The Plastic Flow of Iridium

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The use of iridium as a crucible material has necessitated the development of technology for refining the metal to a high level of purity, and also the establishment of optimum conditions for fabricating the metal into finished products. The latter is of great importance insomuch as iridium cleaves under tension at room temperature but under compression it is deformed in a plastic manner. Manufacturers of iridium products have assumed that its poor malleability is due to the influence of impurities which are very difficult to remove under industrial conditions. Ultra high purity iridium, however, can be forged in much the same way as platinum (1).

At the present time the nature of the brittleness of iridium continues to be a puzzle (2). On the one hand, the cleavage which occurs in iridium is usually considered to be an inherent property, and the influence of impurities only a secondary factor (3). On the other hand, an alternative view of the problem exists in the literature (4); that is, the brittleness is considered to be due to some impurities which embrittle this plastic face-centred-cubic (f.c.c.) metal. For example, if iridium contains more than 10 ppm of carbon then it cracks when rolled; carbon-free iridium however, can be forged without cracking (2). Analysis of the deformation occurring in iridium single crystals (5, 6) and the observation of deformation tracks near cleavage cracks on crystal surfaces (8), have shown that the crystals were deformed by octahedral slip, as is usual for f.c.c. metals. The presence of both deformation and annealing twins in pure iridium and in iridium-0.3 per cent tungsten, however, may be considered as the result of an alternative mechanism, namely plastic flow (4, 8, 9). In this paper the relationships between the plastic deformation of iridium, its brittleness, the role of impurities in its mechanical behaviour, and the optimum regimes for processing iridium workpieces will all be discussed.

The process of manufacturing high purity plastic iridium and its alloys involves a combination of both oxidation-induction melting and electron beam melting. Such a procedure enables materials which are free of non-metallic and gaseous impurities to be obtained. Growing single crystals by electron beam zone melting is the final stage of purification. Large single crystal, or quasi single crystal, work pieces 100 to 150 mm in length and with diameters of 30 to 55 mm are usually produced. An example is shown in Figure 1. Orientated specimens have been cut from large industrial crystals of pure iridium, Oak Ridge alloy iridium-0.3 per cent tungsten, and OZM alloy iridium-3 per cent rhenium-2 per cent ruthenium by spark erosion techniques. Specimens of single crystals, 3 × 2 × 2 mm in size, have been compressed along <100>, <110> and <111> directions, at room temperature. Also, iridium wires have been prepared from single crystal pieces for tensile testing at high temperatures under vacuum.

Experimental Results

The plastic deformation of our iridium single crystals has been described previously (10). Under tensile conditions, strongly orientated anisotropy of both the yield strength and the hardening characteristics during deformation takes place along the "soft" <110> and "hard" <100> crystallographic directions. However, in the case of compression, anisotropy is absent. The deformation mechanism in iridium was investigated by metallographic and transmission electron microscopy, which confirmed the conclusion that iridium deformation occurs by octahedral slip of perfect dislocations having <110> Burgers vector.

A study of single crystal foils by transmission

Fig. 1 Electron beam zone melting is used during the final stage of purification of iridium single crystals. The crystals may have diameters of 30 to 55 mm and lengths of 100 to 150 mm
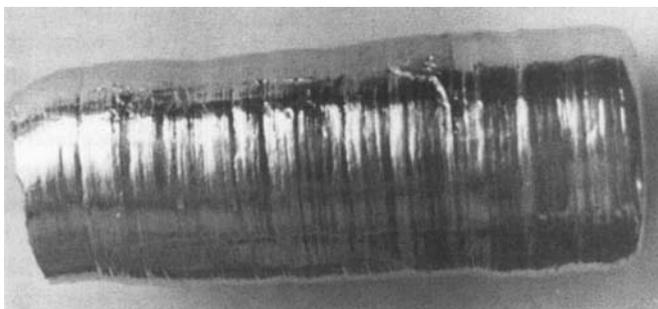
electron microscopy has shown that two types of dislocation structure may be distinguished. Single dislocations, dipoles and dislocation balls are usually observed only near to the edges of very thin foils (Figure 2a) and in thick, almost opaque, areas of foil containing high density dislocation nets (Figure 2b). No deformation, annealing and growth twins were observed in uncracked areas of the single crystal foils studied. Qualitatively, dislocation stuctures in iridium crystals were similar to those normally present in f.c.c. metals, but the density of the dislocations in the iridium was so high that it could only be compared with the density of dislocations in irradiated metals.

As has been reported previously (3), the fracture mode of iridium was not influenced by small concentrations of tungsten in the matrix. Compression tests on iridium alloys have shown that hardening impurities such as tungsten, rhenium and ruthenium result in an increase in yield strength and in hardening during deformation, by comparison with pure iridium, as is shown in Figure 3. The yield strength of the alloys is about 200 MPa, twice that of pure iridium. Metallic impurities do not embrittle iridium; and iridium and its alloys do not fail under compression at room temperature. Our iridium contained more metallic impurities than iridium provided by Johnson Matthey (1), however, in both cases the iridium was plastic and deformed satisfactorily. In contrast, even low concentrations of carbon resulted in the embrittlement of iridium crystals under the effects of compression at room temperature.

The plasticity of polycrystalline wires when tensile tested was found to depend on both the temperature at which the test was carried out and the diameter of the wire, as illustrated in Figure 4. Thus deformation prior to failure of thick wire (1.5 mm diameter) is increased from 3–5 per cent at room temperature to 25 per cent at 500°C. At higher temperatures the plasticity of wire of this thickness does not change.
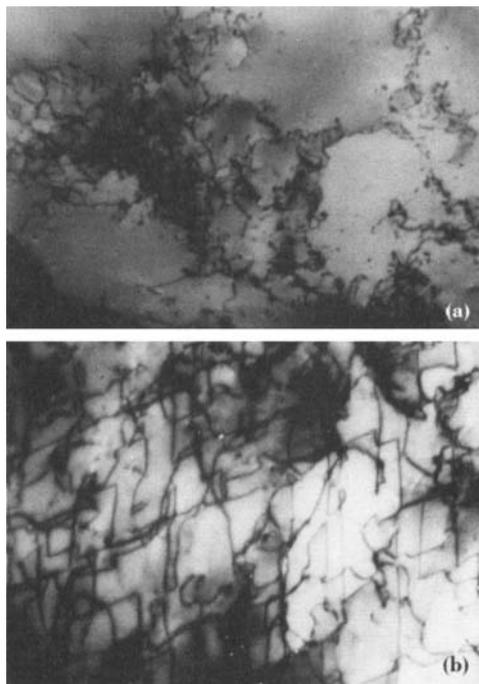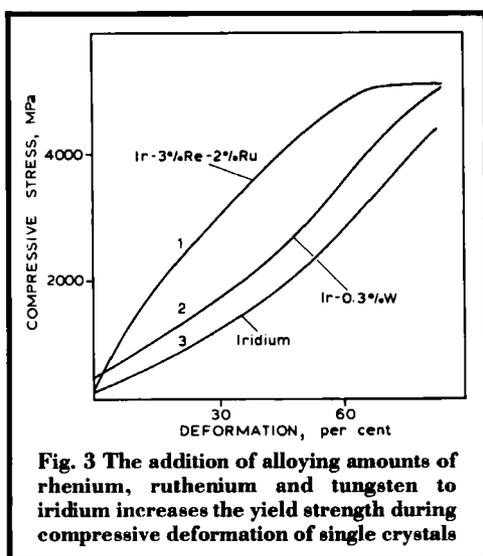

Fig. 2 The dislocation features observed on iridium thin foils: single dislocations, dipoles and dislocation balls only occur close to the edge of very thin foils (a), while high density dislocation nets occur in thicker parts (b)

Fig. 3 The addition of alloying amounts of rhenium, ruthenium and tungsten to iridium increases the yield strength during compressive deformation of single crystals

Similar behaviour of iridum at elevated temperatures has been reported in the literature (11). In the present case the increase in deformation prior to failure at 500°C can only be explained by the increasing dislocation mobility, as recrystallisation in iridium only commences at 1000°C. The plasticity of thin wire (0.3 mm diameter) is decreased from 10–15 per cent at room temperature to 3–5 per cent at 700°C; it then starts to increase to 15–20 per cent at a temperature of 1200°C, see Figure 4. These changes may be connected with the processes of recrystallisation. The increase of plasticity of iridium at these temperatures has been described elsewhere (8). The decreased deformation prior to failure in the temperature range 20 to 700°C cannot be regarded as an inherent feature of iridium insomuch as the phenomena which can cause this to happen are absent in pure f.c.c. metals. This means that the decrease in deformation is determined by external factors. The first of these is the influence of carbon which could have diffused into the iridium during the working of the metal into wire, when carbon is used as a lubricating material. Non-metallic impurities can enhance the dislocation mobility in metals and can therefore accelerate the processes of plastic flow, and lead to cleavage type fractures (7, 12). The second

external factor is the presence of a metal film which appears on the surface of the wire as a result of evaporation of the heating element while the test is carried out under vacuum. Consequently, this can embrittle the iridium and decrease the yield strength. A platinum film on iridium reduces its yield strength (13), a copper film has lowered the yield strength of iridium crystals, which were stretched along the <100> direction, from 100 MPa to only 10–20 MPa.

The degree of roughness of crystal surfaces has an influence on their mechanical properties when they are stretched along the <110> direction. Thus, non-polished crystals with a rectangular cross section cleaved after 15 to 20 per cent deformation at room temperature. A large number of small cracks covered their surfaces. After electropolishing the elasticity of such crystals increased to 30 to 40 per cent. In this case the number of surface cracks on the crystals was significantly reduced, and as a rule these occurred at the edges of the crystal. Electropolished crystals having elliptical sections cleaved after 60 per cent deformation; no surface cracks were observed on them. Crystals with a circular cross section were parted by cleavage after 80 per cent elongation (4).

Fig. 4 Tensile testing of polycrystalline iridium wires has shown the plasticity to depend on both the test temperature and the diameter of the specimens
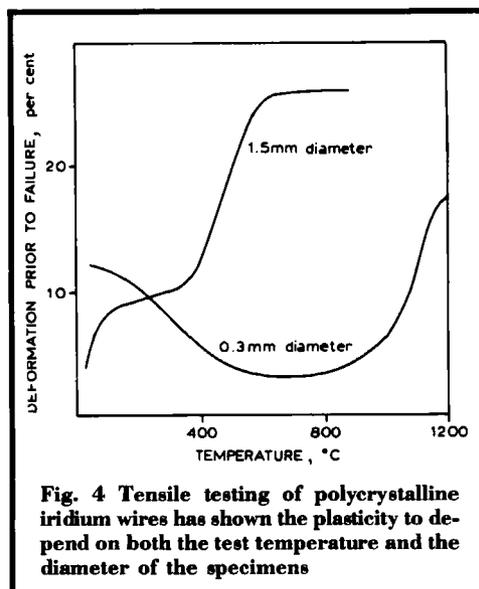
Similar behaviour has been noted for polycrystalline iridium; plane specimens failed without deformation when tensile tested at room temperature and circular wires cleaved after 10–20 per cent deformation.

Discussion

It has been pointed out that iridium single crystals were deformed at room temperature by octahedral slip of perfect dislocations with <110> Burgers vector, as is usual for f.c.c. metals, although some differences do exist between the different metals. Iridium has a very high yield strength compared with that of other pure f.c.c. metals. This may be connected with the low mobility of <110> dislocations. Additionally iridium is significantly hardened during deformation, which may be explained by its ability to accumulate high dislocation densities. Mechanical twinning can be operative at room temperature, but its contribution to flow at such temperatures is insignificant, thus the high hardening of iridium cannot be determined by twinning (4, 6). Anomalous elastic moduli of iridium (14, 15) may be the cause of the differences between iridium and the more usual f.c.c. metals, on the atomic level. This cannot be considered, however, as the direct cause of the tendency of iridium to fracture in a brittle manner, because thin foils of iridium single crystal separate in a similar way to thin foils of plastic aluminium (10).

Of course, the inclination of iridium to cleave of its own accord, without some relationship to its other mechanical properties, looks puzzling. Factors such as the high rate of work hardening during deformation, the large deformation that takes place prior to failure, and the separation of crystals only under the influence of tensile stresses produced during drawing and rolling, permit a very simple hypothesis to be formulated about the brittleness of iridium. It may be supposed that the plasticity of the iridium crystal has been completely exhausted during previous stages of deformation. Indeed, a large dislocation density accumulates in the material at the final stage of flow, thus requiring high stresses for further deformation. Under such conditions the stress concentrations at surface defects, such a notches, can reach the theoretical value needed to promote cleavage cracks. The deformation tracks near to cleavage cracks may be considered as visible indications of the changing stress conditions at these places. It appears to us that these tracks must be seen as twin lamellae because they appear under the influence of high stresses, when the formation of mechanical twins will be more justified than octahedral slip. It is also known that mechanical twinning can accompany the growth of cleavage cracks in body-centred-cubic (b.c.c.) metals at low temperatures, and the fracture mechanism maps for both iridium and b.c.c. metals are similar (11). The latter may be considered as another factor in support of twinning near to cleavage cracks in iridium. In addition, micro cracks in thin iridium foils produce partial dislocations, and as a result micro twin lamellae are formed nearby (10).

The choice between slip bands and twins is not important as they only accompany the growth of long cracks, and they are not the cause of brittle fracture. The failure mechanism for iridium crystals which has been proposed elsewhere (7) is unlikely to apply as the alternative slip is absent ahead of cleavage cracks in crystals which were stretched in the <110> direction, and deformation tracks are absent near to small cleavage cracks (10). In addition, the alternative slip mechanism ignores the large deformation that occurs prior to cleavage. The brittleness of iridium seems to be a consequence of the direct breaking of the atomic bonds at the tip of cracks. The similarity between the failure of iridium crystals and the fatigue fracture of aluminium has been reported (16); in both cases the materials were heavily deformed prior to failure.

Mechanical twinning which does not influence plastic flow in single crystals can contribute to the lower plasticity of iridium polycrystals. For example, brittle cracks can advance along twin lamellae in thin iridium-0.3 per cent tungsten foils. A transmission electron microscopy study of the morphology of iridium

films, which were evaporated in vacuum, has shown that the number of growth twins decreases with increasing crystallite sizes. This tendency results in the complete absence of twin lamellae in single crystal films (17). The analogous behaviour of twins in films of other materials has been observed, for example, in β-silicon carbide (18). Growth twins are dangerous features in foils as they can be the embryo for both deformation and annealing twins (19).

In conclusion, some recommendations can be formulated for the selection of the optimum conditions for processing iridium. The main condition is that the material must be kept free from non-metallic impurities during all stages of manufacture. Grain boundaries are danger points in work pieces, especially if the average grain size is of the order of some millimetres. Therefore it is desirable that single crystal or fine grained polycrystalline work pieces are used. The tensile stresses must be kept to a minimum level; in our case at the mechanical working stage, the large crystals were first forged and after that they were subjected to rolling. The optimal temperature range for processing iridium work pieces is 500 to 900°C as the material is plastic at these temperatures, but recrystallisation does not take place. Also, the processing of iridium in this temperature range can be undertaken in air as intensive oxidation only takes place at 1000°C and above. Processing at temperatures lower than the recrystallisation temperature prevents formation of additional danger points in work pieces such as new grain boundaries and twins.

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Ammonia Sensor Uses Platinum Films

There is a need to measure ammonia gas concentrations under clinical and industrial conditions, and for environmental protection.

Now researchers at the C.S.I.C., Spain, have developed a new ammonia gas sensor device based on Schottky platinum/n-gallium arsenide barrier diodes with discontinuous platinum films which have excellent sensitivity between room temperature and 150°C (L. M. Lechuga, A. Calle, D. Golmayo and F. Briones, *J. Appl. Phys.*, 1991, **70**, (6), 3348–3354).

The devices have a dual metallic configuration consisting of a thick deposited platinum circular dot and a thin porous platinum film evaporated over and outside the contact dot. Gas-induced modification in Schottky diode electrical properties are monitored by measuring changes in the diode capacitance as a function of time.

In synthetic air it was possible to measure ammonia concentrations above 150 ppm with response times lower than one minute.