EFFECT OF Zr, B AND C ADDITIONS ON THE DUCTILITY OF MOLYBDENUM

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Abstract

Through the addition of Zr, Al, C and B at the parts per million level to molybdenum, a significant improvement in ductility of a molybdenum weldment has been produced. This improvement approaches 20% ductility in GTA weldments in 6.5-mm-thick plate compared to the traditional 3% ductility. This improvement has been achieved by improving the normally low fracture stress of grain boundaries. Atom probe tomography revealed segregation of zirconium, boron and carbon to and the depletion of oxygen and nitrogen at the grain boundaries in the base metal.

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Introduction

Molybdenum-based alloys possess a unique combination of physical properties including high strength at elevated temperatures, high thermal conductivity, low coefficient of thermal expansion, and excellent performance in neutron flux environments. However, their use in structural applications has been limited by the very low ductility of welds. For example, weldments made in the best commercially available molybdenum alloys have only ~3% elongation at room temperature.[1] This lack of ductility has been especially apparent for welds made in thick material where triaxial constraint predominates. However, Bryhan has shown that controlled additions of substitutional and interstitial alloying elements can provide almost 20% elongation from gas-tungsten arc (GTA) welds in 6.5-mm-thick material.[1]

In molybdenum-based alloys, the two characteristics thought to have the greatest potential for improving ductility are the distribution and content of interstitial elements and the grain size of the recrystallized metal. For the past 50 years, much of the effort toward improving the ductility of welded molybdenum has focused on either reducing atmospheric element contamination or the addition of substitutional elements such as rhenium. The hypothesis has been that intergranular fracture is caused by contaminants weakening the grain boundaries. Further, because of the strain rate sensitivity of body centered cubic metals and the rapid grain growth during welding, it has been thought that if the grains could be kept relatively small and the boundaries free of contaminants, the ductility of weldments could be improved. Alternatively, contaminants might better be tolerated if an element such as rhenium were added[2].

Previous investigations show that freedom from contamination alone will not assure ductility. Brosse et al.[3] examined the hypothesis that molybdenum exhibits intergranular brittleness even without any contamination of the grain boundaries. This study used electron beam melted and purified (< 2.5 wppm O) single crystals joined along the (100) or (110) crystal axes by electron bombardment. Intergranular cohesion was evaluated by four-point bending. All of the bicrystals exhibited intergranular fracture with less than ~1 wppm of foreign elements at the grain boundaries. It was concluded that the observed intergranular brittleness was inherent in the molybdenum bicrystals and not caused by segregation or precipitation.

Kumar and Eyre[4] correlated interstitial segregation with the degree of intergranular embrittlement in binary Mo-O and ternary Mo-O-C single crystals. With the use of a refining technique, crystals were produced containing 6-9 wppm oxygen with carbon content varying between 0.4 and 320 wppm. All of the samples failed in a brittle intergranular mode, although the samples with the highest carbon content exhibited limited ductility. It was concluded that oxygen readily segregated to the grain boundaries thereby promoting intergranular failure. In addition, it was suggested that the beneficial effect of adding carbon resulted from either (a) reduced driving force for oxygen segregation, (b) increased mobility of screw dislocations through the formation of dislocation kinks, or (c) the formation of carbide precipitates on grain boundaries that reduced the grain boundary energy.

Suzuki et al.[5] evaluated the effect of recrystallization on the ductility of very high purity molybdenum, confirming the conclusions of the two previous investigations. Samples with less than ~1 wppm carbon and oxygen had a lower ductility than an alloy containing 6 wppm oxygen and 30 wppm carbon. Carbon but not oxygen was detected on the grain boundary fracture surface by Auger electron spectroscopy. The addition of carbon produced an increase in grain boundary strength.

The ductility of body centered cubic structures is inversely related to the rate of applied strain. The grain growth that results during the welding of molybdenum can cause subsequent tensile strains to be concentrated in the coarse-grained regions of a weldment. This strain localization will result in an increase in the rate of local tensile strain. Ductility may be reduced due to the depletion of dislocations. The recrystallized grain size influences properties according to the Hall-Petch relationship that indicates that the yield stress of a material tends to increase as the grain size is reduced.[6] Thus, to gain increased ductility from brittle weldments in molybdenum, the base metal, heat affected zone and weld filler metal should have matched mechanical properties. This is not such a concern when the weldment has high ductility or work hardening capacity.

Experimental

The composition of the molybdenum alloy used in this investigation is given in Table 1. The alloy was vacuum arc-cast with a zirconium addition intended to getter the oxygen and nitrogen impurities together with parts per million additions of carbon and boron intended to strengthen the grain boundaries. The 4-pass welding process was performed on 0.25 inch plate in a controlled atmosphere chamber where the oxygen, nitrogen and water vapour impurity levels were each less than 10 wppm. The welding filler metal was molybdneum containing 20, 30 or 47 wt. % rhenium.

Tensile tests were performed at room temperature at strain rates between 8.3 x 10^{-3} and 12.5 x 10^{-6} s^{-1} in stroke control. Strain was measured over two weldment regions to measure strain localization: 25 mm centered over the weld and 8.5 mm over one heat-affected zone.

The distribution of the alloying elements in the microstructure of the base metal of this molybdenum alloy was characterized by a combination of field ion microscopy and atom probe tomography. Microstructural characterizations were performed in the Oak Ridge National Laboratory (ORNL) energy-compensated atom probe and the ORNL energy-compensated optical position-sensitive atom probe.[7] No prior examination or preselection of the field ion specimens in the transmission electron microscope was performed in order to eliminate any possibility of carbon contamination during specimen preparation.

Results and Discussion

The tensile test results are summarized in Table 2. Tests were performed at a standard strain rate of 10^{-4} sec^{-1} and also at faster and slower rates to determine the effect of strain rate. The maximum observed elongation, pertinent to typical engineering use, was 19.5%. Even at 8.3x10^{-3} sec^{-1}, useful ductility was apparent in the material welded with Mo-30% Re.

Fracture was found to occur in either the heat-affected zone or the weld zone. The mode of fracture was transgranular cleavage with only small regions of intergranular fracture, in contrast to the intergranular fracture typical of welds in commercial grade molybdenum alloys. The change of fracture mode in these tensile tests suggests that the alloying additions increased the grain boundary fracture stress above the yield stress.

The grain structure of the base metal is shown in a scanning electron micrograph in Fig. 1. The grain structure was found to be finer than that traditionally observed in wrought molybdenum alloys. A pair of field ion micrographs of grain boundaries in this base metal is shown in Fig. 2. Some bright spots indicative of solute segregation to the grain boundary are evident in these micrographs. However, no grain boundary precipitates were observed. No intragranular precipitates were observed during extensive field evaporation of many specimens. This observation refutes the grain boundary carbide mechanism proposed by Kumar and Eyre.

The concentrations of the alloying additions in the matrix well separated from grain boundaries were determined by atom probe tomography. The oxygen was found to field evaporate in O^{+}, O^{2+}species and MoO^{2+} species. Due to the relatively low concentrations of these elements and the background noise level in the three-dimensional atom probe, the concentrations were corrected for background noise.[7] The results were consistent with the alloy composition.

An atom map of a region of a specimen containing a grain boundary is shown in Fig. 3. In this type of representation, a sphere is used to represent the positions of individual atoms. Only zirconium, oxygen, carbon and boron atoms are shown for clarity. It is evident that significant segregation of zirconium, carbon and boron to the grain boundary has occurred. In addition, the oxygen and nitrogen + silicon level at the grain boundary was significantly reduced from the matrix level. The oxygen depletion is in contrast with previous image atom probe elemental maps of oxygen segregation to a grain boundary in molybdenum.[8] The Gibbsian interfacial excesses of the solutes at this grain boundary were determined by selected volume analyses of grain boundary and matrix regions and the results are given in Table 3. These results quantify the segregation information shown in Fig. 3.

These atom probe tomography results have demonstrated that oxygen and possibly nitrogen segregation to the grain boundaries does not occur in this alloy and may be inhibited by due to the presence of zirconium, carbon and boron. Intergranular failure is thereby inhibited through the significant reduction of the oxygen level at the grain boundary.

Conclusions

A combination of zirconium, carbon and boron additions in the parts per million range have improved the ductility of molybdenum weldments from ~3% to ~20%. Segregation of zirconium, carbon and boron and depletions of oxygen and nitrogen at grain boundaries was observed in the base metal by atom probe tomography.

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References

1. A. J. Bryhan, *Joining of Molybdenum Base Metals and Factors Which Influence Ductility*, WRC Bulletin 312, Feb. 1986, ISSN 0043-2326.

2. J. R. Stephens and W. R. Witzke, *J. Less Common Met*., 29 (1972) 371-388.

3. J. B. Brosse, R. Fillet, and M. Biscondi, *Scr. Metall.*, 15 (1981) 619-623.

4. A. Kumar and B. L. Eyre, *Grain Boundary Segregation and Intergranular Fracture in Molybdenum*, Proc. R. Soc., London, A370 (1980) 431-458.

5. S. Suzuki, H. Matsui, and H. Kimura, *Mater. Sci. Eng.*, 47 (1981) 209-216.

6. W. C. Leslie, The Physical Metallurgy of Steel**s**, Mc Graw-Hill, New York, 1981, p.17.

7. M. K. Miller, Atom Probe Tomography: Analysis at the Atomic Level, Kluwer Academic/Plenum Press, 2000, New York, NY.

8. A. R. Waugh and M. J. Southon, *Surf. Sci*., 68 (1977) 79.

Table 1. Composition of the alloy used in this study.

Element	wppm	appm
Zirconium	1500	1600
Carbon	12	96
Boron	6	53
Oxygen	42	250
Nitrogen	26	178
Iron	6	10
Silicon	3	10
Molybdenum	Balance	Balance

Table 2. Room temperature tensile test results for GTA-welded molybdenum alloy with three levels of Mo-Re filler metal.

Filler metal	Stain rate in 25mm sec^{-1}	Range of percent elongation in gauge length		Avg. yield stress		Avg. tensile stress		Number of tests
		25mm	8.4mm [a]	MPa	ksi	MPa	ksi	
Mo-20Re	$8.3x10^{-4}$	8.2-15.2	10.4-14.0	428	62.0	524	76.0	6
	$8.3x10^{-5}$	11.0	6.0	392	56.8	470	68.1	1
Mo-30Re	$8.3x10^{-3}$	10.0-12.6	7.9-11.6	537	77.9	583	84.5	2
	$8.3x10^{-4}$	19.5	>15.0	481	69.9	544	78.8	1
	$1.25x10^{-6}$	22.6	>15.0	267	38.7	457	66.2	1
Mo-47Re	$1.25x10^{-6}$	10-26	8->15.0	250	36.3	484	70.1	3

[a] 15.0% maximum measurement with the extensometer.

Table 3. Gibbsian interface excesses of solute at the grain boundary shown in Fig. 3.

Element	Gibbsian Interfacial Excess Atoms m^{-2}
Zirconium	7.6×10^{17}
Carbon	1.1×10^{17}
Boron	7.3×10^{16}
Oxygen	-3.9×10^{16}
Nitrogen + Silicon*	-4.3×10^{16}

*These elements cannot be discriminated by their mass peaks in the atom probe.

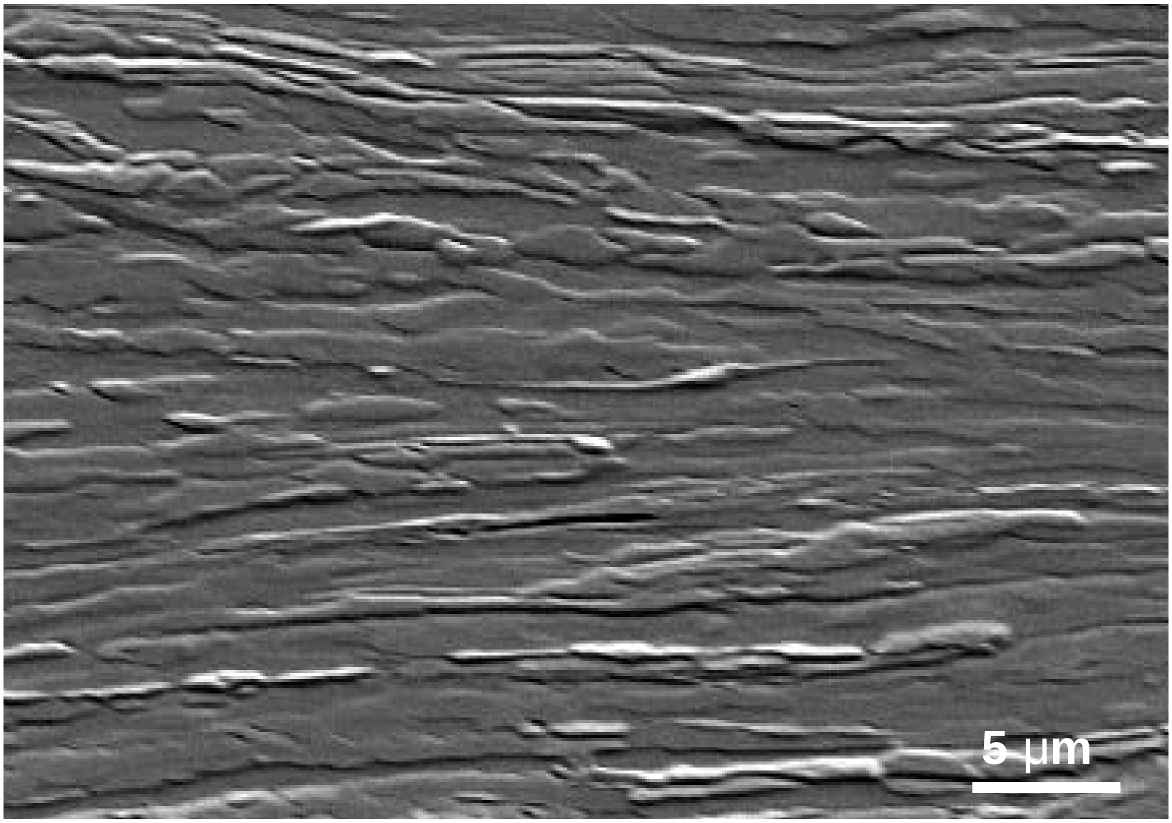

Fig. 1. Scaning electron micrograph of the grain structure of the molybdenum weldment.

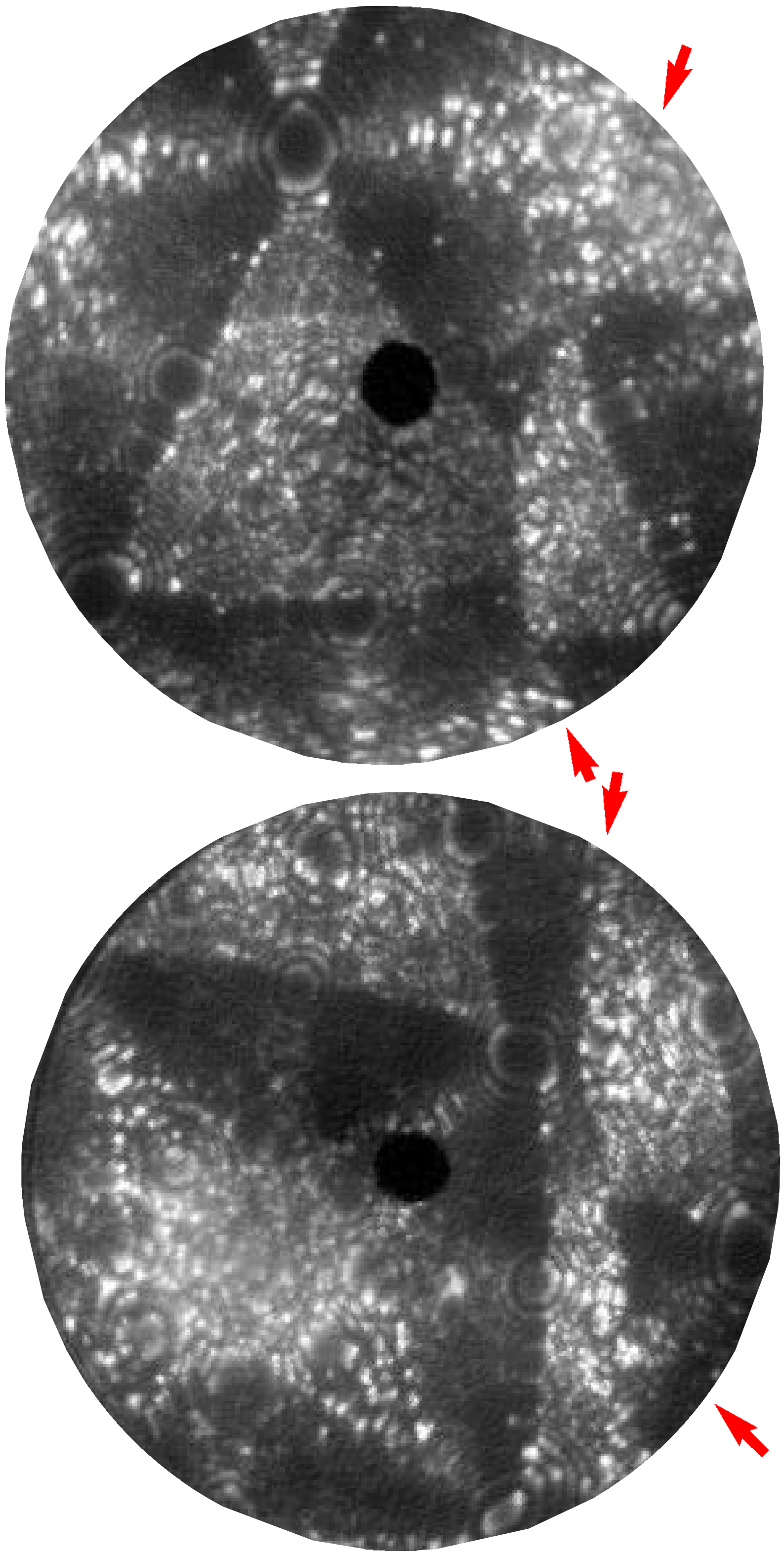

Fig. 2. Field ion micrographs of grain boundaries in the molybdenum weldment.

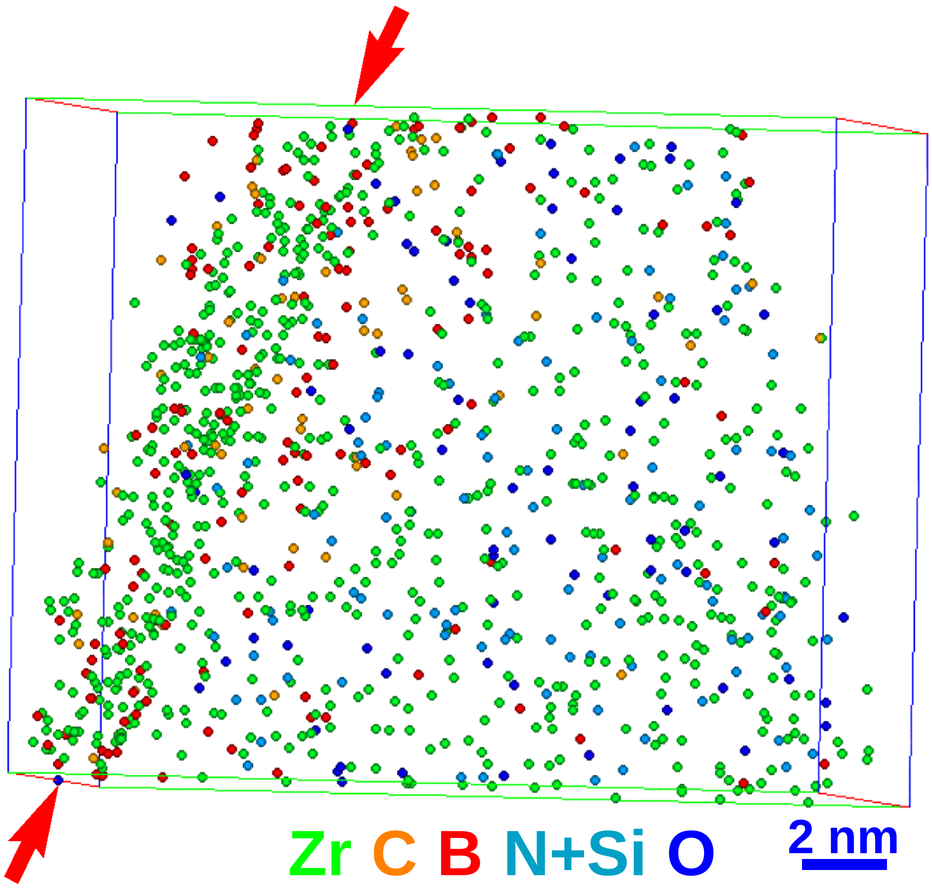

Fig. 3. Atom map of a section of a grain boundary. Zirconium, carbon and boron atoms have segregated to the grain boundary. Oxygen is depleted at the grain boundary.