Mo-Si-B Alloy Development

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ABSTRACT

Mo-Si-B silicides consisting of the phases α-Mo (Mo solid solution), Mo_3Si, and Mo_5SiB_2 exhibit melting points on the order of 2000°C and have potential as ultra-high temperature structural materials. In order to obtain satisfactory oxidation and creep resistance, the volume fraction of the α-Mo phase needs to be kept small. Therefore, in order to maintain satisfactory fracture toughness values, the ductility of the α-Mo phase needs to be improved. One way to do this is to add small amounts (1.5 at%) of Zr to the Mo-Si-B alloys. The room temperature ductility of molybdenum is also improved by the addition of a few vol.% of $MgAl_2O_4$ spinel particles.

INTRODUCTION

In order to increase the thermodynamic efficiency of fossil energy systems, strong, tough and oxidation resistant materials capable of service temperatures well beyond 1000°C are needed. Berczik[1,2] has pioneered alloys consisting of Mo_3Si, Mo_5SiB_2 ("T2-phase"), and a toughening Mo solid solution (α-Mo). The oxidation resistance, creep strength, and room temperature fracture toughness of such Mo-Si-B intermetallic alloys are competitive with the corresponding values for nickel-base superalloys.[3,4] However, so far these properties have not been achieved in one and the same alloy. Further progress needs to be made in improving the room temperature ductility of the α-Mo phase. If that can be achieved, less α-Mo will be needed to reach an adequate value of the fracture toughness. Less α-Mo also translates into improved oxidation and creep resistance. It is shown that the fracture toughness of Mo-Si-B can be improved by microalloying with Zr. It is also shown that the room temperature ductility of Mo can be improved by adding $MgAl_2O_4$

spinel particles. This effect was first demonstrated in 1967 by Scruggs,[5] but has never been independently verified. While we do find such a ductility enhancement, our interpretation of the ductility improvement differs from that proposed by Scruggs.

EXPERIMENTAL PROCEDURES

Alloys were prepared by arc-melting elemental starting materials in a partial pressure of argon (70 kPa) on a water-cooled copper hearth. The purity of the starting materials Mo, Si, Zr and B was 99.95, 99.99, 99.5, and 99.5 weight % (wt%), respectively. Alloy compositions will stated in atomic % (at%) unless otherwise noted. The alloys were re-melted several times in order to improve their homogeneity and drop-cast into 12.5 mm diameter rods or 12.5×6.3 mm rectangular bars. The cast alloys were homogenized by vacuum-annealing for 24 hrs at 1600ºC.

Room temperature fracture toughness values (K_q) were estimated from the controlled fracture of chevron-notched specimens in three-point bending as:

$$K_q = \sqrt{\frac{(W/A)E}{1-\nu^2}}, \qquad (1)$$

where W is the energy required to break the specimen, A is the area traversed by the crack, E is Young´s modulus (329 GPa), and ν is Poisson´s ratio (0.288). The span for the three-point bend testing was 40 mm, and the cross-head speed was 10 μm/s.

Mo-$MgAl_2O_4$ specimens were fabricated from molybdenum (purity 99.95%, particle size 3-7 μm) and $MgAl_2O_4$ spinel powder (-635 mesh size; ≤ 20 μm). B and Zr were added to strengthen the grain boundaries [6]. They were added as Mo_2Zr and MoB (-325 mesh size; ≤ 45 μm) 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 hrs in argon in rotating bottles containing ZrO_2 media. Consolidation was carried out in a graphite hot-press in vacuum (mechanical pump) for 1 hr 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 governed 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 cross section of approximately 0.7×3 mm were electro-discharge machined. The 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. Compositions were measured via energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM). 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. One specimen was fractured in a scanning Auger microscope and the chemical composition of features on the fracture surface was analyzed.

RESULTS AND DISCUSSION

MICROALLOYING WITH Zr

Silicon is a potent strengthener of molybdenum. Bruckart *et al.*[7] report that an addition of 1.7 at% Si to Mo increases the room temperature 0.2% yield stress from 509 to 840 MPa. At the same time, the total elongation decreases from 24 to 3%, i.e., Si embrittles Mo. Therefore, if Zr additions to Mo-Si-B reduce the solubility of Si in the α-Mo phase, the fracture toughness is expected to increase. Using EDS, the Si concentration in the α-Mo phase of Mo-12Si-8.5B and

Mo-12Si-8.5B-1.5Zr was determined using the known composition of the Mo_3Si phase as a standard. These concentrations should only be used for comparative purposes since the actual Si concentration in the α-Mo phase is probably lower. While the Si concentration in the α-Mo phase of the alloy without Zr was determined to be 4.0±0.6 at%, that in the Zr-containing alloy was slightly lower, namely, 3.1±0.1 at%. This result suggests the possibility that the beneficial effect of Zr on the fracture toughness of Mo-Si-B occurs via a reduction in the concentration of Si in solid solution. Chevron-notch fracture toughness experiments were carried out with cast and annealed Mo-2.5Si-0.1Zr and Mo-2.5Si-0.5Zr to determine whether Zr does indeed improve the fracture toughness of Mo-Si. The experimental data are summarized in Table 1. The two alloys exhibited comparable fracture toughness values. However, the 0.1Zr alloy fractured transgranularly, whereas the 0.5Zr alloy exhibited partial intergranular failure. For these reasons the experiments with Mo-Si-Zr are not conclusive at this point.

Table 1. Room temperature fracture toughness K_q for Mo-2.5Si-xZr.

Composition, at%	A, mm^2	W, mJ	K_q, MPa m$^{1/2}$
Mo-2.5Si-0.1Zr	5.50	8.36	23.3
"	5.47	7.94	22.8
Mo-2.5Si-0.5Zr	5.57	8.95	24.0
"	6.40	9.66	23.3
"	6.56	9.30	22.6

DUCTILIZATION WITH SPINEL PARTICLES

In the 1960's, Scruggs found that powder-metallurgical Cr becomes more ductile when MgO particles (that transform partially into $MgCr_2O_4$ spinel particles) are added.[8] Under the Fossil Energy Materials Program, M. P. Brady verified this ductilizing effect.[9] He determined that segregation of detrimental impurities such as nitrogen to the particle-matrix interface is one of the factors responsible for ductilization. Scruggs suggested that not only Cr, but also Mo can be ductilized by adding spinel particles.[5] An initial experiment carried out to verify the Scruggs effect seemed successful[3,10]. However, more detailed experiments[10] failed to verify the effect. It turned out that the starting Mo powder was contaminated with oxygen and therefore embrittling MoO_2 formed. In the present work, another series of Mo-$MgAl_2O_4$ alloys fabricated from a new source of Mo powder was therefore prepared and studied.[11]

An optical micrograph of a polished and etched section of Mo-2.5 vol% $MgAl_2O_4$, shown in Figure 1, clearly indicates the grain boundaries and spinel particles. The composition of the spinel particles was verified by EDS. 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 likely that the Zr was oxidized by residual oxygen during hot-pressing and did therefore not getter the residual oxygen contained in the Mo powder.

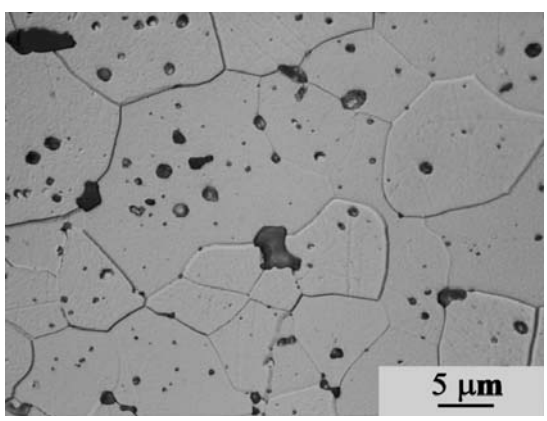

Fig. 1. Optical micrograph of polished and etched section of Mo-2.5 vol% $MgAl_2O_4$, showing the grain boundaries and the dark $MgAl_2O_4$ particles.

A uniaxial tensile (engineering) stress-strain curve for Mo-2.5 vol% $MgAl_2O_4$, tested at a strain rate of 10^{-2} s^{-1}, is plotted in Fig. 2. This figure is representative of all the mechanical tests conducted. In particular, the stress/strain curves showed an upper and lower yield point (except when the fracture strain was very small). Figure 3 shows that the ductility increases significantly as the $MgAl_2O_4$ volume fraction increases from 0.1 to 2.5%. The mechanical property values and grain sizes of the three alloys investigated are summarized in Table 2.

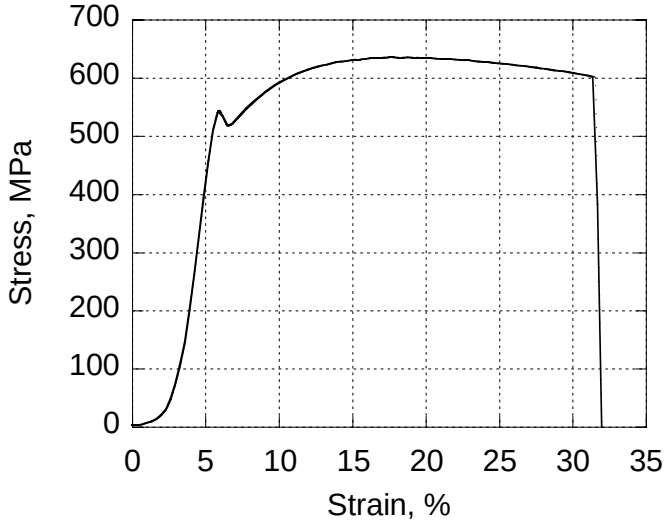

Fig. 2. Engineering stress-strain curve for Mo-2.5 vol% $MgAl_2O_4$ pulled in tension at a strain rate of 10^{-2} s^{-1} at room temperature. The strain in this plot includes the machine compliance and the elastic deformation of the specimen.

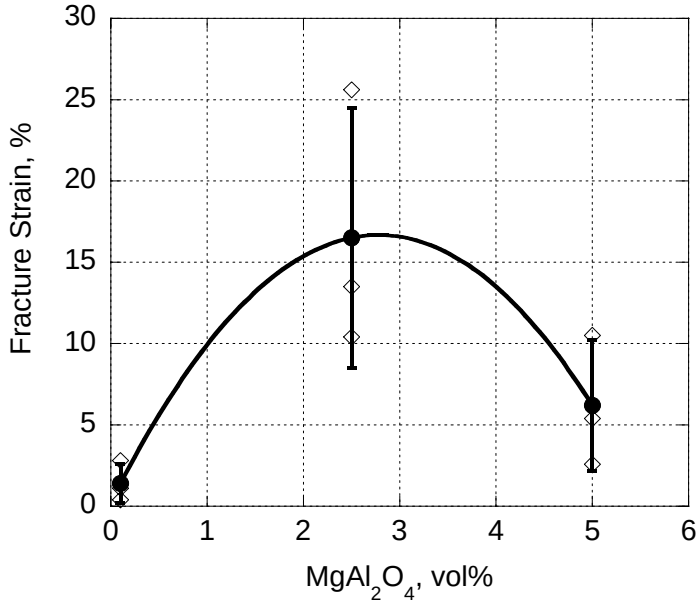

Fig. 3. Room temperature ductility of Mo-$MgAl_2O_4$ as a function of the $MgAl_2O_4$ volume fraction, for a strain rate of 10^{-2} s^{-1}. In addition to the individual data points, average values including error bars with the standard deviation have been plotted.

Table 2. Grain sizes and mechanical test data for the Mo-$MgAl_2O_4$ alloys.

$MgAl_2O_4$, 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±0.8	0.001	462	462	437	560	7.7
0.1	"	"	472	472	447	557	5.8
0.1	"	"	445	445	418	556	12.9
2.5	16.9±1.3	0.001	510	513	489	622	15.5
2.5	"	"	484	489	468	598	26.7
2.5	"	"	474	478	455	580	22.4
5	13.5±0.5	0.001	521	523	511	617	12.8
5	"	"	530	532	518	624	12.4
5	"	"	501	503	488	589	10.7
0.1	21.9±0.8	0.01	506	507	487	540	2.8
0.1	"	"	518	518	485	518	1.1
0.1	"	"	512	512		512	0.4
2.5	16.9±1.3	0.01	548	551	528	645	13.5
2.5	"	"	542	545	518	636	25.6
2.5	"	"	552	555	527	642	10.4
5	13.5±0.5	0.01	558	570	553	627	5.4
5	"	"	578	581	563	655	10.5
5	"	"	594	594	570	607	2.6

The fracture of the Mo-$MgAl_2O_4$ specimens was predominantly intergranular. A scanning Auger micrograph of a fracture surface of Mo-5 vol% $MgAl_2O_4$ fractured *in situ* is shown in Fig. 4. The grain boundary facets revealed carbon and oxygen. However, since carbon and oxygen were also found on cleavage surfaces, adsorption from the ultra-high vacuum environment was probably a factor, and further work will be needed to clarify the grain boundary segregation chemistry.

After tensile testing to fracture, the gauge lengths of the Mo-2.5 vol% $MgAl_2O_4$ specimens exhibited surface microcracks with an average spacing of ~100 to 200 μm. A cross-section through such a surface microcrack is shown in Fig. 5.

Table 2 shows that the Mo grain size decreases with increasing spinel volume fraction. 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]:

$$K_q = 1.12\ [\sigma_{UTS}/(1-c)]\ (2\pi\ \ell\ )^{1/2}. \qquad (2)$$

Here the crack length was approximated by twice the value of the grain size, ℓ , representative of the fact that the largest grain boundary crack will cause ultimate failure. Since the Mo-spinel interfaces are considered weak, the σ_{UTS} values were modified 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 grain sizes and average ultimate tensile stress for each material, and the critical local stress-intensity factors K_q calculated from Eqn. 2 are listed in Table 3. These results indicate that, for a given strain rate, the

values of K_q are nearly independent of the $MgAl_2O_4$ volume fraction, i.e., fracture at a particular strain rate occurs once a critical local stress-intensity factor is reached.

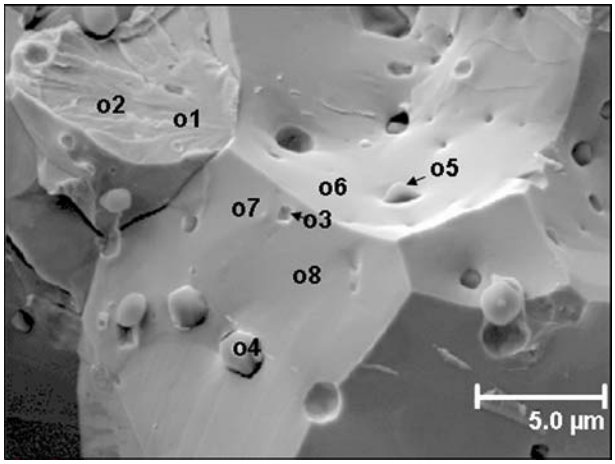

Fig. 4. Scanning Auger micrograph of fracture surface of Mo-5 vol% $MgAl_2O_4$, showing grain boundary facets, a cleavage facet (upper left), $MgAl_2O_4$ spinel particles, and dimples originating from the pull-out of spinel particles.

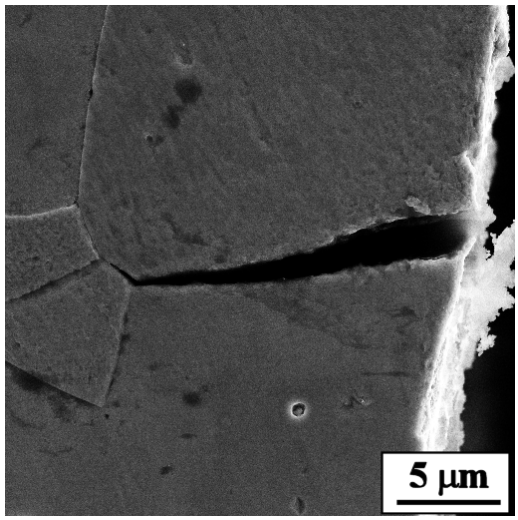

Fig. 5. Cross section through surface microcrack of Mo-2.5 vol% $MgAl_2O_4$ after tensile fracture at 10^{-3} s^{-1} at room temperature.

We have shown that Scruggs' ductility enhancement of Mo by $MgAl_2O_4$ 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 would 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.

Table 3. Evaluation of the local critical stress intensity factor of the microcracks

$MgAl_2O_4$, vol%	Grain Size, μm	Strain Rate, s^{-1}	UTS, MPa	K_q, MPa $m^{½}$
0.1	21.9	0.001	558	7.3
2.5	16.9	"	600	7.1
5.0	13.5	"	610	6.6
0.1	21.9	0.01	523	6.9
2.5	16.9	"	641	7.6
5.0	13.5	"	630	6.8

SUMMARY AND CONCLUSIONS

The room temperature fracture toughness of Mo-Si-B can be improved by alloying with Zr. Possible reasons include a reduction in the Si concentration of the α-Mo solid solution phase. Also, Zr is likely to strengthen the grain boundaries. The Scruggs approach for improving the room temperature ductility of Mo by adding $MgAl_2O_4$ spinel particles has been verified. However, while Scruggs attributed the ductility improvement to gettering of detrimental impurities by the spinel particles, the present data can be interpreted in terms of grain refinement. Several issues remain. In particular it is not known whether the ductility enhancement by spinel particles would occur if the fracture mode would be changed from intergranular to transgranular. It is also not clear in which way the Scruggs mechanism would be influenced by Si in solid solution.

ACKNOWLEDGEMENTS

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