Refining Secondary Iridium by an Oxidative Method

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The majority of investigators reporting on the mechanical properties of iridium have noted its high sensitivity to impurities. The elements which may have caused embrittlement are carbon, oxygen, and the refractory metals tungsten and rhenium. The segregation of these impurities to the grain boundaries in pure iridium has been considered to be the cause of brittleness in samples which failed after less than 5 per cent elongation at room temperature (1). The reduction in metallic impurities, and in carbon and oxygen, to a level of parts per million, allows iridium to be successfully used at temperatures of 1100 K and higher (2).

Iridium crucibles are subjected to repeated thermal cycles for long periods of time at high temperatures. These large iridium crucibles are used to grow single crystals of gallium-gadolinium-garnet and aluminium-yttrium-garnet. The resulting scrap material may be contaminated with platinum, palladium, rhodium, iron, tungsten, molybdenum, magnesium, nickel, silicon, calcium, copper, oxygen, carbon and oxides of aluminium, yttrium, gadolinium, gallium and zirconium. The scrap is likely to contain 95 to 98 weight per cent iridium. The conventional method of producing high purity iridium by chemical refining is extremely labour intensive, and results in significant loss of the metal (3).

A number of alternative methods of purification are known, and one of them is considered here. This process involves oxidation of the impurities during air melting of the scrap iridium in a periclase crucible (periclase contains, in weight per cent, 96 MgO, 1 Al_2O_3, 1.2 CaO, 1 Fe_2O_3 and 0.8 SiO_2). During this process the iridium exhibits extreme inactivity at the high temperatures used, 2715 to 3000 K (4). The reactions of the contaminating materials can be classified into two groups according to their characteristic interactions with oxygen in the air at the melting point of iridium, and at even higher temperatures:

1. Elements which form stable oxides: aluminium, yttrium, gadolinium, gallium, iron, tungsten, carbon, molybdenum, niobium, magnesium, silicon and zirconium.

2. Elements having oxides which dissociate below the melting temperature of iridium, namely: platinum, palladium, rhodium, nickel and copper.

Calculation of the Concentration Equilibrium of Impurity Elements

The possibility of removing the first group of elements from iridium was calculated from the Free Energy of these elements at 3000 K and pressure of 10^2 Pa, and from the resultant equilibrium concentrations of the impurities and the stable oxides. The equilibrium concentrations of the oxides of these elements with liquid iridium was determined from the equilibrium concentration of the impurities, and the final analysis of the liquid iridium. Melting the iridium in a periclase crucible formed a slag based on periclase which allowed better removal of most of the impurities. The calculations were performed on systems consisting of "iridium with impurities-oxygen in air", at temperatures of 2800 to 3000 K, approaching those of the ideal solutions (5). During the calculations, consideration was given to the condensation of the metal and slag phases and also to the migration, in the gas phase, of volatile oxides which have high partial pressures. Atomic adsorption analysis data show that concentrations of oxide impurities in the slag, which did not enter the periclase, were not more than 0.1 weight per cent. Partial

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Element	Initial concentration, at.%	Partial pressure of oxides at 3000 K, × 10² Pa	Equilibrium concentration of impurities in liquid iridium, at.%, in systems		Experimental contents of impurities, at.%
			Iridium-Air	Iridium-Argon	
Al*	0.2	0.813	1.6×10^{-3}	1.5×10^{-2}	4×10^{-4}
Y*	0.05	1.093	4.3×10^{-5}	n.r.	2.6×10^{-6}
Gd	0.15	0.533	2.9×10^{-5}	n.r.	2.4×10^{-5}
Zr*	0.05	0.187	2.6×10^{-5}	n.u.	4.6×10^{-5}
Si	0.01	289.3	1.5×10^{-3}	4×10^{-2}	8.9×10^{-4}
Nb	0.05	19.5	1.7×10^{-3}	n.u.	1.9×10^{-5}
Fe	0.8	169.3	8.6×10^{-2}	2.2×10^{-1}	1.2×10^{-1}
Ca	0.01	0.2	4×10^{-3}	n.r.	3.4×10^{-5}
W	1.5	45322	3.7×10^{-4}	n.u.	4.3×10^{-3}
Mo	0.3	19995	2×10^{-3}	n.u.	1.5×10^{-4}
Ga•	0.1	2266	1.5×10^{-2}	5×10^{-1}	7×10^{-3}
C	0.1	1013	9.1×10^{-5}	n.u.	n.o.
O	0.5		4.9×10^{-1}	n.u.	n.o.
Cu	0.06	58.65	n.u.	2.3×10^{-3}	2.2×10^{-3}
Ni	0.03	738.5	n.u.	8.5×10^{-3}	3.2×10^{-3}
Pd	0.01		n.u.	2.3×10^{-2}	2.2×10^{-2}
Mg	0.01	48	2.7×10^{-1}	4×10^{-4}	7×10^{-4}

* Al, Y, Gd, Zr, Ga-additive elements found in charge as oxides
n.u. — impurities could not be removed
n.o. — contents of elements were not determined
n.r. — equilibrium contents of additives were not calculated

pressures of gas forming oxides in the given temperature range have been studied previously (6). Calculated values of the maximum equilibrium concentrations of the impurities in iridium after induction-oxidation melting are given in the Table.
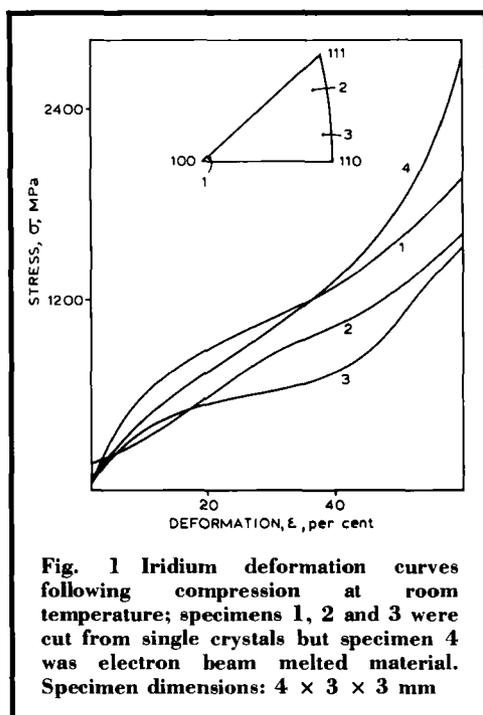
In addition, iridium purification could occur by evaporation of some impurities from the melt. These processes are limited by the fact that melting takes place at atmospheric pressure, but contaminants from both groups with high partial vapour pressures were removed from the iridium.

In previous work the systems "iridium with impurities-inert gas (argon)" were studied at temperatures of 2000 to 4000 K and at pressures of 9.8×10^{-2} to 1.3×10^{-8} MPa, and the evaporation of elements such as platinum, rhodium, aluminium, magnesium, tungsten, iron, nickel, copper, silicon, zirconium and carbon were described (7). Calculations were performed on the basis of the "maximum entropy" principle: entropies of the gaseous phase and of the components in the condensed state. The low concentrations of impurities allow calculation of ideal solutions. The results of the calculations are given in the above Table.

Experimental Studies of Impurity Behaviour

In order to compare theoretical and experimental data, a series of oxidation-induction melting experiments were performed on iridium scrap containing the impurities listed in the Table. Melting was carried out in air using a periclase crucible with porosity of less than 4 to 5 per cent. The iridium was maintained in

Fig. 1 Iridium deformation curves following compression at room temperature; specimens 1, 2 and 3 were cut from single crystals but specimen 4 was electron beam melted material. Specimen dimensions: 4 × 3 × 3 mm

the liquid state for a period of 30 minutes, at a temperature of around 3000 K. Before the metal was cooled in the crucible, 20 to 30 g samples of molten iridium were taken for control measurements. The compositions of the impurities were established by mass spectroscopy. The selected regimes allowed measurements to be made of impurities present in the iridium at concentrations of the order of $10^{-7} - 10^{-8}$ atomic per cent. The experimental data are also presented in the Table.

The experimental concentration values for aluminium, yttrium, gadolinium, zirconium, silicon, iron, molybdenum, gallium, copper, nickel, palladium and magnesium, agree well with the calculated data. On the basis of these results, it is possible to conclude that iridium refining can be carried out by the following methods:

1. The oxidation of impurities which form stable oxides during the induction-oxidation melting process. These, together with the oxides in the furnace charge, then enter into the slag. The removal of aluminium, yttrium, gadolinium, zirconium, silicon, niobium, iron and calcium from the iridium was carried out by this method.

2. The formation of oxides of the contaminants which have high partial pressure, such as tungsten, molybdenum, gallium, carbon, and which evaporated during melting.

3. The removal of impurities such as copper, nickel, palladium and magnesium which occurred due to evaporation because they have higher partial pressures than iridium.

For calcium and niobium, the level of purity obtained was higher than that calculated. This may be due to the formation of chemically stable oxides with MgO, resulting in a sharp fall in CaO and NbO activities in the slag and a decrease of calcium and niobium concentrations in the melt. The final concentration of tungsten was higher than the calculated value. This result shows that tungsten removal is dependent on the kinetics of the reaction for its removal from the melt. When air was introduced into the iridium melt the tungsten formed a volatile oxide and its removal was increased (8).

Discussion of the Results

The agreement of the calculated data with figures obtained experimentally showed that the method of calculation used, and the assumptions made, were correct. Effective removal of contaminants from iridium results from better contact of the melt with the periclase crucible, thus binding part of the oxides, and intensive mixing of the melt with the help of an electromagnetic field. However, during induction-oxidation melting platinum and rhodium, which have properties similar to those of iridium, were not removed from the iridium. Also only a partial reduction in the concentration of the impurities of iron, gallium, palladium, oxygen, copper and nickel occurred. These elements can be removed more effectively from iridium by electron-beam melting, after which the concentrations of platinum and rhodium decrease to $10^{-3} - 10^{-4}$ atomic per cent, and residual impurities to $10^{-4} - 10^{-5}$ atomic per cent. The metal impurities which are removed in this way from

iridium scrap have been picked-up during single crystal growth in crucibles and from iron-based apparatus used during the formation of these large crucibles.

After induction-oxidation melting iridium can be worked. The results of compression studies carried out at room temperature are given in Figure 1.

Samples cut from a coarse grained ingot produced by induction melting were also investigated. This material was cold worked into single crystals that were found to be strong, which may be due in some way to the increased concentration of elements such as oxygen and iron in the iridium.

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Protecting Tantalum by Platinum Implantation

Tantalum is a suitable material for use in corrosive environments, due to the formation of a dense highly resistant oxide film on its surface. In hot concentrated mineral acids, however, it is attacked and although the loss of material may be acceptable in some circumstances the associated electrochemical evolution of hydrogen can cause serious problems. Tantalum readily forms hydrides, which are brittle and therefore cause loss of mechanical strength which could, perhaps, result in component failure.

It is known that palladium and platinum can protect tantalum from embrittlement, it is also known that a titanium surface modified by ion implantation with an electrocatalytically active metal can be effective in reducing corrosion. Now a communication from the University of Heidelberg, Germany, reports the results of an investigation of tantalum following platinum ion implantation, and its effect on hydrogen embrittlement ("Electrocatalytic Protection against Hydrogen Embrittlement of Tantalum in Strong Acids by Platinum Ion Implantation", W. Ensinger and G. K. Wolf, *Surf. Coat. Technol.*, 1992, **51**, (1–3), 41–44).

Even a very small amount of platinum implanted in the surface of tantalum has a significant influence on the embrittlement by hydrogen, as determined by a mechanical bend test. Both the amount of platinum implanted, and the rate at which it was implanted had an effect on sample life; a low charging current and a high implantation dose being the most effective conditions. Implanted platinum reduces hydrogen adsorption electrochemically, it also decreases the entire corrosion process, including the cathodic hydrogen evolution reaction, and is effective for a long time in extremely corrosive environments, even though only a shallow layer of tantalum is modified. Thus tantalum implanted with platinum has greater scope as a constructional or protective material.

The Chemistry of the Platinum Group Metals

The fifth International Conference on the Chemistry of the Platinum Group Metals will be held at the University of St. Andrews, Scotland, from 11th to 16th July, 1993. The conference will be organised by the Dalton Division of the Royal Society of Chemistry and provides an important opportunity for researchers in the field to meet and discuss recent developments.

Topics to be covered include applications of platinum group metals in organic synthesis, materials science, biology and medicine; their electrochemistry; advances in homogeneous catalysis, co-ordination chemistry, clusters, particles and the solid state.

People wishing to contribute or to receive further information should contact Dr. John F. Gibson, Secretary (Scientific), Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England.