JOURNAL OF MATERIALS SCIENCE **40** (2005) 5983–5987

On the inherent fracture mode of iridium at room temperature

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Experimental data that allow the determination of an inherent fracture mode of the refractory fcc metal iridium at room temperature are considered in this paper. High purity iridium and Ir-3 wt%Re-2 wt%Ru are chosen as the model substances. Brittle transgranular fracture is the sole fracture mode exhibited by the samples at room temperature. Neither recrystallization in 10^{-5} Torr vacuum nor the geometry of applied stress or grain size induce the brittle intercrystalline fracture in these materials.

1. Background

Iridium exhibits certain properties that make it unique among the metals with the face centered cubic (fcc) crystal structure. For example, single crystals of Ir are highly plastic but cleavable [1–3], while polycrystalline iridium exhibits poor plasticity and brittle intergranular fracture (BIF) as its primary fracture mode [4–7]. This does not seem puzzling, since it behaves like an embrittled fcc metal [8]. Some researchers explain these properties on the basis of impurities [4, 7, 9]. On the other hand, iridium formally obeys some cleavage criteria [2, 10, 11]. Of course, the term "inherently brittle fcc metal" sounds somewhat provocative, but the high melting temperature of iridium (2443°C) points to strong interatomic bonds and other possible peculiarities of its atomic structure [10, 12–16]. First principle calculations suggest that low cohesive strength of the grain boundaries (GBs) may be considered an inherent property of iridium, with impurities simply enhancing this tendency [15, 17]. This fcc metal has been classified as intrinsically brittle according to the classification of fracture behavior by Rice [18]. Direct experimental study of impurity segregation to cracked GBs in iridium [19] supports these hypotheses on the nature of GB brittleness. Unfortunately this circumstance makes experimental verification of the inherent fracture mode in polycrystalline iridium (it is accepted that this should be BIF) practically impossible, since a very low impurity level (it is less than 10 ppm of carbon) caused zero plasticity [9] and, hence, the critical concentration of a dangerous contaminant cannot be surely measured on the fracture surface of a bulk sample with absolute accuracy.

Tensile tests over a wide temperature range of plastic iridium (i.e. free from dangerous impurities) and Ir-3 wt%Re-2 wt%Ru alloy wires have shown that the fracture mode is brittle transgranular fracture (BTF) [20, 21]. Unfortunately, this experiment cannot be accepted as verification of the inherent fracture mode in iridium, since GBs are absent in the material, which is a severely deformed single crystal. A recent study of the fracture mode in polycrystalline iridium sheets confirms that their fracture mode can be 100% BTF. However, recrystallization in low vacuum (10^{-2} Torr) generates BIF regions, whose portion increases with rising grain size [22]. Of course, these results agree with the scenario of inherently low cohesive GB strength, but they also support the impurity induced model of BIF. Indeed, an appearance of BIF zones on the fracture surface of recrystallized samples may be explained by the influence of non-metallic impurities which penetrate into the iridium matrix from the environment or the surface [23, 24].

In other words, no reliable findings have yet been obtained that would allow the determination of the inherent fracture mode in polycrystalline iridium. The simplest scenario would be one in which BTF is the sole fracture mode for polycrystalline samples, since this does not depend on both the recrystallization history of the material and the geometry of the applied load. Indeed, in this case the problem of the low cohesive GB strength should be automatically removed from consideration as BIF is absent on the fracture surface. In the present paper, the technique of such an experiment and its results are described.

2. Experimental procedure

High purity polycrystalline iridium and Ir-3 wt%Re-2 wt%Ru alloy were borrowed from the Ekaterinburg Non Ferrous Metal Processing Plant. Neither material contains dangerous non-metallic impurities, such as carbon or oxygen, since they were manufactured using a pyrometallurgical process route including oxidative melting in a periclase magnesia crucible, electron beam melting in a horizontal crystallizer, and massive single

0022-2461 © *2005 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-1296-1

crystal growth by electron beam melting as the final step [25]. The model materials provide an opportunity to determine the role of metallic impurities on the fracture behavior of iridium. They should not influence *a priori* the fracture mode of an fcc metal [26]. Some findings for iridium support this point of view [20, 22, 27]. "Monocrystalline" ingots can consist of a small number of coarse crystallites, but this does not influence the workability of the iridium. Sheets obtained from such coarse-grained work pieces exhibit a layered morphology where the layers are grains from the initial ingot, since recrystallization annealing was not included in the processing schedule. Recrystallization erases the layered morphology, causing a grain structure to appear in the material.

Samples prepared both from single crystalline and coarse-grained ingots were studied. They were cut from rolled sheets of 0.5 mm thickness. Their shape was that of a double spoon, with a size of 2 × 8 mm. Electropolishing of the samples was not carried out, since this procedure leads to etching of GBs and, therefore, induces BIF. In the initial state, the grain size of samples prepared from massive single crystals was about 50 to 100 μm, whereas the grain structure was not revealed in the samples with layered morphology. Samples were annealed in evacuated quartz ampoules (10^{-5} to 10^{-4} Torr, oil diffusion pump has been used) at 1200°C for 20, 40, 60, 80, 100 or 120 min. After that they were quenched in water (the ampoules were break during quenching). All samples were initially subjected to tensile strain at 20°C (traverse rate ~1 mm/min, elongation ~3%). Subsequently, their elongated portions were bent up to failure (cyclical "bending-unbending") at room temperature. Furthermore a small number of samples with the size 20 × 2 × 0.5 mm were cut from the "monocrystalline" ingot which showed the coarse grained structure. The middle parts of some of them contain GBs which intersected the sample from edge to edge. Such samples were elongated or bent up to failure at room temperature. Fracture surfaces of the samples were examined using a Philips XL-30 scanning electron microscope.

3. Experimental results

The results may be briefly outlined as follows: the fracture mode of all tested samples is BTF. No BIF regions, such as seen in the images in [10, 22, 27], were revealed on the fracture surfaces studied here. No qualitative differences between the pure metal and the alloy were found. Therefore, for economy of journal space, the data for the pure Ir are presented to illustrate the fracture surfaces of samples having the usual grain structure, while the data for the Ir-3 wt%Re-2 wt%Ru alloy are presented to illustrate the fracture surfaces of the samples with the layered morphology.

In the initial state, fracture surfaces of the samples prepared from massive single crystals contain cleaved crystallites, while some boundaries between them have cracked (see Figs 1a and 2a). Naturally, the geometry of loading does influence the number, length or orientation of GB cracks. The grain size in both pure iridium and the alloy, which was estimated on the fracture

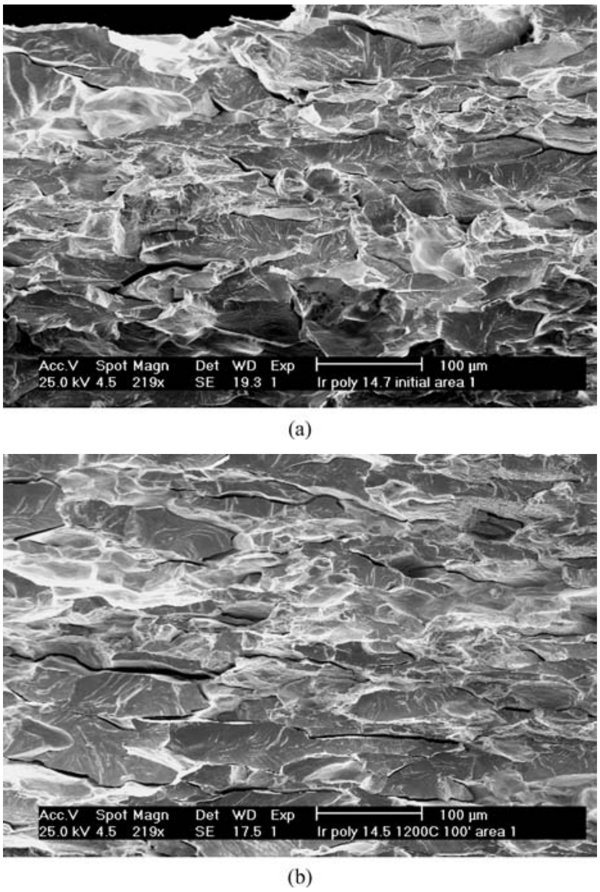

Figure 1 Fracture surfaces of polycrystalline Ir samples after tension (elongation ~ 3%): a—initial state; b—test after annealing (100 min at 1200°C in oil vacuum 10^{-5} Torr).

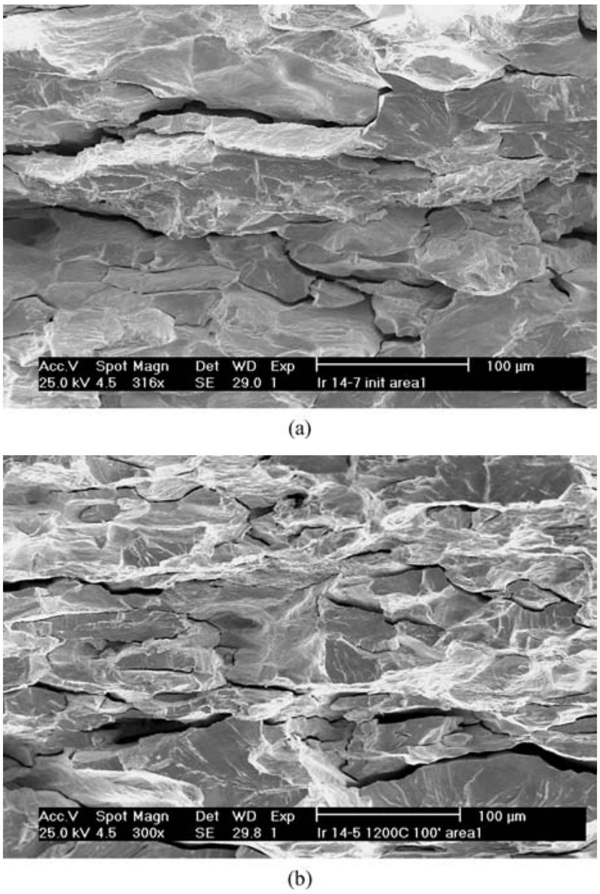

Figure 2 Fracture surfaces of polycrystalline Ir samples after bending (one cycle prior to failure): a—initial state; b—test after annealing (100 min at 1200°C in oil vacuum 10^{-5} Torr).

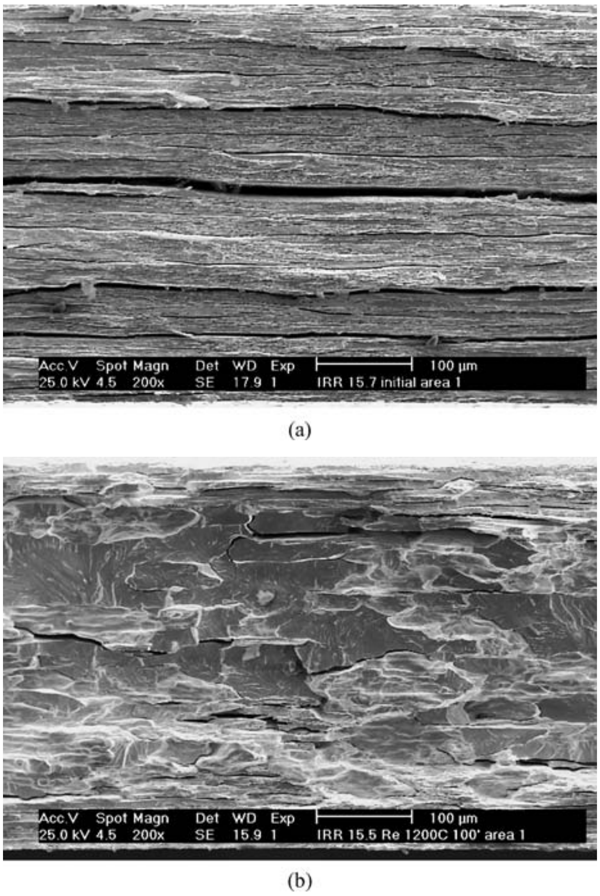

Figure 3 Fracture surfaces of Ir-3% Re-2% Ru polycrystalline samples after tension (elongation ~ 3%): a—initial state (layered morphology—sheet was prepared from coarse grained monocrystalline ingot); b—test after annealing (100 min at 1200°C in oil vacuum 10^{-5} Torr).

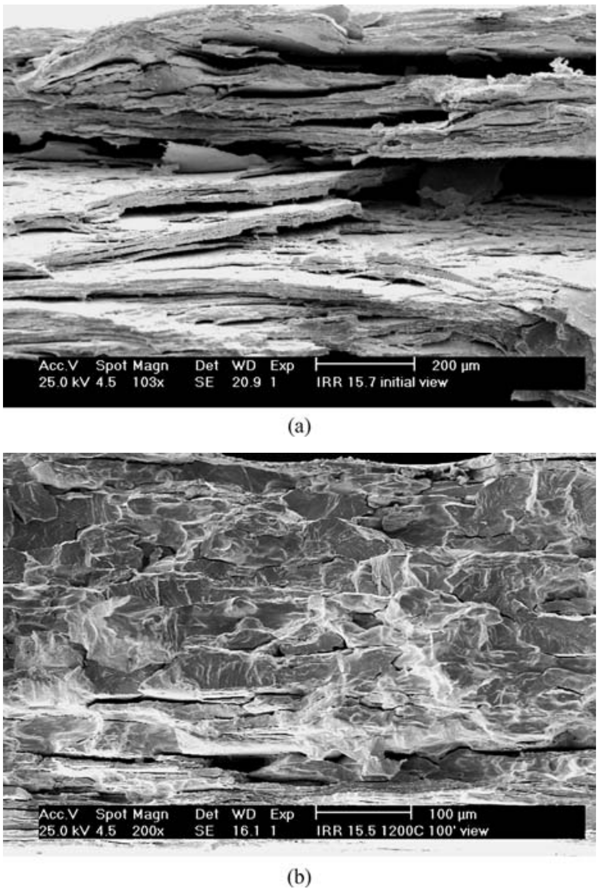

Figure 4 Fracture surfaces of Ir-3% Re-2% Ru polycrystalline samples after bending (one cycle prior to failure): a—initial state (layered morphology – sheet was prepared from coarse grained monocrystalline ingot); b—test after annealing (100 min at 1200°C in oil vacuum 10^{-5} Torr).

surface, was between 50 and 100 μm. Samples prepared from coarse-grained "monocrystalline" ingots also displayed BTF inside every layer as well as interlayer cracks (Figs 3a and 4a). The number and size of interlayer cracks also depend on the geometry of applied stress.

The first 20 min of annealing do not lead to the appearance of a new grain structure and, as a result, the fracture surface morphology of the samples remains the same. A new cellular structure with an average grain size of 50 to 100 μm forms in the materials after 40 min annealing. Further annealing causes additional growth of the crystallites. From this point, the fracture surfaces of samples prepared from massive single crystals and coarse-grained "monocrystalline" ones, which initially exhibited the layered structure, continue to show the same appearance—their fracture surfaces are identical to the morphology described at the beginning of this section (see Figs 1b, 2b, 3b, and 4b). All grains cleave and some GBs are also cracked. However, the fracture surface morphology does not depend on the geometry of applied stress.

Fracture surfaces of the sample cut from the coarse grained "monocrystalline" ingot are shown in Fig. 5: a—the sample fails under tension in the area where the GB is absent; b—the sample fails under tension near GB; c—the sample fails under bending near GB. In all cases BTF is the fracture mode of the iridium sample. Neither BIF nor GB cracking is observed here.

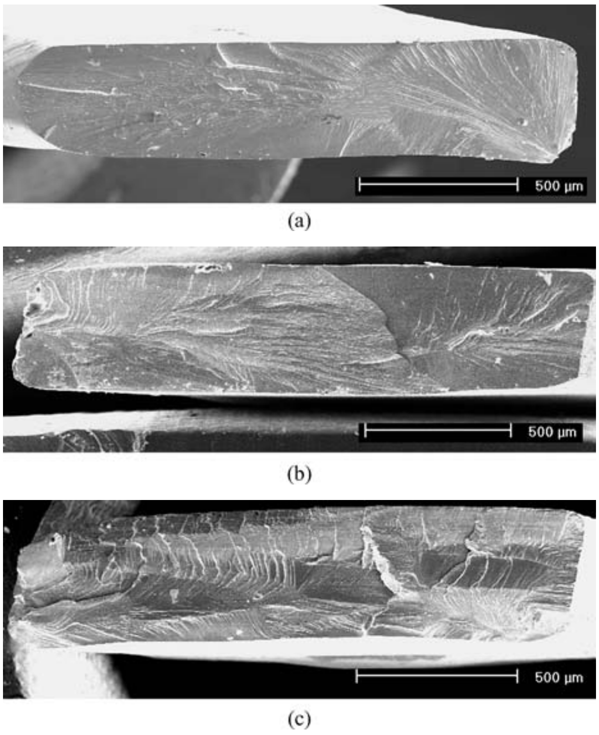

Figure 5 Fracture surfaces of the bi-crystalline Ir sample: a—"single crystalline" area (tension); b—GB intersected fracture surface (tension); c—GB intersected fracture surface (bending).

4. Discussion

The experimental data presented here lead to the conclusion that BTF is the sole, i.e. inherent, fracture mode of iridium in both mono- and polycrystalline states. Hence, it may be really classified as intrinsically brittle fcc metal [18]. Although it sounds unusual, this fracture mode does not mean that the tested material possesses poor plasticity, since the high purity iridium (i.e. free from dangerous impurities) never fails under compression [2, 3, 28]. This statement should not be considered as contradictory to the empirical knowledge of deformation and fracture of fcc metals [26], since detailed information on the mechanical properties of iridium was absent when the theory was formulated. Indeed, ductile rupture (necking to a point or a line) at room temperature is an inherent fracture mode at room temperature of fcc-metals whose melting points are lower than 1900°C, whereas BTF is the fracture mode (at low temperatures!) of fcc metals having melting points over 2000°C. Iridium wires show some degree of a necking at elevated temperatures (over 900°C) [20, 21]. Mechanical properties of another refractory fcc metal (rhodium) [11] support this point of view. The possible scenario of transgranular cleavage in iridium single crystals, according to which brittle cracks appear due to severe work-hardening of the fcc metal matrix during preliminary plastic deformation [22, 28, 29], may be extended to the case of the polycrystalline aggregate. However, exploration of the physical mechanisms of this phenomenon requires detailed transmission electron microscopy (TEM) of the dislocation structure in polycrystalline iridium.

The last feature of the fracture behavior of polycrystalline iridium that will be discussed here is GB cracking on the fracture surfaces of polycrystalline samples. It is clear that the number and shape of cracks depend on the sample shape and the geometry of applied load. Cracks advance on planes oriented close to the fracture surface normal and their growth direction is approximately parallel to the working surfaces of the sample. Macroscopic layered structure or morphology only reinforces this tendency in comparison with a typical polycrystalline material, but the main cause of such behavior is the addition of a wedging stress to the tensile load, which occurs under tension of small samples in a standard testing machine. The bending of layered samples, which causes the number of cracks on the fracture surfaces to increase, confirms this supposition. The possible cause of GB cracking may be the prevention of dislocation motion at GBs in iridium at room temperature [30], where <110> dislocations should have low mobility [31]. However this scenario should be examined in a TEM study. On the other hand, intergranular cracking may be the consequence of low cohesive strength of GBs in iridium, but exotic geometry of the cracks and absence of BIF regions on fracture surfaces are strong arguments against this explanation.

5. Conclusion

Brittle transgranular fracture is the sole inherent fracture mode of iridium at room temperature.

Acknowledgements

Helpful discussions with Dr. Alexander Yermakov, professor David Lupton, and professor Semyon Klotsman are gratefully acknowledged. It is also a pleasure to acknowledge the help of Mr. Vladimir Cheremnykh in the SEM study of fracture surfaces. This research was partially supported by the Russian Foundation for Basic Research (# 04-03-32073).

References

1. C. A. BROOKES, J. H. GREENWOOD and J. L. ROUTBORT, *J. Appl. Phys.* **39** (1968) 2391.
2. C. N. REID and J. L. ROUTBORT, *Metall. Trans.* **3** (1972) 2257.
3. A. YERMAKOV, P. PANFILOV and R. ADAMESKU, *J. Mater. Sci. Lett.* **9** (1990) 696.
4. B. L. MORDIKE and C. A. BROOKES, *Platinum Metals Rev.* **4** (1960) 94.
5. P. HAASEN, H. HIEBER and B. L. MORDIKE, *Zt. Metallkde* **56** (1965) 832.
6. G. REINACHER, *Metall* **18** (1964) 731.
7. C. A. BROOKES, J. H. GREENWOOD and J. L. ROUTBORT, *J. Inst. Metals* **98** (1970) 27.
8. M. H. KAMDAR, "Treatise on Materials Science and Technology. Embittlement of Engineering Alloys," edited by C. L. Briant and S. K. Banerji (Academic Press, 1983 in Russian, Moscow, "Metallurgia" 1988) Vol. 25, p. 333.
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. C. GANDHI and M. F. ASHBY, *Acta Metall.* **27** (1979) 1565.
12. J. M. MACLAREN, S. CRAMPIN, D. D. VVEDENSKY and M. E. EBERHART, *Phys. Rev. Lett.* **63** (1989) 2586.
13. S. CRAMPIN, K. HAMPEL, D. D. VVEDENSKY and J. M. MACLAREN, *J. Mater. Res.* **5** (1990) 2107.
14. YU. N. GORNOSTYREV, M. I. KATSNELSON, A. G. MIKHIN, YU. N. OSETSKII and A. V. TREFILOV, *Phys. Metals Metall.* **77** (1994) 154.
15. 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.
16. L. YAKOVENKOVA, B. GREENBERG, YU. SHAMANAEV and L. KARKINA, 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. 423.
17. S. P. CHEN, *Phil. Mag.* **66A** (1992) 1.
18. J. R. RICE, *J. Mech. Phys. Solids.* **40** (1992) 239.
19. B. FISCHER and D. F. LUPTON, *Private Communication* 1996.
20. P. PANFILOV, V. NOVGORODOV and A. YERMAKOV, *J. Mater. Sci. Lett.* **13** (1994) 137.
21. J. MERKER, B. FISCHER, D. F. LUPTON, R. WEILAND and J. WITTE, in Proceedings of the XIII International Conference on Processing and Fabrication of Advanced Materials (PFAM XIII), (Singapore, 6–8 December 2004), in press.
22. P. PANFILOV and A. YERMAKOV, *J. Mater. Sci.* **39** (2004) 4543.
23. V. N. KAIGORODOV, S. M. KLOTSMAN, A. V. ERMAKOV, V. K. RUDENKO, A. N. TIMOFEEV and N. I. TIMOFEEV, 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. 101.

24. Y. TATEYAMA and T. OHNO, *Phys. Rev. B* **67**, 174105 (2003).
25. N. TIMOFEEV, A. YERMAKOV, V. DMITRIEV and P. PANFILOV, "Metallurgy and Mechanical Behavior of Iridium" (Ekaterinburg: Urals Branch of Russian Academy of Science, 1996) (in Russian).
26. R. W. K. HONEYCOMBE, "The Plastic Deformation of Metals" (London, Edward Arnold, 1972).
27. L. HEATHERLY and E. P. GEORGE, *Acta Mater.* **49** (2001) 289.
28. P. PANFILOV, A. YERMAKOV, V. DMITRIEV and N. TIMOFEEV, *Platinum Metals Rev.* **35** (1991) 196.
29. 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.
30. P. PANFILOV and A. YERMAKOV, *Platinum Metals Rev.* **45** (2001) 179.
31. 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.

Received 20 December 2004
and accepted 31 March 2005