

## Research Progress on Brittleness of Iridium

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**Abstract:** Due to the high melting point, excellent high temperature strength and anticorrosive property, iridium is the unique material which can be used under extremely hostile environments. However, iridium exhibits an anomalous brittle fracture behavior, a mixed brittle intergranular fracture (BIF) and brittle transgranular fracture (BTF), even though it is of face-centred cubic (fcc) crystal structure. A great deal of efforts have been made to explore the embrittlement mechanisms since the anomalous fracture behavior was recognized in 1960 s, up to now, there has not been a reasonable conclusion yet. This paper emphatically reviewed the possible embrittlement mechanism of iridium, including impurity-induced brittleness, intrinsic brittleness and special defect structure induced embrittlement, discussed the research status quo about the deformation and failure mechanisms of iridium. Finally, the research direction and research method of the embrittlement mechanism of iridium were forecasted.

**Key words:** iridium; BTF; BIF; intrinsic brittleness

Iridium (Ir) is one of the platinum group metals (PGMS). It is not only the most anticorrosive among all metals, but also has a high melting point (2443 °C) and is the only metal to maintain good mechanical properties in air at temperatures above 1600 °C<sup>[1-3]</sup>. Due to its high melting point, excellent high temperature strength and anticorrosive properties, iridium is the unique material used under extremely hostile environments. For example, it is used for crystal growth crucibles, nuclear fuel containers in thermoelectric generators, coatings of advanced rocket thrusters, automotive spark plugs, etc. In recent years, the application requirements of iridium in industry have progressively increased, and the price for iridium also has increased rapidly (Table 1). Unfortunately, iridium exhibits poor workability (even at elevated temperatures), and is very difficult to be fabricated<sup>[1,5]</sup>. The brittleness substantially restricts its industrial applications.

Iridium belongs to face-centred cubic (fcc) metals. Generally, metals with fcc lattice are considered to be high plasticity, and the fracture mode has also been widely accepted as ductile fracture. However, the fcc-metal iridium

is somewhat strange, as its fractures in a brittle manner (Fig.1): at room temperature, high pure iridium single crystal is a highly plastic material, but it fails by brittle transgranular cleavage (with the features of river patterns) after considerable plastic deformation (the elongations up to 80% under tension<sup>[5]</sup>), and the necking is absent. Under compression, the anisotropy of single iridium is vanishing<sup>[6,7]</sup>. Obviously, the brittle fracture of ductile materials rules out empirical theories. Iridium in polycrystalline state displays a brittle-ductile transition as a function of temperature<sup>[8]</sup>, which is the typical character of body-centred cubic (bcc) metals and its alloys, and exhibits both brittle intergranular fracture (BIF) and brittle transgranular fracture (BTF) at temperatures up to 1000 °C even in inert environments and at moderate strain rates<sup>[9,10]</sup>. But fine-grain iridium, prepared from a massive single crystal, never fails under compression<sup>[7]</sup> and can be forged like platinum<sup>[11]</sup>.

The anomalous fracture behaviors had been recognized since 1960s, and grabbed the attention of researchers. Although a great deal of efforts has been made to explore

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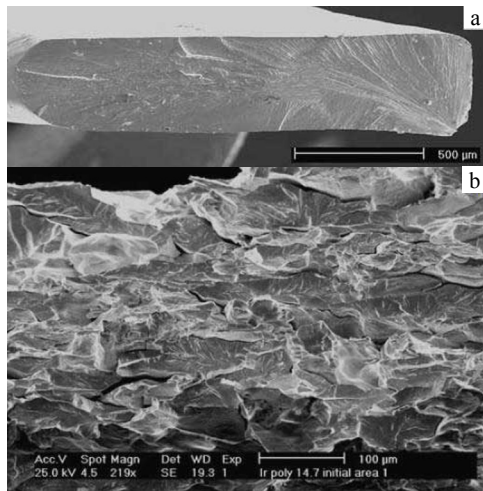
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**Table 1** Variation in price and consumption of iridium (t) over industry branches in 2006~2011<sup>[4]</sup>

Consumption	2006	2007	2008	2009	2010	2011
Chemical industry	1.0	0.7	0.7	0.7	0.4	0.4
Electronic, electrical engineering	0.9	0.8	0.5	0.2	2.3	2.3
Electrochemistry	1.1	0.7	0.8	1.0	2.3	2.3
Others	1.1	1.0	1.3	0.9	1.2	1.4
Average price (USD/troy ounce)	350	447	450	425	606	950

Fig.1 Fracture surface of iridium <sup>[6]</sup>: (a) single crystal and (b) polycrystalline

the mechanism of unusual fracture, up to now there is still a big controversy on the factors which control fundamental mechanisms in the materials science community. The deformation and failure mechanisms of iridium are not clear. And the nature of both BTF and inclination to GB brittleness continues to be unsolved. At the first international symposium on iridium, Professor P. E. Panfilov (Urals State University, Russia) commented that “It is unbelievable that there is a face-centred-cubic metal whose properties continue to be puzzling at the end of the twentieth century”<sup>[12]</sup>.

Although some physical properties of iridium are generally in agreement with empirical cleavage criteria, its fundamental mechanisms are not clarified, and controversial with each other in the literatures. At present, the main viewpoints of embrittlement mechanism of iridium are as following.

## 1 Impurity-Induced Brittleness

Grain boundaries (GBs) are important components of polycrystalline materials and the segregation of harmful impurities usually deteriorates the performance of materials. It is well known that the BIF in fcc metals is mainly attributed to the influence of the segregation of dangerous

elements to GBs. Iridium is one of refractory metals (refractory metals are difficult to be refined and their mechanical properties are very sensitive to the influence of non-metallic impurities<sup>[13]</sup>). In addition, high pure iridium single crystal exhibits high plasticity. Hence, the brittleness of polycrystalline iridium might be an impurity-induced brittleness.

Early studies<sup>[5,14]</sup> suggested that a small quantity of harmful impurities (such as C, P, Si) have a great effect upon critical resolved shear stress, and might also affect the Peierls-Nabarro (P-N) force resisting the movement of dislocations. Thus, the brittleness of iridium is due to the effect of impurities, not only on GBs but also in the interior of the grains. In contrary, Hecker<sup>[15]</sup> et al. showed that impurity segregation to GBs was not necessary for grain boundary fracture by analysis of freshly fractured grain boundaries using Auger electron spectroscopy. Hence, they concluded that brittle transgranular cleavage and BIF of iridium are intrinsic and not caused by impurities. However, Handley<sup>[11]</sup> suggested that the sensitivity of iridium to dangerous impurities is so high that standard procedures did not allow detecting the critical level of impurities on fracture surfaces of iridium samples. For example, the presence of very small amounts of impurities (10 μg/g is the critical level for carbon) will result zero plasticity. Therefore, this makes it extremely difficult to be verified by direct experiment<sup>[16]</sup>.

Indeed, the segregation of dangerous impurities or the diffusion of harmful impurity atoms on GBs in recrystallization annealing can induce GBs brittleness, as GBs are the most probable sites for crack growth. Although that is the most logical explanation for the BIF of polycrystalline iridium in common sense, many experimental studies<sup>[16-19]</sup> indicated that the fracture mode of high purity polycrystalline iridium and its alloys is a mixture of BIF and BTF, and the fracture surface of fine grained polycrystalline iridium without non-metallic impurities can consist of approximately 100% BTF, despite the fact that the plasticity of iridium with (or without) non-metallic impurities will become worse after recrystallization annealing in vacuum. So impurities (C, Si, P, etc.) can exacerbate GBs brittleness, but its influence is only a secondary factor for BIF. Hence, BTF may be the inherent fracture mode of polycrystalline iridium, while BIF in iridium is considered as an impurity-induced fracture mode, as no environmental factors have so far been implicated in the brittle fracture of iridium.

Now, it is clear that impurities and most non-metals (metal impurities (such as Fe, Ni, Al, Cr) do not induce brittleness<sup>[7,20]</sup>, and some metal elements are beneficial for ductility, such as Liu<sup>[21]</sup> discovered that doping with “10<sup>-6</sup> levels” of Th can suppress grain-boundary fracture and increase the ductility at high-strain rates), can considerably

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