition element taken from Group III or IV. This is shown in the Table.

Intermetallics and Their Application

Generally high stability compounds of the platinum group metals have received little attention, reference only being made to them as prime examples of the Engel-Brewer approach to metallic bonding. However, their stability and high melting or decomposition temperatures make them attractive materials for use in demanding environments. To limit the scope of transition metal combinations with the platinum group metals, only those elements from Groups IVB and VB will be considered with occasional reference to other combinations worthy of mention.

A general lack of ductility restricts the use of these materials for structural components, although a number of exceptions have been reported in the literature. In particular a number of isostructural phases with narrow ranges of compositional stability in the systems of niobium and tantalum with iridium and rhodium are known to have somewhat higher degrees of ductility than would normally be expected of intermetallic compounds.

The constitution of the tantalum-iridium system was first reported by Ferguson et al (2)

An Indication of the High Temperature Stability of Some Platinum Group Intermetallics Resulting from Predictions Made by the Engel-Brewer Concept				
Transition Series	Group III		Group IV	
	Compound	Melting Point °C	Compound	Melting Point °C
3d	TiIr$_3$	2115	VIr$_3$	2100*
4d	ZrIr$_3$	—	NbIr$_3$	2435
5d	HfIr$_3$	2470	TaIr$_3$	2450

* decomposition temperature

in 1963 from which confirmation was then made on a number of terminal solid solutions and intermediate compounds. The iridium-rich compound α–TaIr$_3$ melts congruently at 2450°C. Three other phases γ, α$_1$ and α$_2$ were also reported all of which are stable up to at least 1860°C. The phase α$_1$, nominally TaIr, decomposes peritectically at 2120°C and shows a respectable degree of ductility and toughness. The tantalum-rhodium system (3) shows close resemblance to the tantalum–iridium system and similar properties were recorded for α$_1$ (TaRh), although no explanation could be given. The compound TaRh decomposes peritectoidally at 1860°C. Ritter et al (4) reported the constitution of the niobium–rhodium system in 1964 and it was used to form the basis for a comparative evaluation of the intermediate phases of the related systems tantalum–iridium and tantalum–rhodium. Although a number of these phases were reported to be hard but ductile, none had stability above 1430°C. The isostructural phase α$_2$ in the niobium-iridium system is known to have similar mechanical properties to the α$_1$ phase in the tantalum–rhodium and tantalum–iridium systems.

A measurable degree of ductility and high stability are obviously two criteria which have some relevant importance to high temperature coating technology. However, the improvement in oxidation resistance of the refractory elements niobium and tantalum at temperatures above 1000°C by alloying with a variety of suitable elements has proved to be somewhat ineffective. Single phase α–Nb containing 5 atomic per cent iridium shows only a marginal improvement over pure niobium.

Although further alloying with elements such as tungsten, titanium and nickel might well be foreseen, the interesting combination of strength, ductility and high decomposition temperatures of a number of alloys of niobium and tantalum with the platinum group metals are such as to warrant further attention.

Of the many and varied coating methods developed for high temperature corrosion protection of nickel and cobalt-based alloys, pack aluminising remains one of the most economical and convenient processes. The mode of degradation of aluminide coatings is well understood and has prompted the development of superior coatings containing precious metal diffusion barriers (5–9). There still remains some controversy as to the mechanism by which elements such as platinum and rhodium can effectively increase the durability of conventional aluminide structures. The stability and oxidation resistance of the platinum and rhodium aluminides is, however, an important consideration. Figure 1 shows a typical platinum-aluminised
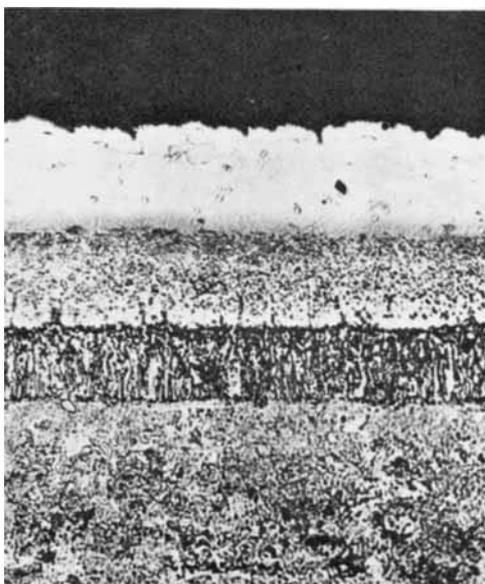
Fig. 1 A typical platinum-aluminised structure is shown in the photomicrograph. The diffusion zone consists basically of a platinum-rich surface layer, an intermediate nickel-rich layer and, at the diffusion zone/substrate interface, a layer which has a more characteristic aluminised structure

structure while the type of component which could benefit from this coating process is shown in Figure 2.

Precious metals are now being considered as beneficial additions to CoCrAlY and NiCrAlY clad coatings. Yttrium, hafnium and the rare earths have been used for some time in these protection systems and are known to create fine dispersions of inert oxides which improve scale adherence by pinning mechanisms. The addition of platinum and/or rhodium to the MCrAlY compositions where M is cobalt, nickel or iron, may well contribute to this mechanism by the formation of discrete intermetallic particles at the protective oxide/coating interface. As yet there seems to be no experimental evidence to corroborate this particular theory although work has been conducted on CoCrAlY coatings which shows that the presence of platinum can have a substantial effect upon the adherence of alumina scales (10, 11).

Some of the highest melting point compounds as predicted by the Engel-Brewer theory are those which combine a platinum group metal, in particular platinum or iridium with zirconium and hafnium. Holcombe (12) has suggested that the compound $HfPt_3$ may be used for containing reactive oxides. More recent work by Ficalora et al (13) on both $HfPt_3$ and $ZrPt_3$ showed no deterioration when oxidised in air at $1000°C$ for 5 hours. Fine dispersions of $ZrPt_3$ and $ZrRh_3$ in rhodium–platinum alloys are thought to
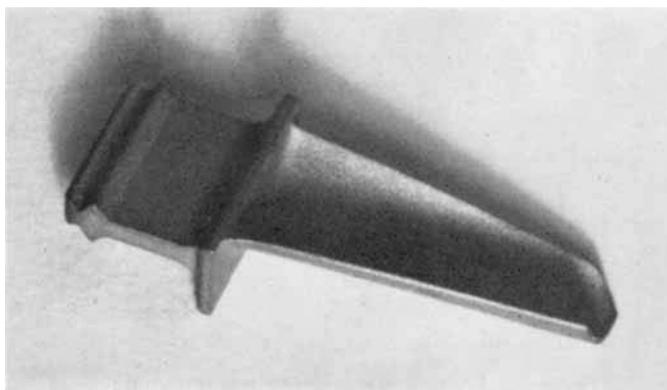

Fig. 2 High temperature applications are one of the more obvious uses for the intermetallic compounds of the platinum group metals

improve significantly high temperature creep strength (14). Obviously there is scope for an improvement in the high temperature mechanical properties of other alloy systems by platinum-group intermetallic dispersion strengthening. In particular it would be interesting to speculate whether small additions of zirconium or hafnium to the ductile phase compositions in the niobium–iridium (rhodium) and tantalum–iridium (rhodium) systems would: (a) improve oxidation resistance by the formation of complex mixed oxide scales of the type $Zr(Hf)O_2.Nb_2O_5$, having some plasticity and; (b) improve the overall creep properties of the alloys by selective dispersion of intermetallic compounds of the form $Zr(Hf)_x(PGM)_y$. Certainly Barrett and Corey (15) have suggested that fine dispersions of inert platinum group metals in oxides which have very high volume ratios would form a unique basis for a protection system.

Apart from exploiting these intermetallics as high temperature materials, a number of alternative applications can be suggested based on the prediction that low temperature ($<400°C$) properties are comparable with those of the compounds Mo_5Ru_3 and W_3Ru_2 (16, 17). These two compounds produced as thin films have hardness values comparable with sapphire and are virtually inert in the presence of toxic etchants up to temperatures around 550°C. Ficalora et al (13) reported similar results, although mainly qualitative, on the chemical inertness of $HfPt_3$ in various etchants. Equally attractive is the possible application of the platinum-group intermetallics as bearing and electrical contact materials utilising their high melting point and corrosion and wear resistant properties and as general wear resistant coatings for high quality cutting tools and extrusion or wire drawing dies.

It seems evident from the literature that the high temperature intermetallics of the platinum group metals are still somewhat novel and that their potential has yet to be fully appreciated.

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Palladium for Electrical Contacts

The use of electrodeposited palladium instead of gold on electrical contacts appears economically attractive at the present time. At the Annual Technical Conference of the Institute of Metal Finishing held recently at Windermere, in a session devoted to noble metals, this was one of the topics discussed.

In a paper, "High Speed Plating Solutions for Selective Electroplating", F. I. Nobel and R. T. Hill of Lea-Ronal dealt with the special plating solutions required to produce the desired results when plating both selectively and continuously. For palladium plating it has been established that proprietary solutions, at present being successfully used in barrel and rack plating operations to plate electrical contacts, can be modified for use in spot plating machines by increasing the metal content from about 8 to 10 grams per litre to 15 to 25 grams per litre. With the correct conditions 5 microns of sound bright palladium, as good as barrel plating, can be deposited in 15 seconds.