Deformation of Zone-melted Iridium Single Crystals

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Iridium is known to possess properties which make its use at high temperatures attractive despite its high cost. It has a high melting point, 2443°C, and maintains its strength to high temperatures. In addition, it is extremely resistant to chemical attack and is consequently being increasingly used as a crucible material. Unfortunately iridium is very difficult to fabricate, showing a brittle behaviour characteristic of more complex structures and completely unexpected in a face-centred-cubic metal. Face-centred-cubic metals such as copper and aluminium are ductile even at low temperatures. The reason for this lack of ductility is not known but it has been suggested that it is due to impurities in the bulk or in grain boundaries. In the present investigation the characteristic deformation parameters of zone-refined iridium single crystals are compared with those of other face-centred-cubic metals. In addition a limited number of experiments on polycrystals are described and a comparison made with single crystal behaviour.

Experimental Details

Iridium was obtained in the form of 4 mm. diameter sintered and hot-swaged rods from Johnson Matthey & Co Limited. The initial purity of the material is shown below.

ppm by weight

Pt	Pd	Rh	Al	Ca	Cu	Fe	Pb	Mg	Si	Ag	Na
10	1	100	3	5	1	20	2	2	50	1	30

These rods were then purified and converted to single crystals by the electron beam vertical floating zone method (1). Each rod was zoned

eight times at 3.5 mm./min. in a vacuum of 10^{-5} to 5×10^{-6} torr, using a cathode current of 100 mA. The high thermal conductivity and high density of iridium made it important to limit the zone to a very small length. Before zoning, the rods were annealed at just under the melting point, usually for about 30 hours, until a vacuum better than 10^{-5} torr was attained.

The three stages of specimen preparation are illustrated in Fig. 1. Photograph (a) shows an as-received rod; photograph (b) shows a rod which has been zoned once at a speed of 3.5 mm./min. The trapped gas is, despite prolonged previous annealing, still released rapidly during zone melting so that the surface becomes uneven. Degassing has generally ceased after three passes, when the zone becomes more stable. Before the crystal can be used the unevenness must be smoothed out by zoning several times. During these zone passes the diameter of the crystal is measured with a travelling microscope which moves at the same speed as the cathode, and the diameter of the molten zone is adjusted by moving the upper chuck up or down. A final pass at a constant low speed of 1.2 mm./min. ensures uniform crystallisation conditions along the whole rod as seen in (c). The orientation did not change along the length of a rod by more than $\frac{1}{2}°$. Since the orientations obtained were in the centre of the standard stereographic triangle it was not necessary to use a seed crystal.

Spectrographic analyses of three adjacent sections of a typical zone-refined crystal showed only the following metallic impurities:

Ag	0.5 ppm	Mg	<1 ppm
Cu	<1 ppm	Si	<1 ppm

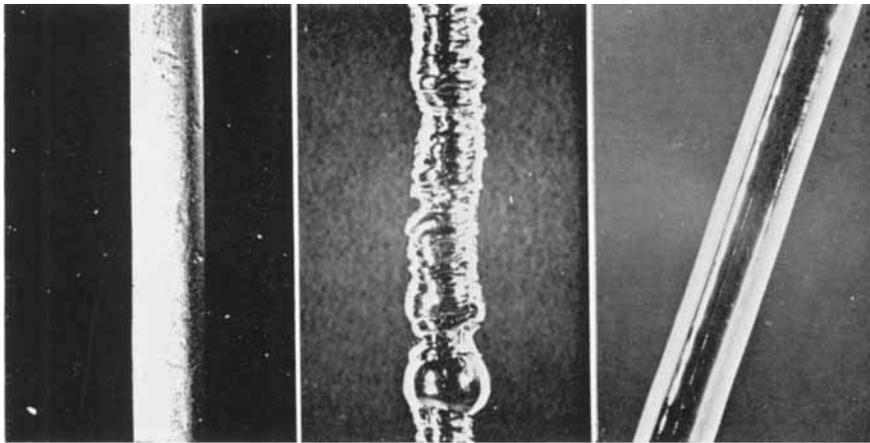*Now at Department of Materials Technology, University College of North Wales, Bangor

Fig. 1 Various stages in the production of a single crystal; (a) as received, (b) zoned once, (c) final crystal

Although tensile tests would have been preferable it was necessary to use compression tests because of the limited amount of material available. The reproducibility of compression tests is not as good as that of tensile tests particularly at high strains when the specimen deforms non-uniformly.

All experiments were carried out in an Instron Universal Testing Machine (Type TT-BML). The temperatures were obtained using oil or isopentane thermostats. A strain rate of 7.0×10^{-5} sec^{-1} was used.

The grown crystals were embedded in wax on a specially designed carrier and cut into lengths of about 15 mm. using a paraffin cooled, diamond impregnated wheel. The cutting machine permitted exactly parallel cuts to be made so that the end surfaces needed only to be polished lightly before the crystal was deformed.

It was assumed that the same slip systems operate for iridium as for other face-centred-cubic metals: $(111)\ <110>$. In a compression test the crystal axis moves towards the normal to the slip plane if the specimen is relatively short compared with its diameter (2). The relationships used to convert the load-extension curves to shear stress—shear strain curves were (3):

$$\text{Shear stress } \tau = \frac{P}{A_o} \left(\frac{l}{l_o}\right)^2 \sin \chi_o \cdot \cos \lambda \qquad (1)$$

$$\text{Shear strain } a = \frac{1}{\cos\lambda_o} \sqrt{\frac{\sin^2\chi_o}{\cos^2\lambda_o} + \frac{l_o^2}{l^2} - 1} - \frac{\sin\chi_o}{\cos\lambda_o} \qquad (2)$$

where P =load, A_o =original cross-sectional area, λ_o =initial angle between crystal axis and slip direction, λ =angle during deformation, χ_o initial angle between crystal axis and slip plane, l_o =initial length of specimen, $l =$ length during deformation.

At low strains the crystal maintained its cylindrical shape but at high strains friction at the platten crystal interface prevented deformation here so that only the middle of the crystal deformed and the crystal became barrel-shaped. At this point a compression test becomes unreliable. This difficulty prevented an evaluation of τ_{111} (T, $\dot{a}$) the stress at which dynamic recovery first takes place, and hence a calculation of γ, the stacking fault energy (4).

Deformation Results

Fig. 2 shows stress-strain curves of iridium single crystals of the orientation indicated, deformed at these different temperatures, 78, 273 and 473°K.

It is apparent that for all metals copper (5), silver (6), nickel (4) and iridium the stress-strain curves exhibit the same basic characteristics. An initial period of easy slide (low rate of work hardening) is followed by a period of rapid linear work hardening. The curves
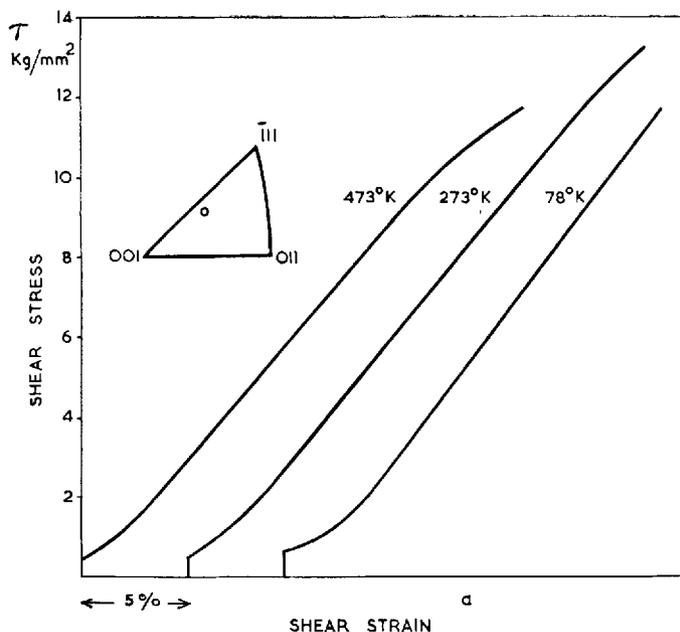
Effect of Annealing in Different Atmospheres

The effects of various gases on iridium at high temperatures were investigated by annealing single crystals in these gases and noting any change in the mechanical properties at room temperature. Nitrogen, air and argon were chosen, and the annealing treatment was twenty hours at 900 to 1000°C. The hardness change of such crystals is shown below:

Gas	Vickers Hardness (2kg load)
Argon	205 ± 5
Nitrogen	205 ± 10
Air	207 ± 5
As zoned	203 ± 5

The indentation, which was made on the cylindrical surface, measured about 0.1 to 0.15 mm. (diagonally). The scatter of

flatten off on onset of dynamic recovery. The major inaccuracy in the evaluation of the parameters was due to non-uniform diameter of the specimen along its length. Despite the smoothing out passes a variation of ± 4 per cent in the diameter could still be detected. From the stress-strain curves the following data were obtained: τ_o, critical resolved shear stress as a function of temperature and θ_{II}, the rate of work hardening in stage II, divided by the shear modulus G(T), also as a function of temperature; these data are plotted in Fig. 3. The values for the shear modulus were taken from Köster (7, 8).
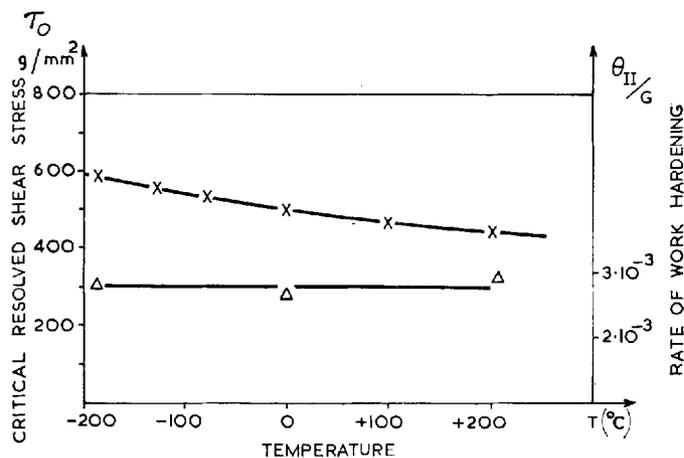

Fig. 3 The critical resolved shear stress (X), and the rate of work hardening θ_{II} divided by shear modulus G ($\triangle$), as a function of temperature for zone-refined iridium single crystals.

measurements on such a surface is higher than that for flat surfaces and consequently an average of five measurements was made. All the specimens after annealing remained shiny with the exception of the specimen annealed in air which showed a hard, brittle, blue-black oxide layer (probably IrO_2). This surface layer was very thin and did not seem to affect the bulk hardness. These annealed crystals were then deformed at the same rate as the vacuum prepared crystals. The stress-strain curves for vacuum prepared and atmosphere annealed single crystals were identical in all respects.

Recrystallised Specimens

The experiments described so far have all been undertaken on single crystals. Two techniques were used to produce poly-crystals suitable for compression testing:

(a) a deformed single crystal was cold-rolled to produce a rectangular rod and subsequently annealed in the electron bombardment furnace; the percentage reduction is estimated to be 30 per cent;

(b) a zoned rod was rotary swaged at about 1100°C in air to a smaller diameter (10 per cent reduction) and recrystallised in the electron bombardment furnace.

It would be expected that the second type of operation produced an impurer specimen than the first. The recrystallised specimens were coarse grained and several became single crystals despite the heavy deformation.

Normal stress-strain curves could be measured only up to the maximum permitted load of the Instron machine (Fig. 4). At this point a compression of 2 per cent had been attained. By using a hydraulic press a much larger load could be applied. The maximum deformation attained before cracking was 30 per cent. As can be seen the poly-crystalline iridium is also reasonably ductile and the yield stress $\sigma_0 = 2\tau_0$ is as low as can be expected considering the values obtained for single crystals (Fig. 2). There was no difference between the two types of poly-crystalline specimen.
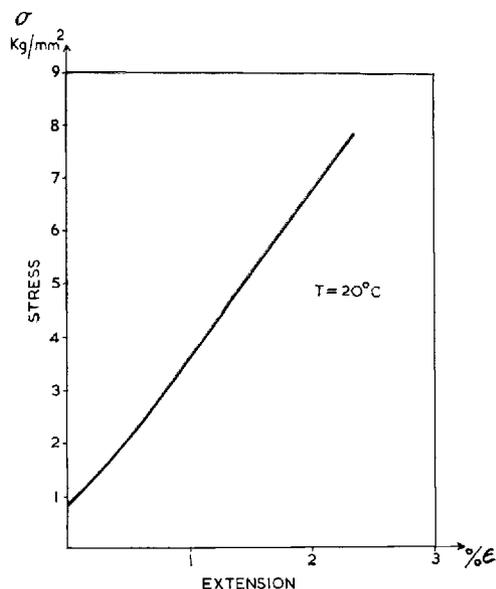

Fig. 4 Load-extension curves for recrystallised iridium

Discussion

The single crystals of iridium investigated here were ductile. Stress-strain curves over a wide range of temperature were similar to those of other face-centred-cubic metals. The only difference was that the absolute magnitude of the critical shear stress of iridium is somewhat larger than of, for example, copper, silver and gold. This can only partly be accounted for by the high shear modulus. The temperature dependence of the yield stress was similarly small. θ_{II}/G was $\approx 1/370$ and independent of temperature as observed for other face-centred-cubic metals. This strong similarity between iridium and other face-centred-cubic metals rules out the suggestion that in iridium other deformation mechanisms are operative. The annealing of single crystals in air and nitrogen in an attempt to contaminate the crystals and thus influence the mechanical properties produced no change in the properties. These impurities could, however, produce grain boundary weakness and consequently two procedures were used to produce polycrystals. The polycrystals were, however, equally ductile at room temperature whether or not swaged in air at

elevated temperature in the course of preparation. The polycrystals were not as ductile as the single crystals but withstood considerable deformation at low rates of deformation. At high rates of deformation they showed a greater tendency to brittle behaviour but in any case withstood rolling 30 per cent in one pass at a speed of 10 cm/sec. The fracture tended to be intercrystalline.

The impurities present are very much lower than those usually necessary to produce grain boundary weakness but it may be that the significant impurities are non-metallic or otherwise not easily determined.

In a similar investigation on rhodium, Calverley and Rhys (9) were able to deform zone refined single crystals by 90 per cent without intermediate anneal and yet the annealed polycrystalline wires could only be deformed to a very limited extent before inter-

crystalline fracture occurred. These authors were also forced to the conclusion that grain boundary segregation of unknown impurities is the cause of embrittlement.

The authors are indebted to Johnson Matthey & Co Limited for providing the iridium specimens and for carrying out the analyses.

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Ethylenediamine Complexes of Ruthenium

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So far as is known, no ethylenediamine complexes of ruthenium have been isolated. The reaction between ethylenediamine and chloro complexes of ruthenium such as ammonium chlororuthenite or ruthenium trichloride results in the formation of dark brown viscous solutions from which it seems impossible to separate any crystalline derivatives. A technique earlier discovered and used to prepare ammino derivatives of ruthenium II has now been successfully used to produce an ethylenediamine complex of ruthenium II, $[en_3Ru],ZnCl_4$. This compound should provide a suitable starting-point for the preparation of other ethylenediamine complexes, particularly of ruthenium III since in its reactions it appears to be analogous to the ammino complex $[(NH_3)_6Ru], ZnCl_4$.

In a Ph.D. Thesis (London University, 1955) Lever, and at the International Conference on Co-ordination Chemistry, London, 1959 (Special Publication of the Chemical Society, No. 13, 1959, 135–136) Lever and Powell described the preparation of hexam-

minoruthenium dichloride, $[(NH_3)_6Ru]Cl_2$ and the chlorozincate $[(NH_3)_6Ru],ZnCl_4$ by the reduction of ruthenium chloro complexes with zinc dust in ammoniacal ammonium chloride solution. It has now been shown that by cautiously adding zinc dust to a solution of ruthenium trichloride in 25 per cent ethylenediamine, boiling under reflux, filtering, cooling, and carefully acidifying the solution to pH 1–2 crystals of $[en_3Ru],ZnCl_4$ can be separated. (Found Ru 20.55, Zn 13.37, N 17.22, Cl 29.10, C 14.93, H 4.93 per cent; $[en_3Ru],ZnCl_4$ requires Ru 20.69, Zn 13.39, N 17.21, Cl 29.02, C 14.75, H 4.95 per cent).

It has, so far, not been possible to investigate fully the reactions of this compound but it has been found to behave similarly to the analogous ammino complex. Thus, when it is boiled with hydrochloric acid, hydrogen is evolved and a deep blue complex is formed. Mercuric chloride and chloroauric acid are both reduced indicating the powerful reducing properties of the compound. It is hoped that, in the future, these and other reactions will be studied and the products isolated and identified.