Reactions between Some Alkali and Platinum Group Metals

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The present knowledge of reactions between the alkali metals, lithium, sodium, potassium and rubidium with the platinum group metals, platinum, palladium, rhodium, iridium, osmium and ruthenium, their reaction products, and the relevant binary phase diagrams, is surveyed. Information is included on the magnetic and electrical behaviour of some alloys, especially those with the higher platinum contents.

Although the alloying behaviour of the platinum group metals with the Group IB elements copper, silver and gold has been studied extensively, little attention has been given to their alloys with the Group IA, alkali, metals. To remedy this situation an investigation of these systems was started at the Forschungsinstitut für Edelmetalle und Metallchemie, and while this work has been in progress several publications have described the crystal structure of various intermediate phases that appear in these systems. Work by K. H. J. Buschow and J. H. N. Van Vucht (1, 12) and W. Bronger and B. Nacken (4, 8) is particularly relevant, and some of their data are included in Table 1.

During the preparation and investigation of these alloys difficulties arise due to the relatively low boiling points of the alkali metals, compared with the high melting temperatures of the platinum metals. For example these temperature differences range from 1330 to 1552°C for lithium-palladium to 688 to 2500°C for the rubidium-ruthenium combination. In addition, the chemical reactivity of the alkali metals increases with the heavier metals, but there is a decreasing tendency to form intermediate phases with platinum group metals. Thus at least eight phases are found in the lithium-palladium system compared with possibly one in the lithium-ruthenium system, and none in any of the systems containing potassium or rubidium. The reactivity of the alkali metals was manifest by the rapid corrosion of many of the alloys on exposure to air. Platinum or palladium alloys with less than 35 atomic per cent lithium could be handled in air without excessive oxidation, but at higher lithium concentrations powdery corrosion products, white to grey-black in colour, were formed. Platinum alloys were found to be more reactive than palladium ones. In general alloys of the heavier alkali metals tarnished more rapidly on exposure to air, even at the lowest alkali metal concentrations, forming a wet hydroxide layer.

Preparation and Investigation

Several methods were adopted for alloy preparation. These involved reacting mixtures of high purity elements under argon in the glove box illustrated in Figure 1. The general experimental procedures were as follows:

(i) With the arc furnace coupled directly to the glove box, palladium and platinum alloys with lithium were produced by arc melting on a water cooled copper hearth in a high purity argon atmosphere. The furnace charges weighed between 1 and 5 grams and consisted either of pressed tablets of lithium pieces and platinum group metal sponge or powder, or alternatively of small pieces of both elements. In the latter case only the platinum metal became molten, then reacted with the lithium.

Table I

Crystallographic Data

| Compound | Composition at.% palladium | Structure | | | Reference | Compound | Composition at.% platinum | Structure | | | Reference |
		Classification symbol (17)	Type	Lattice parameter Å				Classification symbol (17)	Type	Lattice parameter Å	
$LiPd_7$	~85–88	cF32	$MgPt_7$	a = 7.71–7.74	(2,5)	$LiPt_7$	~87.5–88	cF32	$MgPt_7$	a = 7.763–7.758	(7,10)
$LiPd_2$	~60–75	mP8	—	a = 5.35–5.41 b = 2.72–2.73 c = 7.65–7.67 β = 90–91.5	(6)	$LiPt_2$	~66–73	cF32	—	a = 7.678–7.693	(7,9)
$LiPd$	45.5–51.8	hP2	$LiRh$	a = 2.74–2.77 c = 4.13–4.28	(1,2,4)	$LiPt$	—	hP2	$LiRh$	a = 2.73 c = 4.23	(8)
Li_3Pd_2	39.5–41	cP2	CsCl?	a = 2.97	(1–4)						
Li_2Pd	—	hP3	AlB_2	a = 4.23 c = 2.73	(1–3)	Li_2Pt	—	hP3	AlB_2	a = 4.19 c = 2.66	(3,8)
Li_3Pd	—	cF16	BiF_3	a = 6.19	(1)	$Li_{15}Pt_4$?					
$Li_{15}Pd_4$	—	cI76	$Cu_{15}Si_4$	a = 10.69	(1,2)	Li_5Pt? Li_9Pt?					
Li_xPd 9 ≥ x ≥ 5	—	cF?		a = 19.01–19.35	(1)			Evidence by D.T.A. only, see Reference (7)			
$LiRh_3$		ol8	Ir_3Li	a = 2.659 b = 8.602 c = 4.657	(12)	Ir_3Li		ol8	Ir_3Li	a = 2.672–2.672 b = 8.693–8.697 c = 4.670–4.671	(12)
$LiRh$		hP2	$LiRh$	a = 2.649 c = 4.359	(11)	$IrLi$		hP2	$LiRh$	a = 2.649–2.651 c = 4.397–4.399	(12)
$NaPd_2$?	non cubic					$NaPt_2$		cF24	Cu_2Mg	a = 7.50	(9)

(ii) Sintering of specimens was undertaken in closed molybdenum or iron cylinders, sealed by arc welding under high purity argon. Such specimens consisted either of pressed tablets or of capped tubes of palladium or platinum which completely enclosed the alkali metal.

(iii) In differential thermal analyses, molten alkali metals were reacted directly with platinum metal powders enclosed in tantalum or stainless steel tubes. After the tubes, measuring 4 mm in diameter and 15 mm long, had been filled they were closed by flattening the ends which were then folded twice and again compressed.

The alloy samples were investigated by a variety of techniques including metallography, D.T.A., X-ray methods, and by magnetic and electrical measurements. Metallographic examination of prepared microsections was generally unsuccessful, since only the few low lithium content alloys of palladium and platinum which were stable in air gave informative results. X-ray powder diffraction photographs were taken using $Cu_{K\alpha}$ radiation. Despite attempts to inhibit the reaction by coating the powder samples with vacuum grease before they were removed from the glove box, by evacuating the body of the camera, or by attempting—unsuccessfully—to contain crushed samples in capillary tubes, it was not possible to investigate alloys containing high alkali metal concentrations without interference by the air.

For the determination of reactions, transformations and melting temperatures, D.T.A. was performed under a helium or argon atmosphere in the temperature range 50 to 1550°C, with heating and cooling rates of 5 to 10°C per minute. In addition to the normal signals, the start of the reaction that produces an intermediate phase is indicated by an exothermic signal during the first heating cycle. Problems encountered included reactions between the samples and the container materials, and the volatilisation of the alkali metals.

Measurements of magnetic susceptibility, and in some cases of its variation with temperature, were carried out in a Faraday-type

Fig. 1 Samples for examination were produced from alkali metals and platinum group metals of 99 and 99.9 atomic per cent purity, respectively. This argon filled glove box was used both for the preparation of arc melted samples and to enable the constituent elements to be sealed into tubes or cylinders prior to the reaction processes

balance in fields up to 1 tesla. Even though these measurements were made in a helium atmosphere, contact of the samples with air during mounting was unavoidable, and for this reason measurements made on sintered samples (tablets) with their larger surface area proved less reliable than those made on samples prepared by melting, or on the cylindrical diffusion samples (capped tubes). Electrical resistivity and electromotive force measurements were made on a number of deformable lithium-platinum alloys.

Experimental Results

The reactions of the alkali metals with those of the platinum group metals are summarised.

1. Reactions with Lithium

Mainly on the basis of D.T.A. measurements, a phase diagram has been established for the lithium-palladium system, shown here as Figure 2 (2), and a partial phase diagram for
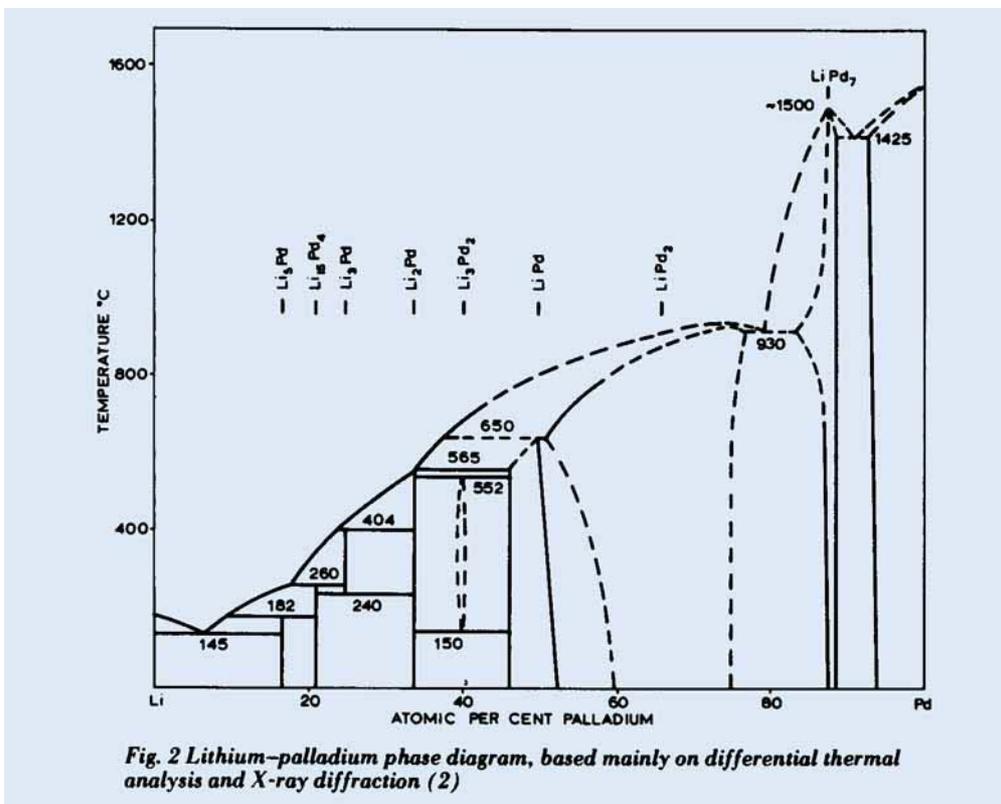
Fig. 2 Lithium–palladium phase diagram, based mainly on differential thermal analysis and X-ray diffraction (2)

lithium-platinum, Figure 3 (3). Crystallographic data for the phases present in these two systems is given in Table I, together with such information as is known for the other systems.

Rhodium and lithium react at about 300°C in a two-stage reaction. When the rhodium concentration is ⩾50 atomic per cent, the solidification of free lithium is not detected on cooling, and it is concluded that complete reaction has occurred.

Iridium and lithium react at 500 and 540°C. The reaction at the lower temperature is more vigorous for smaller iridium concentrations. Lithium again reacts completely when the concentration of the platinum metal is ⩾50 atomic per cent.

It is concluded that the only intermediate phases that exist in the two above systems are RhLi and Rh_3Li, and the analagous IrLi and Ir_3Li phases, respectively (11, 12).

At 450°C ruthenium and lithium react com-

pletely at concentrations above 70 atomic per cent ruthenium, in a slow single stage reaction. From this it is concluded that only one intermediate phase, near Ru_3Li, exists in the system.

Osmium does not react with lithium below 900°C. As the only thermal effects observed were those originating from pure lithium we expect no intermediate phases. At higher temperatures reactions with the container materials, or volatilisation of the alkali metals, started. No appreciable shift of the freezing point of the lithium was detected, indicating virtually no solid solubility.

2. Reactions with Sodium

Palladium and sodium react at 300°C, complete absorption of the sodium being observed at palladium concentrations above 60 atomic per cent, and the phase formed decomposes peritectically at 797 ± 5°C. The X-ray pattern of the phase, which is assumed to be Pd_2Na,

contains weak lines indicating a symmetry lower than cubic.

Platinum reacts with sodium at 300 to 370 and at 350 to 400°C. Sodium is completely used up in alloys containing more than 50 atomic per cent platinum. The reaction was more pronounced at the lower temperature when the platinum concentration was less than 50 atomic per cent. No melting points of alloys were observed below 900°C. We assume two phases of the approximate compositions PtNa and Pt_2Na, the latter being known to exist possibly as a cubic Laves phase. Its lattice constant was confirmed as a = 7.50 ± 0.01 Å (9). However, the seven lines of the diffraction pattern that were observed did not yield conclusive evidence that the phase is in fact a Laves phase, see Pt_2Li (7).

With the other platinum metals sodium does not react below 700°C. At higher temperatures sodium starts to escape from the reaction capsules, indicating no reduction in its vapour pressure.

Depending on the amount of palladium (platinum), reaction product and sodium present, interaction was found with tantalum containers above 750°C, and with stainless steel ones at approximately 1000°C. No indication of an appreciable solid solubility of the platinum metals in sodium was observed.

3. Reactions with Potassium

The platinum metals do not appear to react with potassium. The behaviour of the potassium suggests a fairly easy and rapid reaction with the tantalum and stainless steel containers, probably catalysed by small amounts of hydroxides. In mixtures with platinum and palladium, potassium is lost nearly quantitatively on heating to 800°C. In alloying experiments with the other platinum metals volatilisation was observed as low as 500°C. This may indicate a small solubility of potassium in palladium and platinum.

Magnetic and Electrical Properties

Magnetic measurements were made only on palladium and platinum. The samples were in the form of sintered compacts, melted spheres of approximately 5 mm diameter and, in the case of the heavier alkali metals, on cylindrical diffusion (capped tubes) samples heat treated for 1 week at 300 to 400°C. Susceptibility data are summarised in Table II. Most values are extrapolated from data obtained in two phase regions. Because of experimental difficulties during the preparation of lithium rich lithium-platinum alloys by melting, data in this composition range are relatively uncertain. For sodium, potassium and rubidium alloys measurements were made only on diffusion samples, where the alkali metal was initially encapsulated in a platinum metal cylinder (capped tube). The validity of the results obtained on the diffusion samples tended to be confirmed by the very small loss in weight during heat treatment, and by the fact that no free alkali metal was present after heating. Further confirmation was provided by chemical analyses, and it was concluded that the alkali metal had diffused completely into the surrounding platinum metal.

The diffusion method of sample preparation, at temperatures slightly above the reaction temperature found by D.T.A., was found to be necessary because all the heavier alkali metals evaporated during preliminary melting trials.
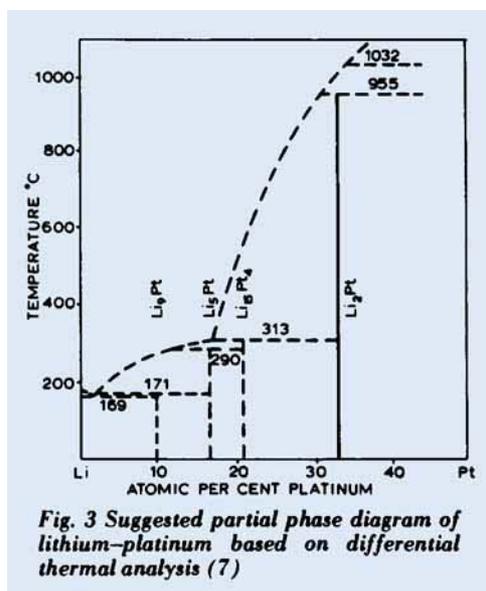

Fig. 3 Suggested partial phase diagram of lithium–platinum based on differential thermal analysis (7)

Table II				
Room Temperature Molar Susceptibilities of Palladium and Platinum Phases with Lithium and Sodium (μemu = 10^{-6}cm^3)				
	Phase	μemu/mole	Phase	μemu/mole
	Palladium	556	Platinum	189
Lithium	LiPd$_7$	245 − 188	LiPt$_7$	83 − 72
	LiPd$_2$	90 − 16	LiPt$_2$	15 − 11
	LiPd	4 − 0	LiPt	2 ± 3
	Li$_3$Pd$_2$	0 ± 2		
	Li$_2$Pd	0 − 24	Li$_2$Pt	2 ± 2
	Li$_{15}$Pd$_4$	6 ± 2	Li$_{15}$Pt$_4$	7 ± 3
	Li$_6$Pd	28 ± 2	Li$_6$Pt	11 ± 4
			Li$_9$Pt	16 ± 3
Sodium	NaPd$_2$	~240	NaPt$_2$	~50

Furthermore unacceptable uptake of molybdenum was found in potassium alloys sintered in direct contact with molybdenum capsules at temperatures above 600°C.

An estimate of the solid solubility of the alkali metals in platinum and palladium was obtained by a graphical method. This implies that the molar reduction of the susceptibility by dissolution of the heavier alkali metals is identical to that for lithium, that is by an amount typical for a single electron metal. In this way the solid solubility of sodium in palladium was estimated as 2 to 2.5 atomic per cent, and in platinum as about 1 atomic per

cent. Potassium dissolves in solid palladium to about 0.4 atomic per cent, and in platinum to less than 0.1 atomic per cent, the limit of detection, while rubidium has a solubility limit below 0.1 atomic per cent in both palladium and platinum. In fact there is no deviation in the susceptibilities measured from those expected from the additively computed values for a simple physical mixture.

The decrease of susceptibility with increasing alkali metal content observed in binary systems which form intermetallic compounds correlates with the decrease in the variation with temperature of the susceptibility (as measured for PdLi

Table III				
Resistivity of Some Platinum Rich Lithium-Platinum Alloys				
Composition, atomic per cent lithium	State	Resistivity, $\mu\Omega$cm		
		77 K	273 K	373 K
0.0	Homogeneous	1.84	9.85	13.7
0.6	,,	4.84	13.3	17.5
1.3	,,	6.97	16.1	20.5
1.6	,,	9.21	18.7	23.2
2.7	Heterogeneous	7.91	18.7	20.8
5.2	,,	6.89	15.5	19.4

and PtLi alloys (2, 7)) expected from the onset of pure Pauli spin magnetism in phases containing about 50 atomic per cent palladium or platinum.

Wires and strips made from thin sheets of PtLi (platinum-lithium) alloys containing up to 3 atomic per cent lithium were produced easily by cold working, and were used for electrical measurements. These were performed after a final heat-treatment of the samples, for 25 hours at 600°C, in vacuo. Between o and 100°C no deviation in resistivity from linearity was found, however, values at −196°C are lower than if extrapolated from linear behaviour. Data are given in Table III. Within the solubility range of 1.8 atomic per cent lithium, resistivity increases by $5\mu\Omega$ cm/at.%Li and its temperature coefficient of resistance is lowered by 1×10^{-3}/K/at.%Li. Corresponding values for a palladium-lithium sample containing 4.3 atomic per cent lithium are $\rho_{20} = 26\mu\Omega$ cm at 20°C and $\alpha_{100} = 18.7 \times 10^{-4}$/K. Measurements are still being made on this binary system, including the fairly broad $LiPd_2$ phase region. The thermoelectric power of the platinum-lithium alloys increases by 0.15mV/at.%Li between o and 100°C. Temperature variations for four alloys are shown in Figure 4.

Discussion

Bearing in mind the experimental difficulties mentioned, one can say that most probably no intermetallic phases occur in the binary systems of osmium with the alkali metals. No evidence was found for the existence of intermetallic phases in the corresponding systems of ruthenium, iridium or rhodium with alkali metals heavier than lithium, nor in platinum and palladium with those heavier than sodium. Mutual solid solubilities seem to be negligible in most cases, exceptions again being palladium and platinum. Solution of palladium or platinum in lithium leads to a reduction of the melting temperature by about 35 or 10°C, respectively. No similar effect could be found for any of the other systems examined. Palladium, and to a minor extent platinum also, dissolves small amounts of alkali metal, the
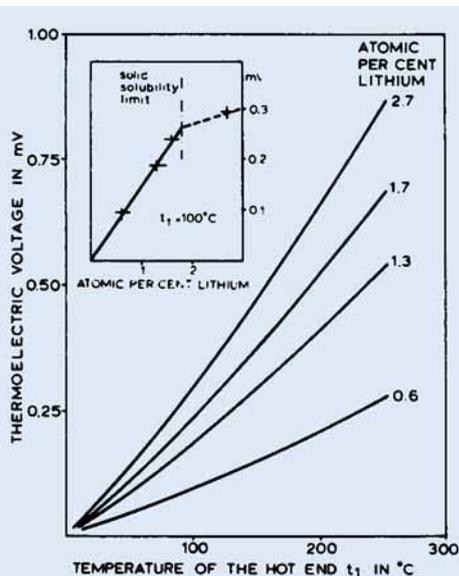

Fig. 4 *Thermoelectric voltages between lithium–platinum alloys and platinum (cold end at 0°C). The observed increase in the thermoelectric power is comparable with the one caused by copper*

amount decreasing from lithium to potassium as could be expected from their molar volumes. Magnetic susceptibilities of platinum and palladium are reduced by alloying with the alkali metals, which is typical for a monovalent metal. This is valid for solid solutions as well as for the intermediate phases. From the magnetic behaviour, no intermediate phases are expected for binaries containing potassium or rubidium.

Room temperature susceptibilities of platinum and palladium alloys with non-magnetic metals plotted against electron concentrations fall on the same curve (13, 15 and 16), see Figure 5. For the alloys containing more than 2 atomic per cent lithium there is an increasing deviation to smaller values near an electron concentration of 0.02, the lines for the lithium alloys following the initial slope up to Pt_7Li, or the solid solution limit for the lithium-palladium alloys (6 atomic per cent lithium). In terms of the Friedel theory of band structure modification in the host metal, when alloyed with electron donor metals (14), the smaller gradient of the reference curve is
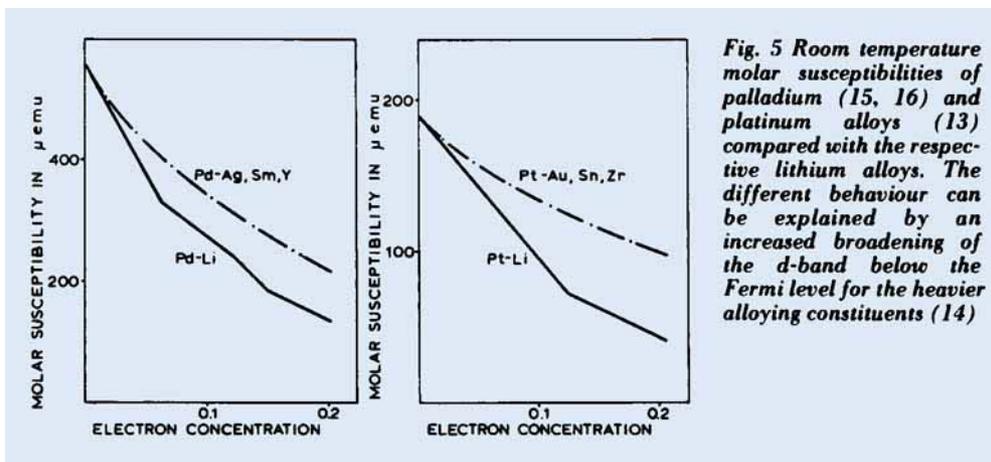
Fig. 5 Room temperature molar susceptibilities of palladium (15, 16) and platinum alloys (13) compared with the respective lithium alloys. The different behaviour can be explained by an increased broadening of the d-band below the Fermi level for the heavier alloying constituents (14)

understood as an increased broadening of the d-band below the Fermi level, with increasing content of solute metal. In lithium alloys, possibly the very low mass of the donor metal leads to a partial removal of the perturbation centres by the lattice vibrations at room temperature. As a result, the number of electrons necessary to fill the d-band remains small over a wide concentration range.

Structural determinations of the more reactive phases could be carried out by the method of Van Vucht and Buschow (1). Following pulverisation in an argon filled glove box their samples were loaded into special holders, having beryllium windows to permit X-ray diffraction measurements to be made under vacuum.

Sample preparation by chemical methods, for example the reaction of alkali hydrides with the platinum metals and—if necessary— dehydrogenation of the ternary hydrides formed (4, 8), probably yield samples which are more homogeneous than those produced by melting. This chemical method is particularly suitable in critical cases when the temperature interval between the boiling point of the alkali metal and the melting point of the platinum group metal is wide. On the other hand low temperature diffusion in sealed capsules also appears to be a promising method of preparation. Since the reactivity of intermetallic phases with high alkali metal concentrations is higher than that of the alkali metal alone, a dry inert atmosphere is essential during investigations.

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