

J. H. Schneibel^a, M. P. Brady^a, J. J. Kruzic^b, R. O. Ritchie^c

^aMetals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, USA

^bDepartment of Mechanical Engineering, Oregon State University, Corvallis, USA

^cDepartment of Materials Science and Engineering, University of California, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, USA

On the improvement of the ductility of molybdenum by spinel (MgAl_2O_4) particles

Dedicated to Professor Wolfgang Blum on the occasion of his 65th birthday

In a 1967 patent, D. M. Scruggs found that the room temperature ductility of molybdenum is improved by adding several volume percent of MgAl_2O_4 spinel particles. The present work substantiates Scruggs' claim – with increasing MgAl_2O_4 volume fraction the ductility of Mo– MgAl_2O_4 is found to pass through a maximum near 2.5 vol%. Scruggs postulated that gettering of detrimental impurities was responsible for this effect. In the present work, fracture initiated at microcracks that formed on the Mo– MgAl_2O_4 specimen surfaces during tensile testing. The ductility maximum is interpreted in terms of the change in the microcrack size (which is assumed to scale with the grain size) and the ultimate tensile stress, as the MgAl_2O_4 volume fraction increases. Fracture occurs once a critical local stress-intensity factor, which is approximately independent of the MgAl_2O_4 volume fraction, is reached.

Keywords: Molybdenum; Ductility; Spinel; Metal–matrix composite

1. Introduction

The ductile-to-brittle transition temperature (DBTT) for molybdenum is near room temperature [1]. Because trace impurities and microstructure influence the DBTT, molybdenum and its alloys may be either ductile or brittle at room temperature. The DBTT can be reduced (or the room temperature ductility increased) by (a) reducing the grain size [1], (b) maintaining an atomic C/O ratio > 2 in order to have strong grain boundaries that resist intergranular fracture [2, 3], or (c) by rolling followed by a recovery anneal [1]. A novel procedure to improve the ductility of molybdenum has been proposed by Scruggs: incorporation of brittle MgAl_2O_4 spinel particles in molybdenum [4]. Normally, additions of brittle particles reduce the ductility of a material. This is well known from the literature on metal–matrix composites: void growth models describing this effect, as well as experimental data, have been documented by Clyne and Withers [5]. Scruggs, however, found that Mo containing several vol.% of MgAl_2O_4 particles exhibited higher room temperature ductility than nominally pure Mo. It ap-

pears that his work on Mo was motivated by earlier findings that showed that the room temperature ductility of chromium was improved by additions of MgO, much of which transformed into MgCr_2O_4 spinel during processing. Chromium is embrittled by nitrogen, and Scruggs suggested that its ductility was improved due to the removal of detrimental nitrogen by the $\text{MgO}/\text{MgCr}_2\text{O}_4$ particles. Recently, Brady et al. [6] repeated Scruggs' experiments using more advanced techniques than were available to Scruggs. They discovered that nitrogen was not in fact incorporated in the bulk of the $\text{MgO}/\text{MgCr}_2\text{O}_4$ oxide particles; instead evidence was found for N, C and S segregation/precipitation at the particle–matrix interfaces. In addition, they examined several particulate additions that did not form spinels, such as La_2O_3 , TiO_2 , and Y_2O_3 . Even though these particles showed evidence for interfacial segregation/precipitation, the corresponding Cr materials were, with the exception of Cr-2 wt.% TiO_2 , brittle in tension at room temperature. Therefore, Brady et al. concluded that other factors such as the propensity of the particles for providing crack nucleation sites, as well as particle-induced increases in the yield stress, may negate the beneficial effect of the impurity management by the particles.

Similar to the case of Cr, Scruggs attributed the high ductility of Mo– MgAl_2O_4 to the gettering of detrimental impurities. However, he did not pursue experiments to verify this mechanism. Also, his use of the ductility of nominally pure Mo as a baseline is problematic. Depending on its trace impurity content and metallurgical history, pure Mo can be ductile or brittle at room temperature. As soon as a small volume fraction of spinel is added, the trace impurity concentrations in the matrix, the location of the trace impurity atoms, and the grain size may change significantly. In order to explore the reported MgAl_2O_4 ductilization effect, it is preferable to show that, starting at a small spinel volume fraction, the ductility increases monotonically with the spinel volume fraction. With such an approach, it is more likely that the trace impurity concentration and grain size will change in a continuous and well-defined manner as MgAl_2O_4 is added. It is the aim of the present work to perform such experiments with the objective of clarifying the mechanism behind the purported ductilizing effect of MgAl_2O_4 .

2. Experimental procedure

Specimens were fabricated from molybdenum (purity 99.95 %, particle size 3–7 μm) and MgAl_2O_4 spinel (–635 mesh size; $\leq 20 \mu\text{m}$) powders. B and Zr were added to strengthen the grain boundaries [7]. They were added as Mo_2Zr (–325 mesh size; $\leq 45 \mu\text{m}$) and MoB (–325 mesh size; $\leq 45 \mu\text{m}$) powders. Batches of 300 g each of Mo– MgAl_2O_4 materials with MgAl_2O_4 volume fractions of 0.1, 2.5, and 5 % (0.035, 0.89, and 1.81 wt.%), and Mo_2Zr and MoB additions corresponding to 0.16 at.% (0.15 wt.%) Zr and 0.09 at.% (0.01 wt.%) B were blended for 8 h in argon in rotating bottles containing ZrO_2 media. Consolidation was carried out in a graphite hot-press in vacuum (mechanical pump) for 1 h at 1800 °C and 21 MPa. The carbon content of the consolidated Mg–5 vol% MgAl_2O_4 material was determined by combustion analysis to be 0.024 at.% (0.003 wt.%). The oxygen concentration was not measured because it was determined almost exclusively by the volume fraction of the MgAl_2O_4 particles.

Tensile specimens with a gauge length of 12.7 mm and a rectangular gauge section of approximately $0.7 \times 3 \text{ mm}$ were electro-discharge machined. Their gauge sections were ground with successively finer SiC paper with a final grit size of 600. Mechanical tests were carried out at constant crosshead speeds at room temperature. Engineering stresses and strains were evaluated from plots of the load vs. the cross-head displacement. Engineering strain rates of 10^{-3} and 10^{-2} s^{-1} were employed.

Metallographic sections and fracture surfaces were examined using optical and scanning electron microscopes. Etching was carried out with Murakami's reagent. Grain sizes were determined as the mean lineal intercept length. In order to obtain an error estimate, three micrographs with typically 200 intercepts each were evaluated for each material. Metallographic sections and fracture surfaces were examined in a scanning electron microscope (SEM) including compositional analysis by energy-dispersive X-ray spectroscopy (EDS). One specimen was fractured in a scanning Auger microscope, followed by chemical analysis of the features on the fracture surface.

3. Results

An optical micrograph of a polished and etched section of Mo–2.5 vol.% MgAl_2O_4 , shown in Fig. 1, clearly indicates the grain boundaries and spinel particles. The composition of the spinel particles was verified by EDS. The specimen surface also exhibits dimples which are either residual porosity left over from the hot-pressing or were formed by the pull-out of spinel particles. Multiphase agglomerates, typically 50 μm in size and containing ZrO_2 , were also found, and are thought to be the remnants of Mo_2Zr particles that reacted with residual oxygen to form ZrO_2 . It is quite possible that the Zr was oxidized by residual oxygen in the hot-press and did therefore not getter residual oxygen contained in the Mo powder.

Uniaxial tensile (engineering) stress–strain data for Mo–2.5 vol.% MgAl_2O_4 , tested at a strain rate of 10^{-2} s^{-1} , are plotted in Fig. 2. This figure is representative of all the mechanical tests conducted, in that the stress/strain curves showed an upper and lower yield point (except when the

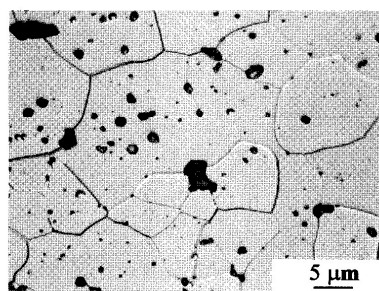


Fig. 1. Optical micrograph of polished and etched section of Mo–2.5 vol.% MgAl_2O_4 , showing the grain boundaries and the dark MgAl_2O_4 particles.

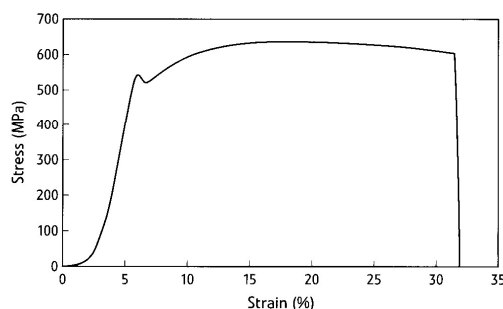


Fig. 2. Engineering stress–strain curve for Mo–2.5 vol.% MgAl_2O_4 pulled in tension at a strain rate of 10^{-2} s^{-1} at room temperature. The strain in this plot includes the machine compliance and the elastic deformation of the specimen.

fracture strain was very small). The grain sizes and mechanical test results are summarized in Table 1. The 0.2 % yield stress increases linearly with the MgAl_2O_4 volume fraction (Fig. 3), whereas the variation in ductility is more complex (Fig. 4). In particular, the ductility increases significantly as the MgAl_2O_4 volume fraction increases from 0.1 to 2.5 %. While the ductility values in this work were not determined directly by measurements at the gauge length, they are deemed reliable enough to verify this trend. Figure 4 suggests that the ductility decreases for 5 % MgAl_2O_4 .

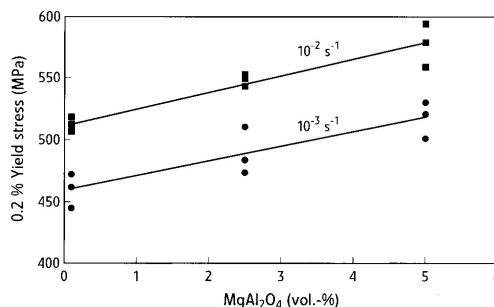


Fig. 3. Yield stress of Mo– MgAl_2O_4 vs. MgAl_2O_4 volume fraction, for strain rates of 10^{-3} and 10^{-2} s^{-1} .

Table 1. Grain sizes and mechanical test data for the Mo–MgAl₂O₄ alloys.

MgAl ₂ O ₄ (vol.%)	Grain size (μm)	Strain rate (1/s)	0.2 % Yield stress (MPa)	Upper yield point (MPa)	Lower yield point (MPa)	UTS (MPa)	Elongation to fracture (%)*
0.1	21.9 \pm 0.8	0.001	462	462	437	560	7.7
0.1	21.9 \pm 0.8	0.001	472	472	447	557	5.8
0.1	21.9 \pm 0.8	0.001	445	445	418	556	12.9
2.5	16.9 \pm 1.3	0.001	510	513	489	622	15.5
2.5	16.9 \pm 1.3	0.001	484	489	468	598	26.7
2.5	16.9 \pm 1.3	0.001	474	478	455	580	22.4
5	13.5 \pm 0.5	0.001	521	523	511	617	12.8
5	13.5 \pm 0.5	0.001	530	532	518	624	12.4
5	13.5 \pm 0.5	0.001	501	503	488	589	10.7
0.1	21.9 \pm 0.8	0.01	506	507	487	540	2.8
0.1	21.9 \pm 0.8	0.01	518	518	485	518	1.1
0.1	21.9 \pm 0.8	0.01	512	512		512	0.4
2.5	16.9 \pm 1.3	0.01	548	551	528	645	13.5
2.5	16.9 \pm 1.3	0.01	542	545	518	636	25.6
2.5	16.9 \pm 1.3	0.01	552	555	527	642	10.4
5	13.5 \pm 0.5	0.01	558	570	553	627	5.4
5	13.5 \pm 0.5	0.01	578	581	563	655	10.5
5	13.5 \pm 0.5	0.01	594	594	570	607	2.6

* The elongation to fracture was evaluated from the load vs. cross-head displacement curves; it was not directly measured

While this result is not statistically ensured, it is consistent with the notion that the ductility must eventually decrease if enough MgAl₂O₄ is added.

The fracture of all Mo–MgAl₂O₄ specimens was predominantly intergranular. A scanning Auger micrograph of a fracture surface of Mo-5 vol.% MgAl₂O₄ fractured in situ is shown in Fig. 5. The grain boundary facets revealed carbon and oxygen. However, since carbon and oxygen were also found on the cleavage surfaces, adsorption from the ultra-high vacuum environment was probably involved, and further work will be needed to clarify the grain boundary segregation chemistry. After tensile testing to fracture, a previously polished surface showed intergranular microcracks (Fig. 6a). The high local strains experienced in the Mo matrix during decohesion at intragranular MgAl₂O₄ particles are illustrated in Fig. 6b. A cross-section through

a surface microcrack is shown in Fig. 7. The surface microcracks exhibited an average spacing of ~ 100 to $200\ \mu\text{m}$ along the gauge length.

4. Discussion

As the spinel volume fraction in MgAl₂O₄ is increased, the grain size decreases and the yield stress increases. According to Hazzledine [8], the “indirect” hardening due to the decreasing grain size is expected to be more important than the “direct” hardening due to the interaction of dislocations with the particles themselves. The yield strength values are

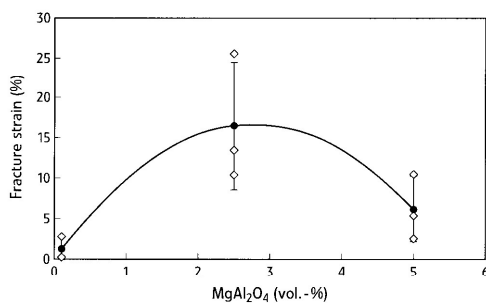


Fig. 4. Room temperature ductility of Mo–MgAl₂O₄ as a function of the MgAl₂O₄ volume fraction, for a strain rate of $10^{-2}\ \text{s}^{-1}$. In addition to the individual data points, average values including error bars with the standard deviation have been plotted.

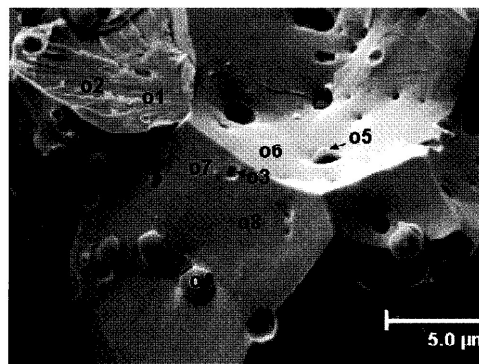


Fig. 5. Scanning Auger micrograph of fracture surface of Mg-5 vol.% MgAl₂O₄, showing grain boundary facets, a cleavage facet (upper left), MgAl₂O₄ spinel particles, and dimples originating from the pull-out of spinel particles.

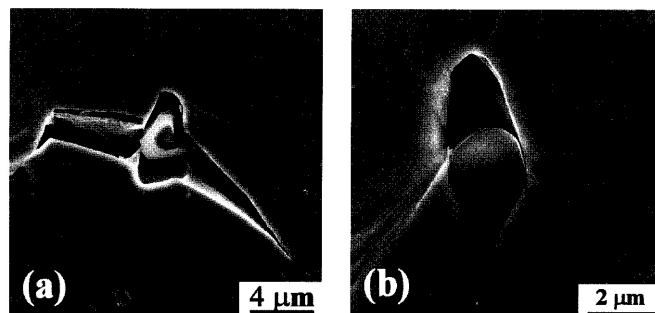


Fig. 6. SEM micrographs of polished surface of Mo-2.5 vol.% MgAl_2O_4 after a room temperature tensile test showing (a) grain boundary fracture at a spinel particle and (b) particle-matrix decohesion in the grain interior.

consistent with a Hall-Petch relationship (Fig. 8). They are also consistent with published data for pure Mo. However, the Hall-Petch slope of the present data appears to be lower than that for pure Mo.

In spite of substantial scatter in the ductility values, the mechanical test data for the Mo- MgAl_2O_4 alloys show clearly a ductility increase as the MgAl_2O_4 volume fraction is raised from 0.1 to 2.5 %. The fracture mode was predominantly intergranular. In molybdenum, the segregant most likely to cause grain boundary embrittlement is oxygen [2, 3]. Compared to the oxygen concentration of MgAl_2O_4 , i.e., 57 at.% oxygen, the residual oxygen content in the Mo powder is negligible. Any changes in the oxygen concentration of the spinel particles due to gettering of residual oxygen in the Mo would therefore be too small to be experimentally verifiable. For this reason no attempt was made to precisely analyze the bulk oxygen concentration of the spinel particles.

Reductions in the detrimental oxygen segregation at the grain boundaries with increasing MgAl_2O_4 volume fraction may be a factor contributing to the ductility maximum. The data to assess this possibility are presently not available. However, the reduction in the grain size with increasing spinel volume fraction could also play a role. In general, the ductility of nominally pure Mo increases as the grain size decreases, which is related to the influence of the grain size on the DBTT. Essentially, above a certain grain size, the DBTT is above room temperature and brittle behavior is observed; at smaller grain sizes the DBTT is below room temperature and ductile behavior is observed. For example,

when the grain size of Mo is decreased from 100 grains/ mm^2 ($\approx 100 \mu\text{m}$) to 500 grains/ mm^2 ($\approx 45 \mu\text{m}$), the reduction in area after tensile testing at room temperature increases from 6 to 67 % [1]. This grain-size effect has been related to the mechanisms causing crack initiation and final brittle fracture (e.g., crack nucleation at dislocation pile-ups or twins). Smaller grain sizes tend to allow higher applied stresses and strains before brittle fracture occurs [9]. While similar arguments can be applied to Mo- MgAl_2O_4 , it may at the same time be considered as a metal-matrix composite (MMC) containing brittle particles. As the spinel volume fraction increases, one would expect the ductility of this MMC to decrease [5]. In general, the ductility decrease depends also on the size and size distribution of the particles, as well as their spatial distribution. Since the goal of the present experiments was to keep these parameters constant, they will not be considered here. The ductility, or fracture strain, ϵ_f , is thus a function of two variables: the grain size ℓ and the MgAl_2O_4 volume fraction c (whereby ℓ is a function of c). The change in the ductility as a function of the MgAl_2O_4 volume fraction c can be written as:

$$d\epsilon_f = \frac{\partial \epsilon_f}{\partial \ell} d\ell + \frac{\partial \epsilon_f}{\partial c} dc \quad (1)$$

or

$$\frac{d\epsilon_f}{dc} = \left(\frac{\partial \epsilon_f}{\partial \ell} \right) \left(\frac{d\ell}{dc} \right) + \frac{\partial \epsilon_f}{\partial c} \quad (2)$$

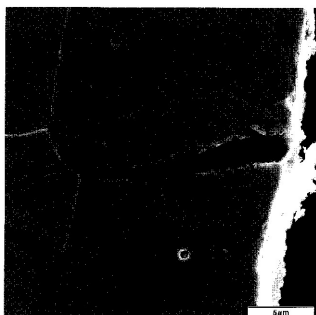


Fig. 7. Cross section through surface microcrack of Mg-2.5vol.% MgAl_2O_4 after tensile fracture at 10^{-3} s^{-1} at room temperature.

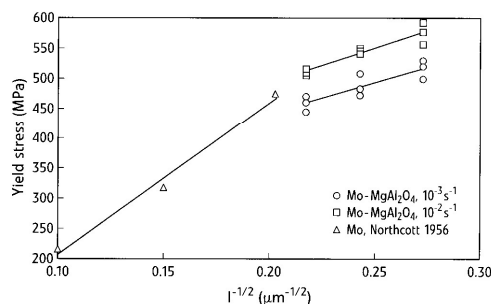


Fig. 8. Hall-Petch plot of the yield stress data, including published data for pure Mo [1].

Table 2. Evaluation of initiation fracture toughness of surface microcracks

MgAl ₂ O ₄ (vol.%)	Grain size μm	Strain rate (s ⁻¹)	UTS (MPa)	K_q (MPa m ^{1/2})	K_q (mod) (MPa m ^{1/2})
0.1	21.9	0.001	558	7.3	7.3
2.5	16.9	0.001	600	6.9	7.1
5.0	13.5	0.001	610	6.3	6.6
0.1	21.9	0.01	523	6.9	6.9
2.5	16.9	0.01	641	7.4	7.6
5.0	13.5	0.01	630	6.5	6.8

If, for small volume fractions, the product on the right-hand side of Eq. (2) is sufficiently large, the ductility increases initially. For higher volume fractions, the second term corresponding to embrittlement by the spinel particles will eventually outweigh the first one and the ductility will decrease. In order to verify Eq. (2), significantly more experimental data would be required.

The above interpretation does not consider the particular fracture mechanism; specifically, it does not take into account the microcracks that form on the specimen surfaces as they are deformed. The ductility observed in the present experiments appears to be determined by sudden fracture that occurs when one of these microcracks reaches a critical local stress-intensity factor required for propagation. The fact that visual inspection of the specimens did not show any evidence for necking is in agreement with this sequence of events.

The surface microcracks were not associated with the oxidized Mo₂Zr particles (which might also be a nucleation site for fracture). The length of the microcracks is expected to scale with the grain size. Grain sizes typically exhibit a log-normal size distribution [10], and the individual grain-boundary facets are expected to exhibit a similar distribution. Final fracture is expected to originate at the largest cracked surface facet in the gauge length. It is also conceivable that occasionally two or more facets are oriented such that a crack initiating at the surface propagates immediately along these facets without stopping at the end of the first one. Qualitatively, the low probability for forming the largest microcrack may be the reason for the substantial scatter in the ductility values. The scatter of the ductility values may thus be analogous to the Weibull statistics for the fracture stress in ceramics [11], except that in ceramics the largest flaw leading to fracture pre-exists in the material, whereas in Mo–MgAl₂O₄ the surface flaws are created during the tensile tests.

Assuming that the size of the largest surface crack in a specimen (which is responsible for final fracture) scales with the grain size, the local critical stress-intensity factor for an edge crack can be estimated as [12]:

$$K_q = 1.12 \sigma_{\text{UTS}} (\pi 2\ell)^{1/2} \quad (3)$$

Here the crack length was approximated by twice the value of the grain size, ℓ , representative of the fact that the largest grain facet crack will cause ultimate failure. The grain sizes and average ultimate tensile stress for each material, and the critical local stress-intensity factors K_q calculated from Eq. 3 are listed in Table 2. Since the Mo spinel interfaces appear to be weak (see Fig. 6b), the σ_{UTS} values were mod-

ified by assuming that the spinel particles do not carry any load, i. e., by dividing σ_{UTS} by $(1 - c)$, where c is the spinel volume fraction. The resulting modified values for the local stress-intensity factor, K_q (mod) are also listed in Table 2. These results indicate that, for a given strain rate, the values of K_q are nearly independent of the MgAl₂O₄ volume fraction, i. e., fracture at a particular strain rate occurs once a critical local stress-intensity factor is reached.

Whereas the above result is encouraging, it would be difficult to reverse the argument, i. e., to determine the strain at which the critical local stress-intensity factor is reached, as this would require detailed knowledge of the crack-tip stress field as a function of strain. This information is not available and would be difficult to generate. Presently, all that can be said is that the ductility maximum observed for Mo–2.5 vol.% MgAl₂O₄ can be interpreted in terms of the dependence of the length of the surface microcracks, and the ultimate tensile strength, on the MgAl₂O₄ volume fraction. Whereas the surface microcracks become smaller with increasing MgAl₂O₄ volume fraction, the ultimate tensile strength tends to level off or decrease after an initial increase.

We have shown that Scruggs' ductility enhancement of Mo by MgAl₂O₄ spinel additions does occur, although the effect can be interpreted in terms different from those originally proposed. Additional experiments are worthwhile in order to substantiate the current mechanism. For example, if one clad the present materials with a well-bonded, ductile material in order to inhibit the surface microcracking, the intergranular microcracking might change from a surface to a subsurface event, presumably leading to higher ductility. Also, suitable alloying might result in strengthening of the grain boundaries which might inhibit the surface microcracking. The fracture mode would then change to cleavage or ductile failure, most likely leading to higher strains to fracture. This leaves open the possibility that mechanisms other than surface microcracking may result in the Scruggs effect.

5. Conclusions

In his 1967 patent, Scruggs attributed the improvement of the ductility of Mo by additions of MgAl₂O₄ spinel particles to the gettering of detrimental impurities. The present work substantiates Scruggs finding that the ductility of Mo–MgAl₂O₄ increases initially with increasing MgAl₂O₄ volume fraction. Whereas Scruggs' interpretation cannot be ruled out, the ductility results can, in contrast to his explanation, also be interpreted in terms of the formation of mi-

crocracks which propagate catastrophically once a critical local stress-intensity factor is reached. The critical stress-intensity factor is estimated from the crack size (which is assumed to scale with the grain size) and the ultimate tensile stress. Unfortunately, it would be difficult to use this interpretation to predict the ductility. Also, it is yet to be seen how the Scruggs effect would change if there was a transition in fracture mode from intergranular to transgranular or ductile fracture.

The authors acknowledge scanning Auger microscopy by H. M. Meyers III. This work was sponsored by the Office of Fossil Energy, Advanced Research Materials (ARM) Program, U.S. Department of Energy, under contract no. DE-AC05-00OR22725 with Oak Ridge National Laboratory managed by UT-Battelle, LLC (for JHS and MPB), and under contract no. DE-AC03-76SF0098 with the Lawrence Berkeley National Laboratory (for ROR).

References

- [1] L. Northcott: Molybdenum, Academic Press, New York (1956).
- [2] J. Wadsworth, T.G. Nieh, J.J. Stephens: *Scr. Metall.* 20 (1986) 637.
- [3] A. Kumar, B.L. Eyre: *Proc. Royal Soc. Lond. A* 370 (1980) 431.
- [4] D.M. Scruggs: Ductile molybdenum composition containing a spinel dispersion, United States Patent 3 320 036, Patented May 16, 1967.
- [5] T.W. Clyne, P.J. Withers: *An Introduction to Metal Matrix Composites*, Cambridge University Press, Cambridge (1993).
- [6] M.P. Brady, I.M. Anderson, M.L. Weaver, H.M. Meyer, L.R. Walker, M.K. Miller, D.J. Larson, I.G. Wright, V.K. Sikka, A. Rar, G.M. Pharr, J.R. Keiser, C.A. Walls: *Mater. Sci. Eng. A* 358 (2003) 243.
- [7] M.K. Miller, E.A. Kenik, M.S. Mousa, K.F. Russell, A.J. Bryhan: *Scr. Metall.* 46 (2002) 299.
- [8] P.M. Hazzledine: *Scripta Metall. Mater.* 26 (1992) 57.
- [9] W.S. Owen, D. Hull: *The Fracture Transitions in Refractory Metals*, in *Refractory Metals and Alloys II*, *Proc. Metall. Soc. Conf.*, M. Semchyshen and I. Perlmutter (Eds.), Interscience Publishers, John Wiley & Sons, New York (1963).
- [10] N.P. Louat: *Acta Metall.* 22 (1974) 721.
- [11] J.J. Petrovic: *Metall. Trans. A* 18 (1987) 1829.
- [12] T.L. Anderson, *Fracture Mechanics Fundamentals and Applications*, 2nd ed., CRC Press, Boca Raton, FL (1995) p. 688.

(Received January 7, 2005; accepted March 16, 2005)

Correspondence address

Dr. Joachim H. Schneibel
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6115, USA
Tel.: +1 865 576 4644
Fax: +1 865 574 7659
E-mail: schneibeljh@ornl.gov