

Brittle Intercrystalline Fracture in Iridium

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Refractory iridium has a unique position among metals due to its resistance to corrosion and its inclination to brittle fracture, the latter only occurring under tension. Since 1960 iridium has been the subject of much research, but this has not led to an understanding of its inclination to brittle fracture under load, although the problem of working iridium has been successfully solved. Grain boundary brittleness during mechanical treatment is the main problem with iridium, and is a continuing and important topic for academic discussion about iridium. Discussion of this problem, begun forty years ago, is continued here.

Due to its excellent high temperature strength and anticorrosive properties iridium is a unique material for use under extremely harsh conditions. For example, it is used for crucibles for growing oxide crystals and for nuclear fuel containers in thermoelectric generators for interplanetary missions (1).

However, in contrast to other face centred cubic (f.c.c.) metals, iridium displays poor workability even at elevated temperatures, and this substantially limits its industrial applications. Its poor workability is historically connected with contaminants that could not be completely removed from the iridium matrix by standard techniques (2). Indeed, the impurity-induced reduction of the cohesive strength of the grain boundary (GB), is the most probable cause for brittle intercrystalline fracture (BIF) in f.c.c. metals.

BIF makes commercial iridium practically unworkable (3), although high purity polycrystalline iridium can be forged like platinum (4). However, brittle intercrystalline cracks can appear on both pure and contaminated boundaries (5) and single crystals of iridium show higher plasticity, but cleave under tension (6, 7). This means that the tendency to BIF may be caused by singularities in the atomic structure of refractory iridium (3).

The problem of GB brittleness while processing iridium would be solved if the boundaries could be removed. However, grain structure does form in iridium containers during service, even if the metal did not contain GBs in its initial state. Therefore knowledge about the causes of BIF is

important for specifying optimal regimes for the manufacture and exploitation of iridium products. The aim of this paper is to discuss possible mechanisms of GB brittleness in iridium.

Physical Model of GB Brittleness in Iridium

It is well known that there are no inherent mechanisms which induce cleavage in f.c.c. metals (8). Iridium may be considered as an exception to this rule since the commercial metal behaves like a brittle crystal and meets some of the formal empirical criteria for cleavage (3, 9). Despite this, no rules can be applied to a metal which shows huge plasticity and simultaneous cleavage (although cleavage takes place in bulk crystals only under tension) (6, 7, 10).

The mechanical behaviour of single crystals of iridium can, however, be explained with the help of three suppositions – all of which have been confirmed by experiment:

- [1] octahedral slip is the dominant deformation mechanism,
- [2] the mobility of $\langle 110 \rangle$ dislocations in iridium is considerably lower than in other f.c.c. metals, and
- [3] other deformation mechanisms, such as mechanical twinning or non-octahedral slip, do not induce cleavage (11).

The strong anisotropy of the yield stress and work hardening under tension; the highly homogeneous distribution of plastic deformation in the sample; and the distinct slip bands from the

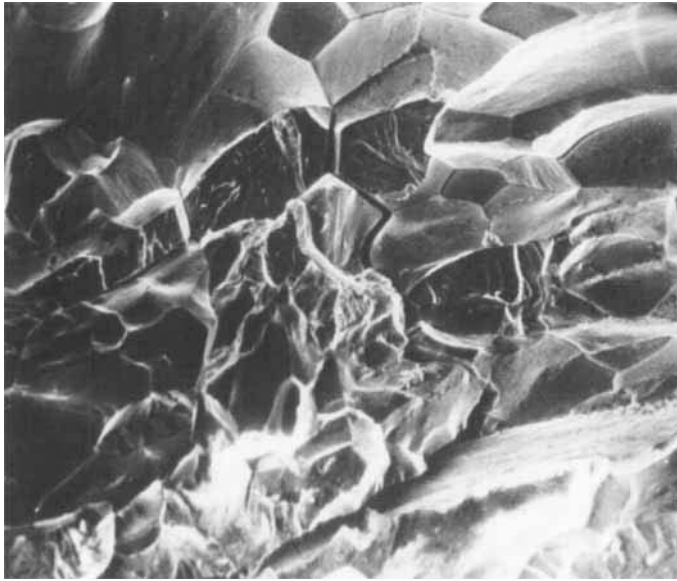


Fig. 1 SEM micrograph showing the fracture surface of fine grain Ir-3%Re-2%Ru alloy, where the ratio between the brittle intercrystalline fracture (BIF) and brittle transcrystalline fracture (BTF) regions is 3:1

Magnification ~ × 500

primary octahedral plane on the working surface allow us to state that at room temperature plasticity in the crystal is exhausted at the easy slip stage, when a 'net' becomes the only permitted dislocation configuration. Because dislocations have low mobility, the net cannot transform into small angle boundaries in spite of the large dislocation density in the iridium material. This is the reason why a neck does not form in iridium single crystals and their fracture surfaces look like brittle transcrystalline fracture (BTF) (3). It seems that the resource of plasticity for single crystal iridium is exhausted when the tensile stress reaches the level at which brittle cracks can appear. For example, iridium crystals fail at 400 to 500 MPa in tensile tests, but under compression, the critical level is not even reached at 2000 MPa (12).

Knowing that GBs have poor cohesive strength can be used as the starting point for discussing brittle fracture in polycrystalline iridium. In commercial metal, only BIF is observed on the fracture surface; this is due to either the segregation of impurities or the weak cohesive strength of the boundaries. The fracture mode of high purity polycrystalline iridium (and its alloys) is a mixture of BIF and BTF, see Figure 1. The proportion of BTF increases as failure proceeds.

For a fine grain aggregate, having maximum

plasticity, the ratio between BIF and BTF on the fracture surface is 3:1 (10, 13). Consequently, the cohesive strength of a pure GB could depend on either the type of boundary or its orientation in the field of the applied stress. The former would mean that there are two kinds of GBs (normal and brittle) in iridium, but TEM studies have shown no differences between GBs in iridium and any other f.c.c. metal (14). Therefore the hypothesis of a specific type of GB is not valid as the basis of a physical model. However, an inherent property, which is directly connected with interatomic forces, never depends on macroscopic parameters – such as mechanical stress.

Mixed brittle fracture appears when a critical crack has some flexibility to move either across the grains or along GBs. As mentioned before, BTF becomes possible only in strengthened crystal grains. Where BIF occurs, grains should also be hardened, since polycrystalline iridium fails after a preliminary deformation which is homogeneously distributed in the sample. Indeed, a neck never appears in the samples at room temperature and octahedral slip bands in the primary plane cover the majority of the grains.

This means that all the grains are filled by dislocation nets, where the dislocation density is considerably lower than in failed single crystals,

due to the difference in elongations prior to failure (2–6% for the grains, and 20–60% for the failed single crystals). The first value corresponds exactly to the contribution of the easy slip stage to the total plasticity of f.c.c. metal, while the second one is an anomalously high value (15).

In addition, the polycrystalline aggregate loses the ability to deform plastically at the easy slip stage, although each crystal grain still possesses a significant amount of plasticity. Failure happens when the dislocation net in the crystal grain tries to compel newly formed $\langle 110 \rangle$ dislocations to move through GBs – which they cannot do. As a result, stress on the GB reaches a critical value when BIF becomes possible.

Experiments have shown that the GB diffusion of impurities occurs in a narrow region around the boundary, where an increased concentration of vacancies is present. For normal f.c.c. metals the width of this so-called diffusion zone (DZ) is about 1–2 interatomic distances. In refractory tungsten, which is also inclined to BIF, the DZ reaches 5, while for iridium the DZ has been estimated as 10–15 interatomic distances (16). Naturally, such a defect-rich layer will hinder the movement of $\langle 110 \rangle$ dislocations through the GB and more so as their mobility is very slow. Both these factors make the anomalous width of the DZ the possible cause of GB brittleness in iridium. Clearly, the inclination to BIF is considerably reinforced if non-metallic impurities, such as carbon, oxygen and hydrogen, are situated within the DZ.

In brittle polycrystals, the majority of cracks appear on the GBs, since the number of boundaries is considerably higher than the number of notch-like defects on the surface. A crack advances along a GB as long as its path coincides with the normal-to-tensile component of the applied stress, but it has a tendency to leave the GB when this condition is not met. As a result, the crack will begin to move across the grain. However, it will always return if the main cleavage plane ($\{100\}$) does not have a suitable orientation.

Brittle transcrystalline cracks have been found in iridium single crystals after an elongation of 5–10 per cent, whereas deformation prior to failure can reach 20–40 per cent (17). This allows us to

state that the presence of transcrystalline cracks in iridium crystals does not mean they lose plasticity. Indeed, the transition of a crack from the GB to the grain may be considered as an effective way to arrest fracture in polycrystalline iridium. The good workability of fine grained work pieces confirms this supposition.

Discussion

A physical model is now proposed to explain brittle fracture in polycrystalline iridium. It is based on the concept of low mobility of the $\langle 110 \rangle$ dislocations and their hindered path on GBs. Iridium is a refractory metal, with a f.c.c. crystal structure, having strong interatomic bonds, but also octahedral slip as the dominant mechanism for deformation. The anomalously high yield stress is a result of strong interatomic bonds while octahedral slip causes the material to have high plasticity. There are no channels for the relaxation of the stress, such as transition from a dislocation net to a cellular structure or for dynamic recrystallisation in iridium at room temperature. Therefore, the ability of iridium single crystals to store high density dislocation nets allows practically unlimited growth of the deforming load – without failure.

An inclination to BTF appears when the tensile component of the applied stress reaches the level at which brittle cracks become possible. The opaque GBs for $\langle 110 \rangle$ dislocations are the stress concentrators in polycrystalline iridium, so that its total plastic deformation at room temperature is close to zero, in spite of the high plasticity of the crystal grain in the aggregate. The considerable width of the DZ in iridium is a possible reason why the GB does not let the $\langle 110 \rangle$ dislocations pass.

Higher temperatures lead to an increase in the mobility of the dislocation: the existing nets begin transforming into a cellular structure and some of the dislocations can pass through the boundaries. Thus, the level of stress on the boundaries is reduced, while the plasticity increases. Indeed, at 400–600°C the elongation prior to failure of fine grain iridium sharply increases (see Figure 2) and necking is observed in the samples; however this does not change the fracture mode (10). An X-ray

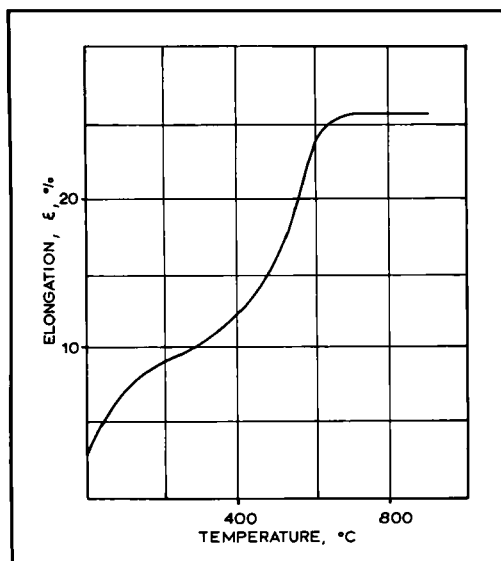


Fig. 2 Temperature dependence of elongation prior to failure for fine grain iridium wire

study of deformed iridium single crystals confirmed the supposition that the mobility of the dislocations starts to grow at 400°C, although recrystallisation only begins at 1000°C (18). At temperatures higher than 1000°C, iridium wire, where no GBs were detected, behaves like a ductile f.c.c. metal and exhibits necking (19), while the neck in a fine grain sample never thins to a point.

The difference in mechanical behaviour may be explained by the assumption that in the first case the high density nets transform to a cellular structure without slowing down on the boundaries (20). The existing GBs hinder this transformation and, therefore, necking to a point does not occur until the temperature is at least 2000°C (21). In addition, the transparency of GBs can increase if they have been doped by heavy metallic impurities, such as tungsten or thorium (22), which reduce the vacancy concentration in the DZ.

An optimised processing scheme for iridium should be able to produce a fine grained metal and be applicable for manufacturing iridium alloys. A few conditions are needed for such a scheme:

- The initial ingot should be free from deleterious contaminants, such as carbon, oxygen and hydrogen.
- From the point of view of the 'brittleness' of

iridium, the tensile stress when processing work pieces should be reduced as much as possible.

- Thermomechanical treatment should be performed at elevated temperatures, but the material should not be allowed to recrystallise under load and during intermediate annealing.

One pyrometallurgical scheme for refining iridium allows massive single crystals of high purity metal and some alloys to be grown* and these can be used as initial work pieces (12). However, this scheme cannot be used to manufacture single crystal ingots for modern iridium base materials, as the alloying elements are removed from the matrix during oxidation and electron-beam melting.

After treatment, the 'single crystalline' metal is in a severely hardened state and GBs are not present (shown by metallographic means). Sheet and rod processed in this way possess the required workability for manufacturing welded crucibles (with plane or stamped bases) and wires with diameters from a few millimetres down to 10⁻¹ mm. BIF is not a problem in this case, as there are no GBs in the material! Experience has shown that there is no strict requirement for the initial ingot to be a single crystal, because coarse-grain work pieces can also be forged without any problem. Thus, if the tensile component of the applied stress is minimal, GB brittleness can be ignored in polycrystalline iridium.

The Oak Ridge family of alloys (Ir-0.3 wt.% W) are iridium doped with tungsten, thorium and/or cerium (9, 13, 22). Tungsten gives a stable fine-grain structure, while the very small additions of exotic elements (such as Th or Ce) suppress the GB brittleness. In view of the fact that the anti-corrosion properties of iridium do not depend on the presence of small quantities of metallic impurities, this technology may be considered as another way for solving the 'iridium problem'.

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* Single crystal work pieces of Ir-3%Re-2%Ru and Ir-0.3%W have been grown.

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Low-Potential Detection of Hydrazine with Rhodium

Hydrazine has a wide variety of uses due to its highly reactive reducing ability. It is used as an intermediate for foaming agents for plastics, polymers, antioxidants, explosives, agricultural chemicals and pharmaceuticals. It finds use as an oxygen scavenger and a rocket fuel. Hydrazine is volatile, flammable and toxic. It also can be easily absorbed by the skin and contact with hydrazine irritates skin, eyes and the respiratory track. Hydrazine is considered to be a hazardous air pollutant and as such its maximum recommended value in trade effluents is 1 ppm.

There have been various methods used to detect and determine hydrazine, including spectrophotometric, optical chemical sensing, flow-injection, liquid chromatography and biosensors. However, the use of electroanalytical methods based on the direct oxidation of hydrazine at conventional electrodes has been hindered due to the relatively high overpotentials.

Now, researchers from the University of Complutense of Madrid, Spain, have used cylindrical carbon fibre microelectrodes (CFMEs) modified with

rhodium for the low-potential detection of hydrazine under flow-injection conditions (J. M. Pingarrón, I. O. Hernández, A. González-Cortés and P. Yáñez-Sedeño, *Anal. Chim. Acta*, 2001, 439, (2), 281–290).

Rhodium metallised CFMEs, combining the advantages of metallised electrodes and cylindrical electrodes, were prepared potentiostatically using RhCl_3 , and characterised by cyclic voltammetry. The electrodes were then tested under flow conditions, beginning at a flow rate of 1.0 ml min^{-1} and an applied potential of +0.3 V. The Rh-CFMEs were found to have good stability during amperometric detection of hydrazine under flow conditions and good electrocatalytic ability for the oxidation of hydrazine and some other organic compounds. The electrode surface did not need to be regenerated. Signal-to-noise ratio was much better at the Rh-CFME than at a Rh-modified glassy C electrode of conventional size. The limit of detection was $6.2 \times 10^{-7} \text{ mol l}^{-1}$ hydrazine ($\sim 20 \mu\text{g l}^{-1}$). This flow-injection method could therefore be used to determine hydrazine in trade effluents.