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The mechanical properties and fracture mechanisms of wrought low carbon arc cast (LCAC), molybdenum–0.5pct titanium–0.1pct zirconium (TZM), and oxide dispersion strengthened (ODS) molybdenum flat products

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Abstract

Molybdenum alloys such as low carbon arc cast (LCAC) unalloyed molybdenum, oxide dispersion strengthened (ODS) molybdenum, and molybdenum–0.5pct titanium–0.1pct zirconium (TZM) molybdenum are of interest for structural applications at high temperatures, but these alloys are poorly characterized with respect to fracture toughness and the ductile to brittle transition temperature (DBTT) in the presence of a notch. Both tensile and fracture toughness testing of these flat rolled molybdenum alloys at temperatures above the DBTT are shown to produce a ductile laminate fracture mechanism, where cracks initiate along grain boundaries in the region of triaxial stresses to leave ligaments of sheet-like grains that are stretched to failure with a high degree of plasticity. The DBTT determined from toughness testing is 50–200 °C higher than determined from tensile testing, which shows the constraining effect of the notch. Use of the *J*-integral test method provided a more consistent and accurate measure of fracture toughness values at temperatures above the DBTT where large amounts of plasticity are observed. A transition was observed from toughness values between 5.8 and 29.6 MPa$\sqrt{m}$ at temperatures below the DBTT to toughness values between 45 and 175 MPa$\sqrt{m}$ for LCAC, 40–215 MPa$\sqrt{m}$ for TZM, and 53–205 MPa$\sqrt{m}$ for ODS. The variation in fracture toughness values at temperatures > DBTT is shown to correlate with size and number density of the ductile laminate features, where high fracture toughness values result from a fine laminate spacing. Since a finer grain size results in a smaller laminate size, the lower DBTT observed for fine grained ODS molybdenum can be understood in terms of the ductile laminate failure mode.

Keywords: Molybdenum; Molybdenum alloys; Fracture toughness; Tensile properties; Toughening mechanisms

1. Introduction

Group VIb refractory metals such as molybdenum are characterized by excellent high-temperature strength, creep resistance, low coefficient of thermal expansion, and high thermal conductivity, but poor oxidation resistance in air at temperatures > 500 °C generally limits the use of these materials to applications where the atmosphere can be controlled [1–6]. When considering the use of molybdenum for structural applications, limitations can be imposed by a ductile to brittle transition temperature (DBTT). Metals that have a body-centered cubic (bcc) structure typically exhibit generous levels of ductility and toughness at a homologous temperature (T/T_m (K)) ≥ 0.3, but brittle behavior is generally observed at a homologous temperature of 0.1, which is near room-temperature for molybdenum [6]. Unnotched tensile or bend tests have historically been used to characterize the DBTT of molybdenum alloys, but fracture toughness tests provide a more conservative measure of DBTT that accounts for sharp flaws that could be present or are formed in service [7–9]. It is well known that the triaxial stress-state resulting from the presence of a notch results in a higher DBTT for bcc metals than determined using an unnotched tensile or bend specimen [7,8,53]. Molybdenum-base alloys have generally been poorly characterized with regards to fracture toughness testing [4,7–16]. The fracture toughness of molybdenum flat products have been measured using plane-strain (ASTM E399) methods [17], but few studies have utilized the *J*-integral method for measuring fracture toughness [18]. In many cases, the size of the specimens used in previous work [7,8] was too small to obtain a valid toughness measurement using ASTM E399 methods at temperatures ≥ DBTT where high fracture toughness values were measured. One goal of this work is to use the

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Table 1
Chemical analysis of the LCAC, TZM, and ODS molybdenum alloys, as provided in material certification reports [7,8]

Material/lot#	C	O	N	Ti	Zr	Fe	Ni	Si	La	Al	Ca	Cr	Cu	Other
ODS molybdenum/ingot #382 heat# LA22963	10	NA	NA	<10	NA	74	12	24	1.6 wt.%	21	320	24	10	<10 Mg <10 Mn <10 Pb <10 Sn
TZM molybdenum/ingot 61722B lot# TZM24080	223	17	9	5000	1140	<10	<10	<10	NA	NA	NA	NA	NA	NA
LCAC molybdenum/ingot 50823 lot# C24728	50	11	4	NA	NA	<10	<10	<10	NA	NA	NA	NA	NA	NA

Unless noted, all compositions given in weight percent ppm; *Note*: the compositions for LCAC and TZM are within the ASTM B386-91 specification for these alloys; ASTM B386-365 for arc-cast LCAC molybdenum and ASTM B386-363 for TZM molybdenum [34]; NA: not available; all material was obtained from H.C. Starck, Cleveland, OH.

J-integral method to measure toughness at temperatures above the DBTT, where a large extent of damage tolerance is observed so that valid toughness measurements can be obtained for thinner specimen sizes.

A number of studies have shown that the DBTT and failure modes of molybdenum alloys are affected by metallurgical variables such as interstitial content, grain size, grain morphology, texture, alloying elements, and distribution of second phase particles [1,6,19–31]. A number of criteria have been used to define the DBTT based on measurements of tensile elongation and/or fracture toughness, but the delineating feature has always been the fracture mode. At temperatures below the DBTT, either transgranular or intergranular quasi-cleavage is observed. Many different types of ductile failure modes have been observed at temperatures above the DBTT, which generally depend on the microstructure of the molybdenum-base alloy. A ductile laminate failure mode, or thin sheet toughening mechanism [32,33], has been shown to be important for wrought molybdenum alloys at temperatures above the DBTT [7,8]. The second purpose of this work is to define the DBTT and failure modes for wrought, commercially available molybdenum flat products using both tensile and fracture toughness tests. The three commercial molybdenum alloys studied are: (1) molybdenum–0.5pct titanium–0.1pct Zirconium (TZM) molybdenum, which contains low amounts of titanium, zirconium, and carbon that produce a coarse distribution of carbides with titanium and zirconium in solid-solution [34], (2) oxide dispersion strengthened (ODS) molybdenum, which contains a fine dispersion of La-oxide ribbons and particles that are elongated by mechanical working [35,36], and (3) unalloyed low carbon arc cast (LCAC) molybdenum [34].

2. Experimental procedures

2.1. Materials

The compositions for LCAC, TZM, and ODS molybdenum are provided in Table 1. All materials were obtained from H.C. Starck, Cleveland, OH as 9.53 (LCAC) or 6.35 mm thick wrought plate in the stress-relieved condition [7,8]. TZM and LCAC were produced using an arc melting process [7,8]. ODS molybdenum plate was produced using powder metallurgy methods [7,8,35,36]. The grain size values for the molybdenum alloys are given in Table 2. Sheet-like, pancaked shaped grains that are aligned in the longitudinal orientation are observed for each of the wrought molybdenum-base alloys [7,8]. However, the sheet-like grains are curved and not perfectly flat in the transverse orientation, and this curved shape results in a slightly larger grain thickness being measured for the transverse orientation relative to the longitudinal orientation.

2.2. Specimen preparation

The SS-1 tensile geometry [8] (nominally 4.445 cm × 0.508 cm × 0.0635 cm) was used for testing in the longitudinal and transverse orientation. The tensile specimens were machined after grinding 0.6 mm of material from each plate surface. The tensile specimens were laser scribed for identification and then electropolished at room-temperature in a solution of four parts concentrated sulfuric acid and one part distilled deionized water using a Type 304 stainless steel cathode and a dc voltage of 6 and 7 V to remove 51–76 μm of material [8]. The 0.25T (2.54 cm × 0.25 cm × 0.25 cm with $a = 1.219$ cm) compact tension (CT) and 1T (5.08 cm × 1.00 cm × 0.50 cm) flexure specimens were prepared in either the longitudinal direction (L–T orientation [37] with the notch perpendicular to the rolling direction), or transverse direction (T–L orientation with the notch parallel to the rolling direction) [7,8]. The molybdenum alloys were tested in the longitudinal stress relieved (LSR) or transverse stress relieved (TSR) conditions. The CT and flexure specimens were laser scribed for identification, and then pickled in a solution of 10 parts acetic acid, four parts nitric acid, and one part HF acid for 5–15 s to remove 25–51 μm of material [7,8]. Specimens were given a final stress-relief heat treatment in

Table 2
Summary of grain size measurements for LCAC, TZM, ODS molybdenum plate

Alloy	Grain width (μm)		Grain length (μm)	
	Average	Standard deviation	Average	Standard deviation
LCAC plate – LSR	14.0	10.4	340	138
LCAC plate – TSR	15.2	10.5	255	113
TZM plate – LSR	3.9	2.5	273	105
TZM plate – TSR	6.1	3.8	132	69
ODS plate – LSR	1.4	0.7	29.0	16.2
ODS plate – TSR	2.0	1.1	13.6	6.6

Note: all of the wrought alloys consist of sheet-like, pancaked grains that are aligned in the longitudinal orientation.