Borides, Silicides and Phosphides of the Platinum Metals

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This paper reviews some recent studies of the borides, silicides and phosphides of the platinum metals. These phases, especially those with a high metal content, have very similar properties. After some general information on the binary systems, brief comments are made on the preparation and properties of the intermediate phases while some features of their crystal chemistry are presented in more detail.

The binary systems of a platinum metal with one of the non-metals boron, silicon or phosphorus (Me-X in which Me=Ru, Rh, Pd, Os, Ir, Pt; X=B, Si, P) are characterised by a comparatively low eutectic temperature (1) which decreases with increasing atomic number of the metal within each transition period. As yet no accurate determinations have been made on the solid solubilities of the non-metals X in the metals Me. It appears however, that these solubilities are quite small. Many systems contain a large number of intermediate phases, most of which have a narrow homogeneity range. Well established phases are collected in the table on page 94. It should be pointed out that the real compositions of most of these phases have not been determined accurately and may deviate considerably from the given formulae which, when having whole numbers as subscripts, correspond to the ideal structural composition.

In addition to the phases included in the table (all of which have been characterised crystallographically) it has been reported that phases with the following approximate compositions exist (for references see reference 5): RhB_{2+}, $PdB_{\sim 0\cdot 7}$, $IrB_{\sim 0\cdot 7}$, $IrB_{\sim 2\cdot 0}$, $PtB_{\sim 0\cdot 7}$, $RuSi_{\sim 0\cdot 7}$, $RuSi_{\sim 1\cdot 5}$, $PdP_{\sim 0\cdot 2}$ and $PdP_{\sim 0\cdot 4}$.

These latter phases, however, have been very incompletely described. Some phases are reported to occur in several modifications. Thus, no less than three modifications of RhSi have been reported but it is not quite clarified whether all of these are true binary phases.

Preliminary experiments in our laboratory and elsewhere have shown that the phases reported are only a fraction of the very large number of intermediate phases in binary systems of a platinum metal with boron, silicon or phosphorus. In particular, the Pd-P system seems to be much more complicated than is indicated in Hansen's Handbook (5).

Preparation and Properties

The borides, silicides and phosphides of the platinum metals are easily prepared by direct reaction between the elements at elevated temperatures. Since this method permits good control of the composition of the samples it is extensively employed in fundamental research. Borides, silicides and phosphides are also formed in reactions between a platinum metal and various compounds of boron, silicon and phosphorus. Thus, silicides may form in reactions between a metal and the volatile oxide SiO (see for instance 13). Therefore, in high-temperature reactions involving platinum metals and their compounds great care should be taken in the use of ceramic tubes containing silica if contamination by silicides is to be avoided.

Intermediate Phases in Binary Me-X Systems

(Me = Ru, Rh, Pd, Os Ir, Pt; X = B, Si, P)

Borides (for additional references see ref. 2)			Silicides (see ref. 2)			Phosphides (for additional references, see ref. 5)		
Ru_7B_3	Rh_7B_3	Pd_3B	Ru_2Si	Rh_2Si	Pd_3Si	Ru_2P (12)	Rh_2P (7)	Pd_3P (10)
$Ru_{11}B_8$	$RhB_{\sim 1\cdot 1}$	Pd_5B_2	RuSi	Rh_5Si_3	Pd_2Si	RuP (6)	Rh_4P_3 (8)	PdP_2 (9)
$RuB_{\sim 1\cdot 0}$ (3,4)				Rh_3Si_{2+}	PdSi	RuP_2 (6)	RhP_2 (9)	PdP_3 (6)
$RuB_{\sim 1\cdot 5}$ (3,4)				RhSi *			RhP_3 (8)	
$RuB_{\sim 2\cdot 0}$ (3,4)								
$OsB_{\sim 1\cdot 0}$ (3,4)	$IrB_{\sim 1\cdot 1}$	PtB	OsSi	Ir_3Si	Pt_3Si	OsP_2 (6)	Ir_2P (7)	$PtP_{\sim 0\cdot 35}$*
$OsB_{\sim 2\cdot 0}$ (3,4)				Ir_2Si	Pt_2Si *		IrP_2 (9)	PtP_2 (11)
$OsB_{\sim 2+}$ (3,4)				Ir_3Si_2(h)	PtSi		IrP_3 (6)	
				IrSi				
				$IrSi_3$				

*There may be more than one phase (probably high- and low-temperature modifications) approximating to this composition

The available information regarding the chemical and physical properties of platinum metal borides, silicides and phosphides is very limited. The reported melting points of some of these phases have been collected in the table below. It may be assumed that the palladium and platinum phases have somewhat lower melting points than the corresponding phases of the other platinum metals. The reactions between a platinum metal and boron, silicon and phosphorus are exothermic but no systematic and accurate determinations of the heats of formation have as yet been made. Since the "affinity" of these non-metals is probably lower for the platinum metals than for the metals of the earlier transition groups, it may be assumed that the heat of formation of the platinum metal borides, silicides and phosphides is of the order of magnitude 10 kcal/g atom non-metal. Most of the phases of platinum metals with boron, silicon or phosphorus are chemically very inert. They are generally not attacked by concentrated acids or even by aqua regia. They have metallic lustre and, with the possible exception of some very metal-rich phases, they are hard and brittle. Thus, in their chemical and physical properties they are similar to the borides, silicides and phosphides of the other transition metals.

Crystal Chemistry

Like all borides, silicides and phosphides, those of the platinum metals are closely packed, with all atoms having high co-ordination numbers. The crystal structures, however, are considerably more complicated than those of the metallic elements. Borides, silicides and phosphides with a high platinum metal content show pronounced structural similarities, especially with regard to the co-ordination around the non-metal atoms. For example the three phases Pd_3B, Pd_3Si, and Pd_3P all possess the cementite (Fe_3C) structure.

Melting Points of Some Transition Metal Silicides and Phosphides

(All values quoted from Hansen (5))

Pd_2Si	1250°C	$PtSi_{\sim 0\cdot 4}$	~986°C *
PdSi	~1100°C	Pt_2Si	1100°C
		PtSi	1229°C
Rh_2P	>1500°C	Ir_2P	~1350°C
Pd_3P	~1047°C	$PtP_{\sim 0\cdot 35}$	590°C *
PdP_2	~1150°C		

*May melt incongruently

The borides of the platinum metals are closely related, and many phases crystallise in the same structure type. However, they differ structurally from the borides of the earlier transition group metals, particularly in the following two respects: first, some platinum metal borides (e.g. Pd_3B, Pd_5B_2, Ru_7B_3, Rh_7B_3) are structurally closely related to carbides while this does not apply to borides of metals in groups IVa, Va and VIa. Secondly, by comparison with the radius sum, the shortest distances between unlike atoms in platinum metal borides are, in general, considerably shorter than is the case for borides of the earlier transition group metals. Analogous observations can be made for silicides and phosphides.

The origin of the rather marked structural differences between borides, silicides and phosphides of the platinum metals, on the one hand, and the corresponding phases of the earlier transition group metals on the other, cannot be satisfactorily explained at present. Clearly, they are not solely dependent on differences in the radius ratio, but are intimately connected with the nature of chemical bonding in these compounds.

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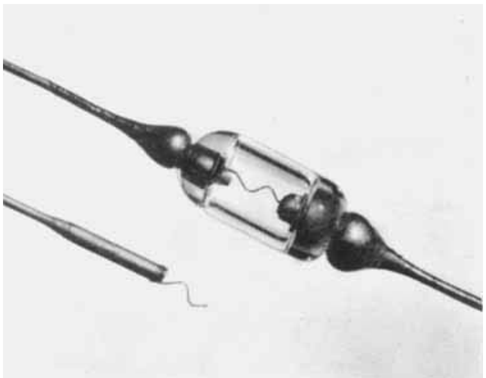
IRIDIUM-PLATINUM WIRE FOR DIODES

The point contact diode is still widely used – particularly in domestic radio and television receivers – because it is cheaper to manufacture than the newer junction types. It is a development of the "cat's whisker" detector used in the early days of broadcasting and consists of a small dice of single crystal germanium with a fine wire or "whisker" in contact with it.



Tungsten is widely used as this material, but the metal forms a stubborn oxide film on the surface. In order to overcome this, and so achieve the required performance of the device, the General Electric Company Limited decided to use 20 per cent iridium-platinum wire for their type GEX 34 diode.

This alloy, which is used in the form of wire ·004 inch in diameter, is hard enough to give the required pressure at the point of contact. In comparison with tungsten it is easier to form and the cutting and crimping tools require less maintenance. Moreover, unlike tungsten, the alloy is completely free from tarnish films.