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On brittle fracture in polycrystalline iridium

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The brittle intercrystalline fracture (BIF) in iridium and low plasticity of this refractory fcc-metal in polycrystalline state for wide temperature range, give occasion to supposition that a metal having fcc lattice can be brittle substance like silicon due to specific features of interatomic bonds. On the other hand, experience has shown that such behavior of fcc-metal should be impurity induced effect. High plasticity of iridium single crystals (by means of octahedral slip), which however cleave under tension, does not support idea on "classic" inherent brittleness of this metal. High sensibility of its mechanical properties to impurities (10 ppm is critical level for carbon!) has been severe restriction for experiments aimed to searching of inherent fracture mode for polycrystalline iridium. In present paper fracture behavior of high purity polycrystalline iridium and iridium, where grain boundaries (GBs) have been contaminated, are considered. Fine grained impurity-free metal exhibits 100% brittle transcrystalline fracture (BTF) and cracked GBs on the fracture surface and this is an inherent fracture mode of polycrystalline iridium. Re-crystallization in vacuum leads to appearance of BIF regions, whose total square can reach 100% of the fracture surface in coarse grain aggregates. Contaminated iridium mainly fails on grain boundaries, at that portion of BIF on the fracture surface (50 ÷ 100%) does not depend on grain size.

1. Introduction

Iridium is a pure face centered cubic (fcc) metal, which formally obeys few empirical criteria for cleavage [1], and, therefore, information about its fracture modes may be important for analysis of mechanical behavior of modern fcc-based materials such as structural intermetallics and metallic composites. Despite contradiction with long-term experience,[1] this refractory fcc-metal ($T_{\text{melt}} = 2443°\text{C}$) exhibits poor plasticity in the polycrystalline state and inclination to brittle intercrystalline fracture (BIF) [3–5], while single crystalline iridium is a high plastic material, whose fracture mode has been shown to be brittle transcrystalline fracture (BTF) [6, 7]. Segregation of impurities on grain boundaries (GBs) is the most logical explanation for the anomaly in polycrystalline Ir, since refining of iridium requires a very complicated procedure [3, 8]. Indeed, high purify iridium can be forged like platinum and practically becomes a "plastic" material [9]. On the other hand, it was proposed that inclination to both BIF and BTF is an inherent property of iridium, while some impurities can reinforce a tendency to brittle fracture [10, 11]. The high ensitivity of its mechanical properties to non-metallic contaminants (e.g. 10 ppm is a critical level for carbon in iridium [9]) makes it extremely difficult to obtain direct experimental verification of these conceptions. The problem may be solved if the fracture behavior of high pure iridium, where GBs are guaranteed to be free from dangerous non-metallic impurities (*carbon and oxygen*), and commercial (contaminated) metal could be compared. Re-crystallized iridium single crystals provide a suitable model material for research aimed at detecting the inherent fracture mode and cause of BIF in polycrystalline iridium.

2. Experimental procedure

High purity iridium and its alloy Ir-3%Re-2%Ru have been supplied by the Ekaterinburg Non-Ferrous Metals Processing Plant. Initial ingots did not contain such dangerous non-metallic contaminants as C, O, N, H, while the level of metallic impurities was lowest: 0.1 ÷ 1 p.p.m. for W, Mo, Nb, Zr, Cu, Gd, Y, Al, Ga, Ni, Pd, Zn, Mg, Ca; ∼10 p.p.m. for Pt, Rh, Fe. Massive single crystals of iridium, its alloy and ruthenium (10 ÷ 55 mm in diameter and 120 ÷ 150 mm in length) have been grown by the means of electron beam melting [12]. Some "single crystalline" (SC) iridium ingots contained a few coarse grains. Heated (1800–2000°C) work pieces were forged by hydraulic hammering to give plates with thicknesses of 10 mm. Broken edges of plates were cut off and it was rolled to sheet. The temperature of the 30-min annealing between the stages of rolling was approximately 800–900°C. This regime guaranteed both relaxation of stress in the work piece and absence of new grains in the matrix, since re-crystallization in iridium starts at 1000°C. No re-crystallization annealing was carried out after final stage of rolling. A sheet was manufactured in

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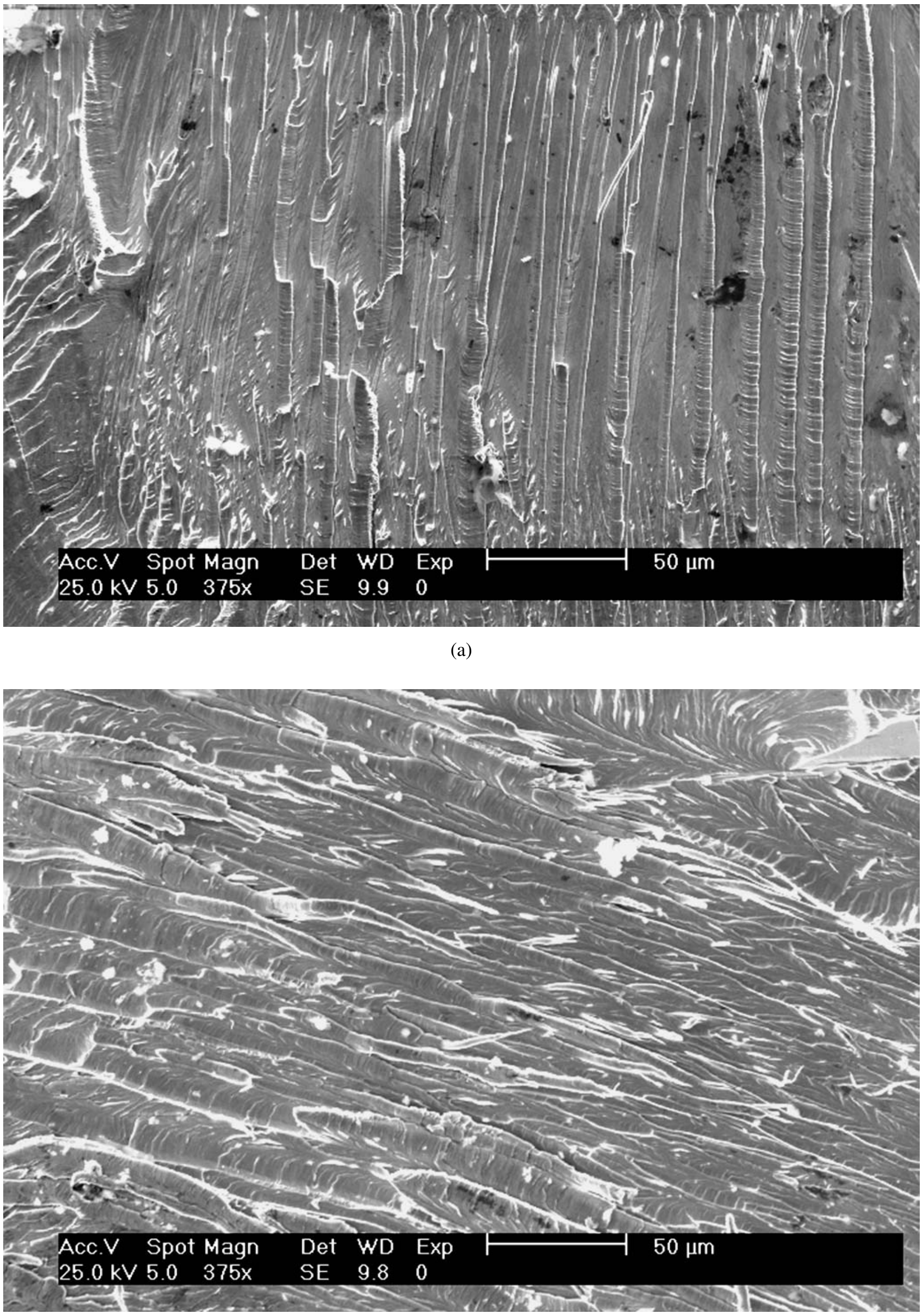
[1] It is well known that pure metal with fcc lattice should be high plastic and ductile substance [2].

the same way from electron beam re-melted (EBRM) iridium containing a few dozen coarse grains. Galvan plastic (GP) iridium has been also prepared. Plate samples (thickness is 1 mm) for room temperature tensile tests were cut from the sheets. Recrystallization annealing of samples was carried out in evacuated quartz (in both "technological"—10^{-2} mm of mercury pole and "oil" vacuum—10^{-5} mm of mercury pole) at 1200°C during 2 h, when new-born grains achieve maximal size and stop to grow. After that, samples have been cooled in water. Fracture surfaces were examined with a help of Philips XL-30 scanning electron microscope.

3. Experimental results

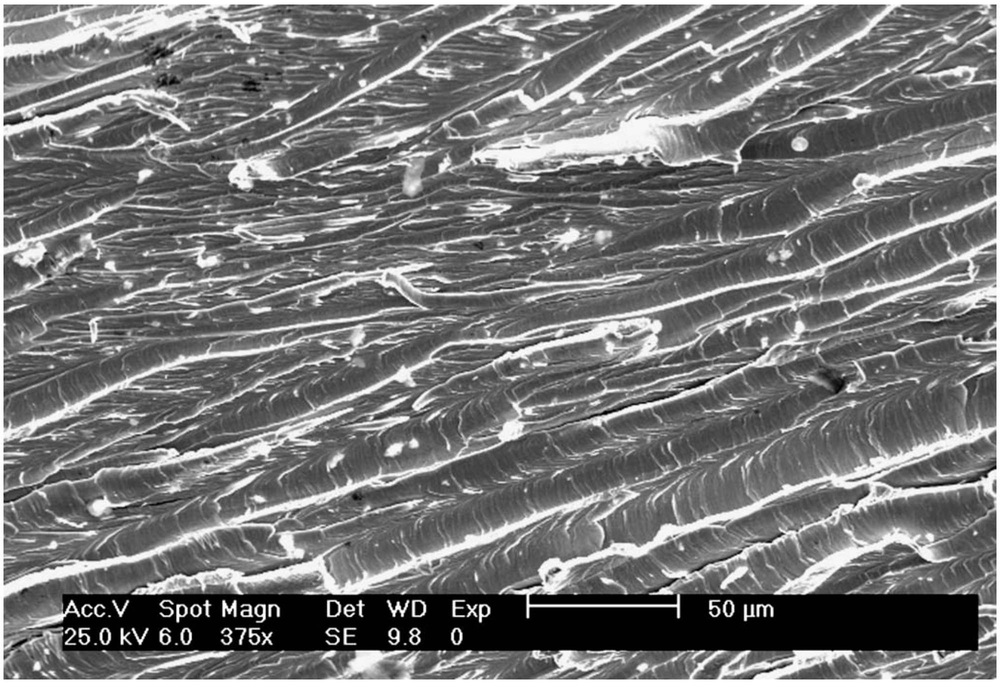
The fracture surfaces of iridium and ruthenium single crystals (Fig. 1a, b and c, respectively) are chosen as standards of BTF for metallic materials. Single crystalline iridium is a highly plastic material, which cleaves under tension along soft directions $\langle 110 \rangle$ at room temperature after elongations of 30–60%, whereas under compression it never separates in spite of the fact that huge plastic deformation (~80%) is accompanied by considerable strengthening [13]. Ruthenium exhibits orientation anisotropy of plasticity because of its dominant deformation mechanism is basal slip [14]. Samples



(a)

(b)

Figure 1 Brittle transcrystalline fracture in deformable single crystals of metals: (a) Ir single crystal (elongation 30%); (b) Ru single crystal (parallel to "*c*"—elongation 20%); (c) Ru single crystal (normal to "*c*"—elongation 0%). (*Continued*)



(c)

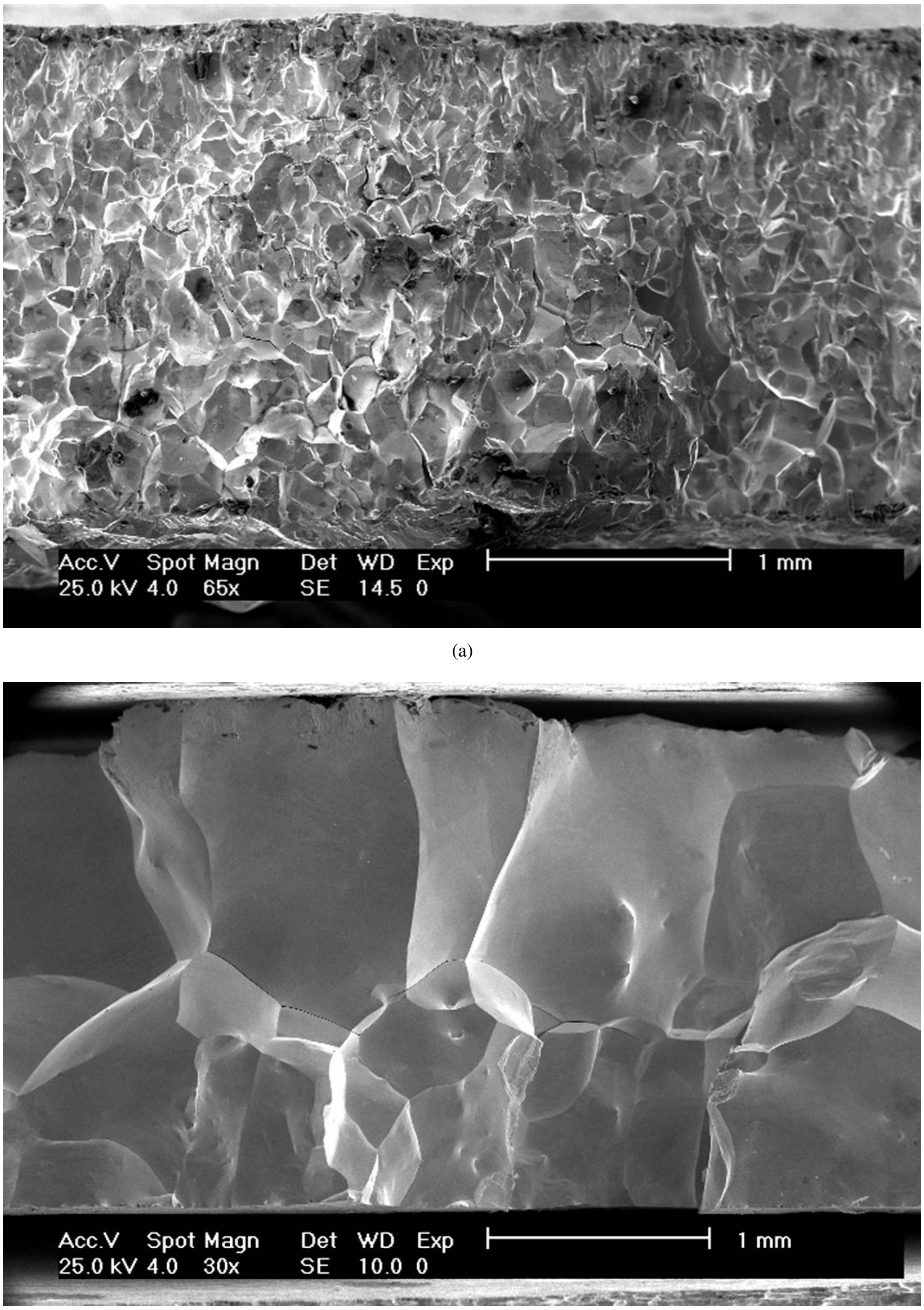
Figure 1 (*Continued*).

stretched along the "*c*" axis, fail in brittle manner after 20% elongation (Fig. 1b), whereas crystals with a tensile axis parallel to "*c*" cleave without preliminary deformation (Fig. 1c). These findings were not depended on impurity content, since the samples have been cut from one massive single crystal of ruthenium. Despite differences in crystallography and preliminary plasticity of samples, all fracture surfaces shown on Fig. 1 look similar. River patterns are the main morphological element of BTF fracture surface, while their orientation depends on crystallography and shape of sample.

Fracture surface of GP iridium is standard of BIF. In this case, iridium behaves as a "truly" brittle substance: it is an unworkable metal, which fails in the grips of the tensile machine and fails after 3–5% of compression. Still it is very soft material: its Vickers microhardness (∼2500 MPa) is similar to that of an annealed single crystal. Fracture surface is 100% BIF (Fig. 2a), where the surfaces of all grains are smooth (undeformed) and some GBs have cracked. Re-crystallization annealing leads to increase of the grain size, but the main features of BIF do not change (Fig. 2b). The cause of BIF in GP metal is GB segregation of non-metallic impurities, which are incorporated into the matrix from the electrolyte. Hence, this is clear impurity-induced fracture of fcc-metal [15].

All samples prepared from sheets and GP metal failed after elongations of 1–5%, which agree with literature data on plasticity of polycrystalline iridium [3–5, 8], but is two times less than the elongation of iridium wire manufactured from single crystalline work-pieces [16]. In spite of low plasticity under tension, polycrystalline metal, prepared from SC work piece, is "plastic" iridium, since it could be compressed without failure as single crystal [13] and such metal is successfully used for manufacture of iridium containers having all needed geometry and size [12]. Its fracture surface is shown on Fig. 3a. The majority of grains on fracture surface fail by means of BTF, although there are regions, which look like BIF between deformed grains. Besides, some GBs have cracked. The ratio between BTF and BIF regions is about 10:1, but sometimes it seems to be that this is 100% BTF. Fracture behavior of Ir-Re-Ru alloy is the same. Fracture surfaces of samples, prepared from both coarse grained ingots, possess layered structures, where the quantity of layers is equal to quantity of grains in the work-piece (see Fig. 3b–d). Layers are situated parallel to the plane of rolling. They have similar thickness and their width is compatible with the width of sample. The fracture mode of iridium inside every layer has been founded to be 100% BTF. Some interlayer boundaries have also cracked. Experiments have shown that the quantity of layers and interlayer cracks on the fracture surface of samples prepared from electron beam re-melted iridium is larger than for the samples from coarse-grain "single crystalline" (CGSC) ingots.

After re-crystallization annealing, plasticity of the materials does not change (1–5% of elongation), but microhardness decreases from 5.000–6.000 MPa down to the "single crystalline" value 2.500–3.000 MPa. In contrast with normal fcc-metals, this procedure could lead to loss of workability of iridium: re-crystallized iridium sheets produced from CGSC and EBRM begin to crack under rolling and stamping. Fracture surfaces of the re-crystallized samples are given on Fig. 4. Regions of BIF are revealed on all fracture surfaces, but their total area and size depend on metallurgical history and impurity content of the sample. The iridium and its alloy prepared from a SC ingots exhibited mixed fracture modes, where the ratio of BTF:BIF varies between 3:1 and 4:1 (Fig. 4a–c). In all cases, the quantity of cracked GBs is small than for un-annealed materials. It should be noted



(a)

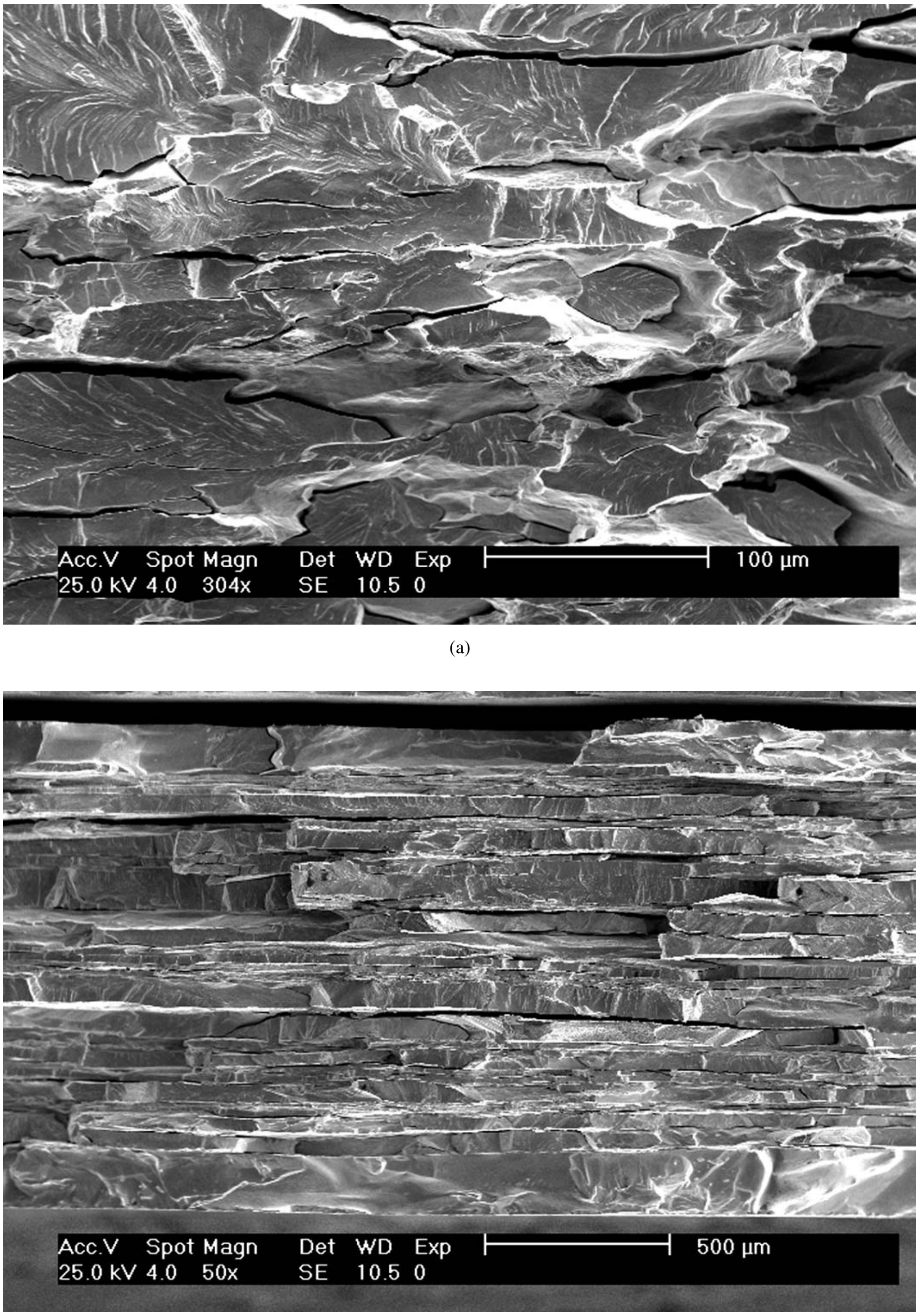
(b)

Figure 2 Brittle intercrystalline fracture in iridium induced by GB segregation of impurities: (a) Galvan plastic metal and (b) Galvan plastic metal (after annealing at 1200°C 2 h).

that grains in Ir-Re-Ru alloy is in 2–3 times smaller than for pure Ir, since alloyed rhenium increases the re-crystallization temperature for iridium from 1000°C up to ∼1100°C and, hence, slows down the kinetics of re-crystallization. Besides, the BTF-BIF proportion for the alloy is close to 4:1. Metal from CGSC ingot possesses the ratio of 1:1, where some of GBs have also cracked (Fig. 4d). After re-crystallization, EBRM iridium showed approximately 80% BIF and small inclusions of BTF (Fig. 4e). In this case, grains have smallest size in the scale of materials, and the length of cracked GBs is comparable to the CGSC metal. Environment (characteristics of vacuum) does not influence on the morphology of the fracture surfaces of studied sampled.

4. Discussion

Polycrystalline iridium and its alloy, prepared from GB-free SC work pieces, were founded to possess the best workability among iridium-based materials. Re-crystallization in vacuum practically does not influence this characteristic of the material. Therefore, it is logical to assume that newly born GBs in high purity iridium



(a)

(b)

Figure 3 Brittle fracture in polycrystalline iridium: (a) sample prepared from massive single crystal; (b) sample prepared from coarse grain single crystalline ingot; (c) Ir Re Ru sample prepared from coarse grain single crystalline ingot; and (d) sample prepared from electron beam re-melted ingot. (*Continued*)

do not content dangerous impurities. The portion of BTF on the fracture surface of re-crystallized samples decreases from 100% up to $60 \div 70\%$, since BTF-BIF ratio in this case depends on grain size and can reach 100% BIF for coarse grained polycrystalline samples.

The opposite tendency has been observed for other electron beam melted iridium materials[2]: initially deformable polycrystalline samples lose workability during re-crystallization. Macroscopic layers in these iridium samples (see Fig. 3b–d) are severely deformed grains of the initial ingot; and interlayer boundaries represent original GBs (which could be contaminated by dangerous impurities), since the manufacture of sheets excludes treatment connected with re-crystallization of iridium. Both materials exhibit 100% BTF, whereas some GBs have cracked. It should be noted that the portion of cracked GBs in CGSC metal is considerably less

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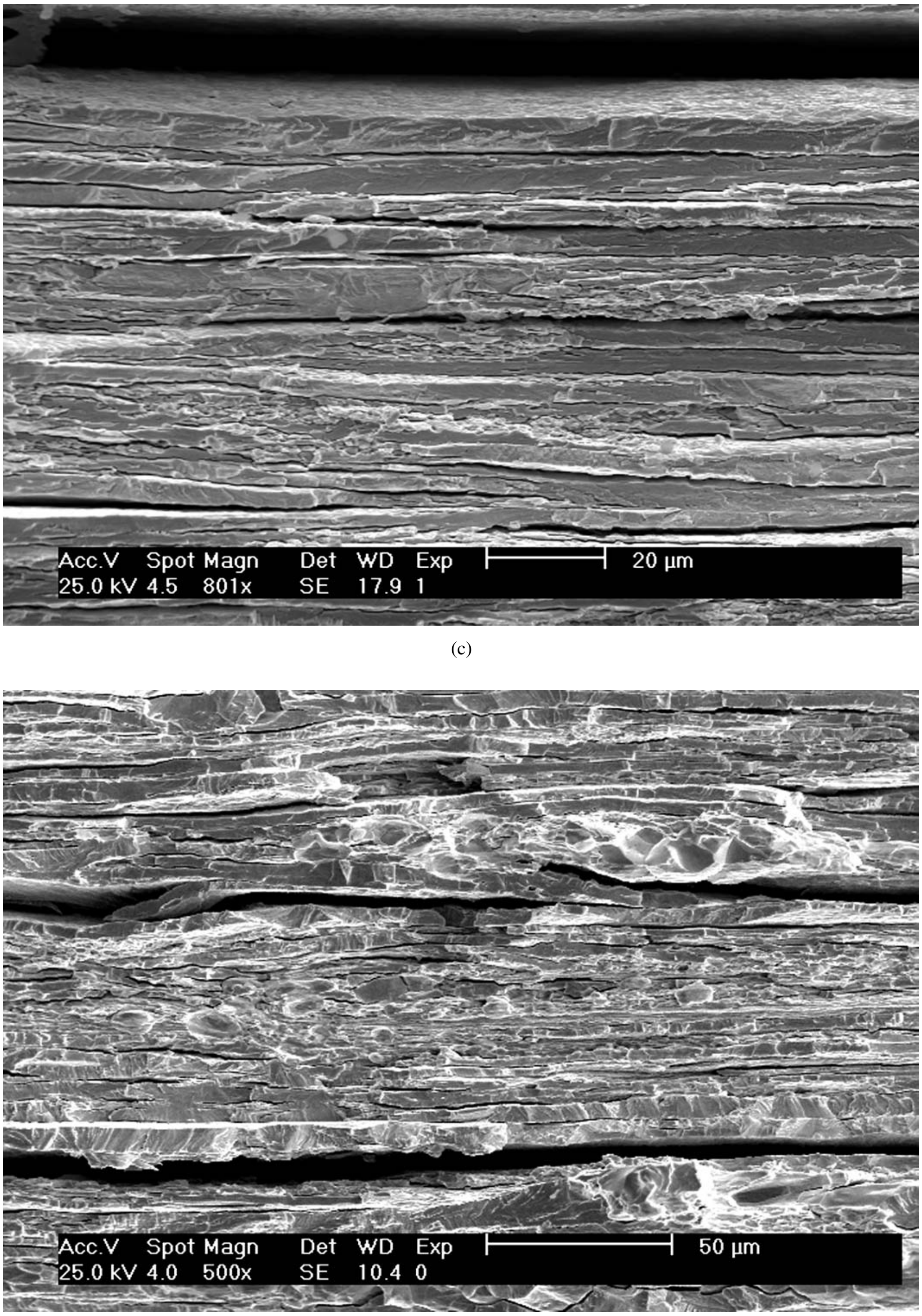
[2] CGSC iridium and Ir-Re-Ru ingots and EBRM iridium.



(c)

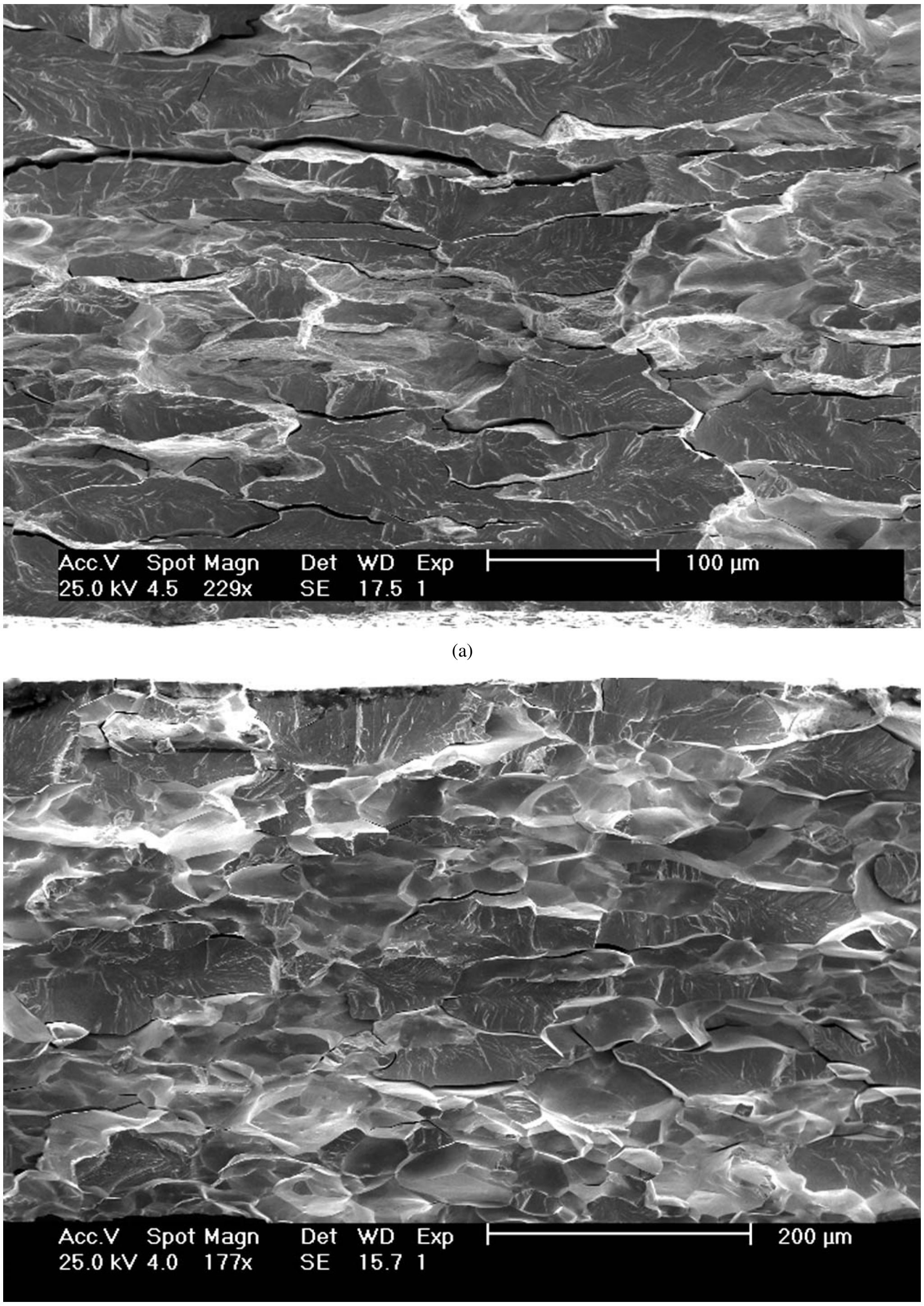
(d)

Figure 3 (*Continued*).

than in EBRM. This is direct subsequence of the fact that purity of iridium ingot after the growing of a single crystal is higher than after conventional electron-beam melting [12]. No layered structure was observed in the re-crystallized samples, because a new grain structure has been formed in all materials. Mixed mode (50% BIF + 50% BTF) and many cracked GBs are detected on the fracture surfaces of CGSC samples (Fig. 4d). In the second case, the majority of grains (∼80%) exhibit BIF, while the quantity of intercrystalline cracks is considerably less than in the initial state (Fig. 4e). Re-crystallized GP metal continues to be unworkable, but stress needed for failure of samples decreases with the rise of grain size. Sometimes, coarse grain samples could ever separate under compression on a number of small pieces including individual grains. In all cases, dangerous impurities from old GBs can segregate on newly born ones in iridium matrix.

Hence, BTF should be associated with plasticity of iridium, whereas the portion of BIF on fracture surface may be considered as measure of its brittleness. BTF with some elements of BIF, such as cracked GBs, may be accepted as inherent fracture mode of polycrystalline iridium. A possible mechanism for GB brittleness in high purity iridium has been proposed [23], but its verification required a detailed transmission electron microscopic study of the motion of ⟨110⟩ dislocations across GBs.

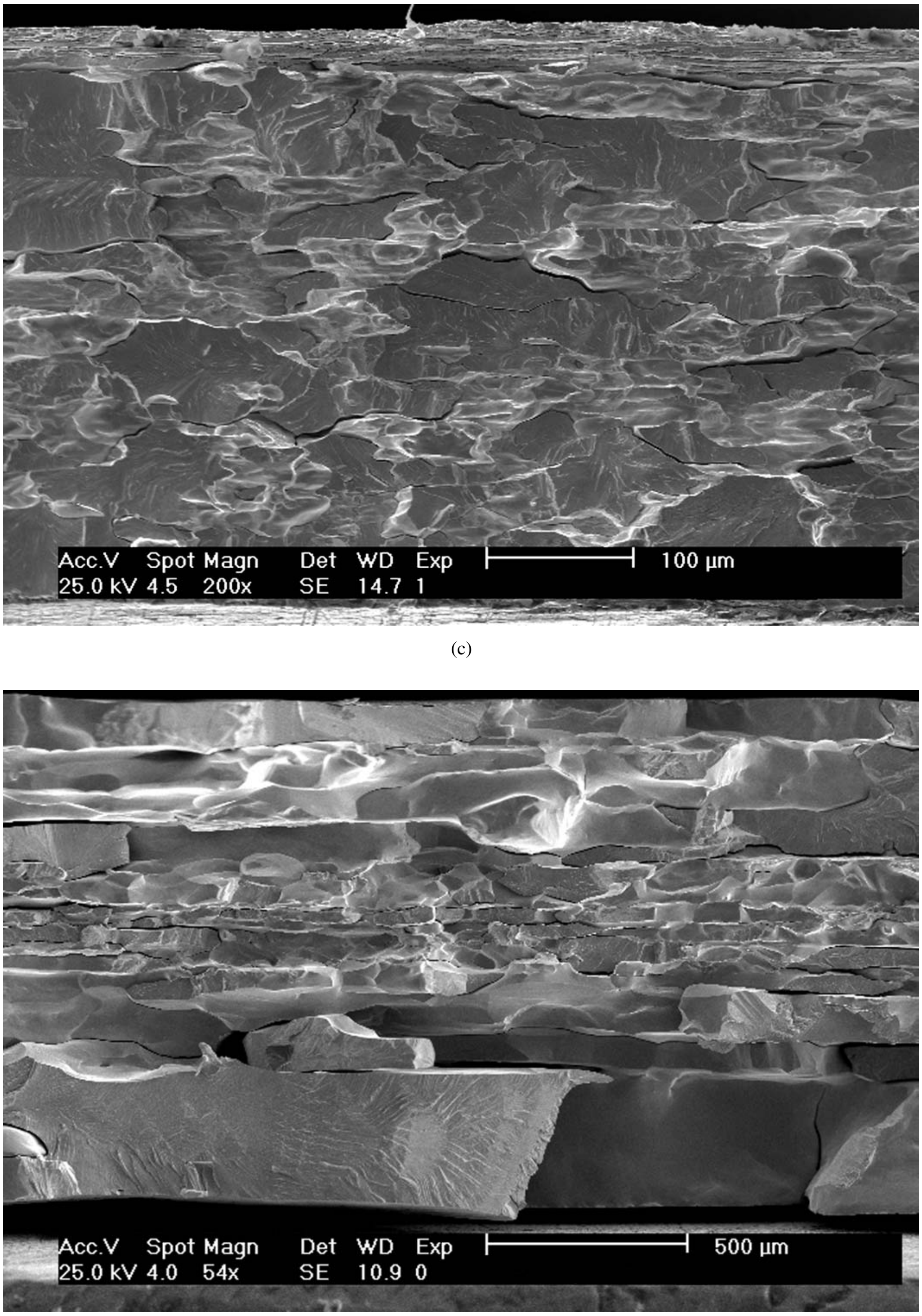
The statement that BTF is a feature of plastic iridium requires to be explained. According to empirical theory, BTF occurs in single crystals, when plastic deformation is impossible [2, 16, 17]. This does not mean that material cannot be deformed at all, but that it becomes a brittle substance when plasticity is exhausted [18]. Under tension along "soft" ⟨110⟩ direction, iridium single crystals exhibit huge elongation (30–70%), which is realized by easy octahedral slip of ⟨110⟩ dislocations, but cleave at the finish. Despite considerable elongation and high dislocation density, the samples remain in the single crystalline state, in as much as dislocation nets, which have filled the volume of material, cannot transform to small angle boundaries due to the low mobility of ⟨110⟩ dislocations in iridium (this features may be connected with the high melting point of



(a)

(b)

Figure 4 Mixture of BTF and BIF on fracture surfaces of re-crystallized iridium (1200°C 2 h in "technological" vacuum): (a) sample prepared from massive single crystal (*annealing in "oil" vacuum*); (b) sample prepared from massive single crystal; (c) sample prepared from massive single crystal of Ir-Re-Ru alloy; (d) sample prepared from coarse grain single crystalline ingot; and (e) sample prepared from electron beam re-melted ingot. (*Continued*)



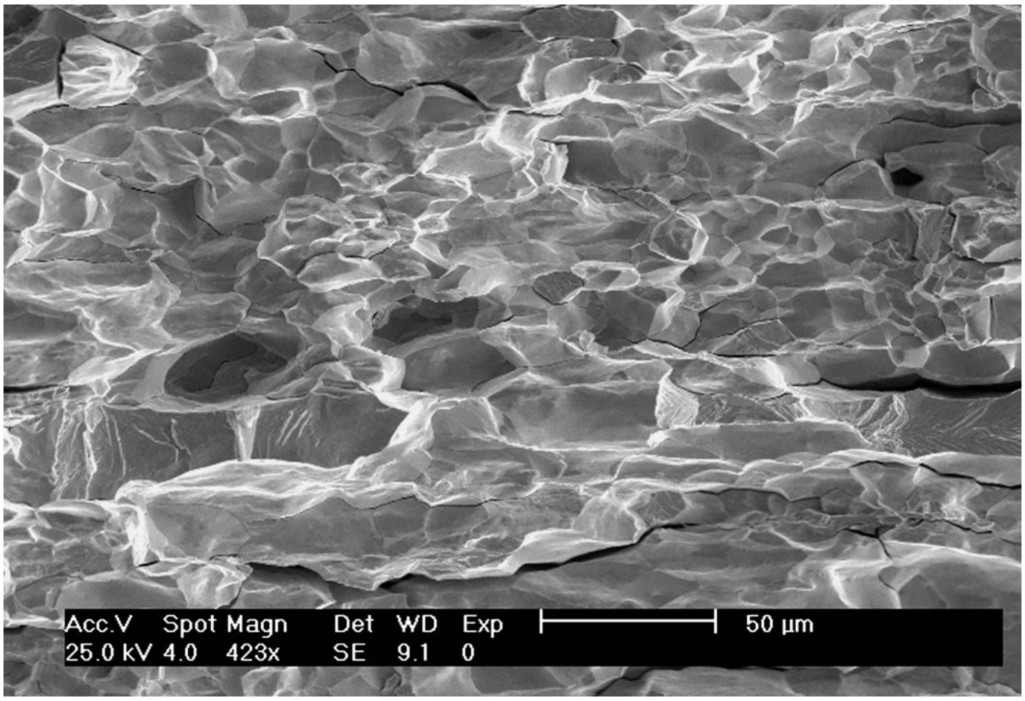
(c)

(d)

Figure 4 (*Continued*).

iridium) [19]. These nets provide barriers for the further motion of $\langle 110 \rangle$ dislocations. As a result, plastic deformation under uniaxial tension becomes impossible and this refractory fcc-metallic crystal cleaves. Under compression (where level of residual stress in a sample is minimal) iridium matrix exhibits highest plasticity accompanied huge work hardening, but it never fails [7, 13].

Cracks produce in brittle material when an external tensile load exceeded some critical value. Therefore, the lifetime of any brittle sample depends on its geometry, the quality of the surfaces and characteristics of surface defects [16]. Mechanically abraded iridium single crystals with rectanglular cross-sections have lots of surface defects and show minimal elongation ∼20%. Electro polishing causes an increase in elongation to 30–40%, while electro polished single crystals having elliptical cross-section (very few surface defects) cleave after 60–70% [20]. This proposed scenario may be checked on ruthenium single crystals stretched along different axes, where fracture surface morphologies are the same in spite of considerable difference in the deformation prior failure. Crystal plasticity is exhausted during preliminary deformation if the tensile axis is parallel to



(e)

Figure 4 (*Continued*).

"*c*", where it cannot be deformed and cleaves as soon as tensile stress is applied normal the "*c*" axis [14]. In the first case, electro polishing of samples leads to some increasing of elongation, but this procedure does not influence the total plasticity of ruthenium single crystals in the second case.

High purity polycrystalline Ir (whose GBs are dangerous impurity free) behaves the same way. Elongation of planar samples is about 3–5%, whereas SC iridium wires, possessing severely hardened microstructure, cleave (100% BTF) at room temperature after ∼10% elongation [21]. Newly born GBs in polycrystalline matrix, which are etched in vacuum, serve as stress concentrators on the surface. Taking into account that cohesive strength of GB in iridium is less than for normal fcc-metal [11], these places are the more suitable for crack appearance when tensile stress applies to a sample. Crack begins advancing along such GB, however its further motion depends on orientation of the boundary relatively a tensile axis. It is clear that GB, which oriented normally to tensile axis, must be the favorable trajectory of a crack in polycrystalline aggregate as it takes place in coarse grained iridium. On the contrary, the nature of BIF in CGSC and EBRM iridium is impurity induced low cohesive strength of GBs.

5. Conclusions

The results obtained here give the basis for the conclusion that brittle transcrystalline fracture with elements of GB cracking,[3] where the ratio between them depends on grain size and can serve as measure of workability, is the inherent fracture mode for polycrystalline iridium. On the other hand, considerable portion of brittle intercrystalline fracture (50 ÷ 100%) on fracture surface of fine grained iridium is the feature of impurity induced fracture, when material has a zero workability. The same tendency is also revealed for the family of Ir-0.3%W alloys, where GBs have been doped by thorium, silicon and other elements: 100% BIF means poor plasticity of material, while appearance of BTF regions on fracture surface points at its rising [25–27]. This is normal for fcc-metals when impurities cause both BIF and poor plasticity [15], while combination of BTF and high plasticity sounds a little bit strangely, however it is sooner linguistic trouble than materials science problem [20].

Acknowledgements

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References

1. C. GANDHI and M. F. ASHBY, *Acta Metall.* **27** (1979) 1565.
2. W. K. HONEYCOMBE, "The Plastic Deformation of Metals" (Edward Arnold, London, 1972).
3. B. L. MORDIKE and C. A. BROOKES, *Platinum Metals Rev.* **4** (1960) 94.
4. P. HAASEN, H. HIEBER and B. L. MORDIKE, *Zt. Metallkde* **56** (1965) 832.
5. G. REINACHER, *Metall.* **18** (1964) 731.
6. C. A. BROOKES, J. H. GREENWOOD and J. L. ROUTBORT, *J. Appl. Phys.* **39** (1968) 2391.
7. C. N. REID and J. L. ROUTBORT, *Metall. Trans.* **3** (1972) 2257.

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[3] Perhaps, this is connected with specific interatomic bonds in iridium [10, 11, 24].

8. C. A. BROOKES, J. H. GREENWOOD and J. L. ROUTBORT, *Journal of Institute of Metals* **98** (1970) 27.
9. J. R. HANDLEY, *Platinum Metals Rev.* **30** (1986) 12.
10. S. S. HECKER, D. L. ROHR and D. F. STEIN, *Metall. Trans.* **9A** (1978) 481.
11. S. P. CHEN, *Phil. Mag.* **66A**(1) (1992) 1.
12. N. TIMOFEEV, A. YERMAKOV, V. DMITRIEV and P. PANFILOV, in "Metallurgy and Mechanical Behavior of Iridium" (Urals Branch of Russian Academy of Science, Ekaterinburg, 1996) p. 119 (in Russian).
13. A. YERMAKOV, P. PANFILOV and R. ADAMESKU, *J. Mater. Sci. Lett.* **9** (1990) 696.
14. P. PANFILOV and A. YERMAKOV, *Platinum Metals Rev.* **38**(1) (1994) 12.
15. M. H. KAMDAR, "Treatise on Materials Science and Technology. Embittlement of Engineering Alloys," Vol. 25, edited by C. L. Briant and S. K. Banerji (Academic Press, 1983 in Russian, Moscow, "Metallurgia," 1988) p. 333.
16. T. YOKOBORI, in "An Interdisciplinary Approach to Fracture and Strength of Solids" (Wolters-Noordhoff Scientific Publications, Groningen, 1971) p. 264 (in Russian).
17. J. F. KNOTT, "Fundamentals of Fracture Mechanics" (London, 1973) (in Russian: Metallurgia, Moscow).
18. P. PANFILOV, A. YERMAKOV, V. DMITRIEV and N. TIMOFEEV, *Platinum Metals Rev.* **35** (1991) 196.
19. P. PANFILOV, in "Iridium. Proceedings of the International Symposium Sponsored by the SMD Division of the Minerals, Metals & Materials Society (TMS) Held During the 2000 TMS Annual Meeting in Nashville, Tennessee, March 12–16, 2000," edited by Evan K. Ohriner, Richard D. Lanam, Peter Panfilov, and Hiroshi Harada (Publication of TMS, USA, 2000) p. 93.
20. P. PANFILOV, in "Iridium. Proceedings of the International Symposium Sponsored by the SMD Division of the Minerals, Metals & Materials Society (TMS) Held During the 2000 TMS Annual Meeting in Nashville, Tennessee, March 12–16, 2000," edited by Evan K. Ohriner, Richard D. Lanam, Peter Panfilov, and Hiroshi Harada (Publication of TMS, USA, 2000) p. 27.
21. P. PANFILOV, V. NOVGORODOV and A. YERMAKOV, *J. Mater. Sci. Lett.* **13** (1994) 137.
22. B. FISCHER and D. F. LUPTON, Private Communication, 1996.
23. P. PANFILOV and A. YERMAKOV, *Platinum Metals Rev.* **45** (2001) 179.
24. YU. N. GORNOSTYREV, O. N. MRYASOV, A. J. FREEMAN, N. I. MEDVEDEVA, M. I. KATSNELSON and A. V. TREFILOV, in "Iridium. Proceedings of the International Symposium Sponsored by the SMD Division of the Minerals, Metals & Materials Society (TMS) Held During the 2000 TMS Annual Meeting in Nashville, Tennessee, March 12–16, 2000," edited by Evan K. Ohriner, Richard D. Lanam, Peter Panfilov, and Hiroshi Harada (Publication of TMS, USA, 2000) p. 137.
25. C. T. LIU, H. INOUYE and A. C. SCHAFFHAUSER, *Metall. Trans.* **12A** (1981) 993.
26. C. G. McKAMEY, E. P. GEORGE, E. H. LEE, E. K. OHRINER, L. HEATHERLY and J. W. COHRON, *Scripta Mater.* **42** (2000) 9.
27. L. HEATERLY and E. P. GEORGE, *Acta Mater.* **49** (2001) 289.

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