

FATIGUE AND FRACTURE BEHAVIOR OF HIGH TEMPERATURE MATERIALS

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FRACTURE AND FATIGUE-CRACK GROWTH BEHAVIOR
IN Mo-12Si-8.5B INTERMETALLICS AT AMBIENT AND ELEVATED TEMPERATURES

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Abstract

Boron-containing molybdenum silicides have received some interest of late due to their superior low-temperature “pest” resistance and comparable high-temperature oxidation resistance to MoSi₂-based silicides; however, like many ordered intermetallics, they are plagued by poor ductility and toughness properties. Of the various multiphase Mo-Si-B intermetallic systems available, alloys with compositions of Mo-12Si-8.5B (at.%), which contain Mo, Mo₃Si, and T2 phases, are anticipated to have higher toughnesses because of the presence of the relatively ductile Mo phase. In this study, we examine the ambient to high (1300°C) temperature fracture toughness (R-curve) and fatigue-crack growth characteristics of Mo-12Si-8.5B, with the objective of discerning the salient mechanisms governing crack growth. It is found that this alloy displays a relatively high *intrinsic* (crack-initiation) toughness at 1200°C (~10 MPa√m), but only limited *extrinsic* R-curve (crack-growth) toughness. Although the lack of extrinsic toughening mechanisms is not beneficial to quasi-static properties, it does imply in a brittle material that it should show only minimal susceptibility to premature failure by fatigue. This relative insensitivity to fatigue was confirmed by fatigue-crack growth testing at temperatures from ambient up to 1300°C.

Introduction

The quest for structural materials that can operate at higher and higher temperatures remains a persistent challenge in materials science. The best prospects in this regard are probably ceramic and intermetallic-matrix composites although, since their cost is prohibitive for many applications, much recent work has focused on their monolithic counterparts. In the intermetallics field,

perhaps the most progress has been made with alloys based on nickel and especially titanium aluminides. These alloys can exhibit significant room temperature ductility, at least compared to other intermetallics, but have the major disadvantage that their operating temperatures would be limited to less than 1000°C, which is too low for certain emerging applications [1]. One candidate material which could be used at significantly higher temperatures is molybdenum disilicide, due to its excellent oxidation resistance, high melting temperature, and relatively easy processibility. However, the structural use of molybdenum silicides is severely limited by their low ductility and poor fracture toughness at ambient temperatures.

In an attempt to enhance the ductility and fracture toughness of these alloys, one approach is through *in situ* ductile-phase toughening. The idea here is to process the silicide with excess Mo; then provided the crack intercepts the resulting primary α-Mo phase, catastrophic fracture can be hindered through the formation of unbroken ductile-particle ligaments in the crack wake. The resulting crack bridging and plastic deformation of the particles, together with crack deflection and interfacial debonding, provide the main contributions to toughness [2-7]. Since molybdenum silicides with Si concentrations less than those of MoSi₂, i.e., Mo₅Si₃ and Mo₃Si, suffer from poor oxidation resistance, boron is added in the current alloy to promote oxidation resistance by forming protective borosilicate glass [8]. It has been reported that the addition of as little as 1 wt.% boron improved the oxidation resistance by as much as five orders of magnitude at moderate to high temperatures (800° to 1500°C) [1]. Consequently, the current alloy was processed with a composition of Mo-12Si-8.5B (at.%), such that it contained the α-Mo, Mo₃Si, and Mo₅SiB₂ (T2) phases. Indeed, the toughness of this material was expected to be higher than that of MoSi₂ due to the presence of the relatively ductile Mo phase. The resulting microstructure indicates that α-Mo forms as isolated particles in the Mo₃Si

Mo₅SiB₂ matrix (Fig. 1).

It is the objective of the present work to examine the fracture toughness (R-curve) and fatigue-crack growth characteristics of this Mo-12Si-8.5B alloy, both at ambient and elevated temperatures up to 1300°C, and to discern the salient mechanisms governing crack growth.

Experimental Procedures

The Mo-12Si-8.5B (at.%) alloy was prepared by arc melting in a partial pressure of argon (70 kPa) and drop-casting into water-cooled copper molds with a diameter of 25 mm. The elemental Mo, Si, and B were 99.95, 99.99, and 99.5 wt.% pure, respectively. Ingots were homogenized *in vacuo* for 24 hr at 1600°C. Further details on the processing and microstructural characterization of this material are reported elsewhere [9,10]. Mechanical property measurements for this alloy at ambient temperature gave three-point bend strength of ~ 500 MPa [10].

Cyclic fatigue-crack growth rate measurements were performed at ambient temperature in a controlled room-air environment and at elevated temperatures in flowing gaseous argon. Testing was performed with disk-shaped compact-tension DC(T) specimens (of width 17.8 mm, and thickness 2.8 mm), containing “large” (> 3 mm) through-thickness cracks. Specimens were cycled with a test frequency of 25 Hz (sinusoidal waveform) at a load ratio ($R = K_{min}/K_{max}$) of 0.1 on a computer-controlled, servo-hydraulic mechanical test frame. Crack growth rates, da/dN , were determined over the range $\sim 10^{-11}$ to 10^{-5} m/cycle under computer-controlled K -decreasing and K -increasing conditions. Data are presented in terms of the applied stress-intensity range ($\Delta K = K_{max} - K_{min}$, where K_{max} and K_{min} are the maximum and minimum stress intensities in the fatigue cycle). Fatigue thresholds, ΔK_{TH} , below which large cracks are presumed to grow at vanishingly small rates, were operationally defined as the maximum value of ΔK at which growth rates did not exceed 10^{-10} m/cycle.

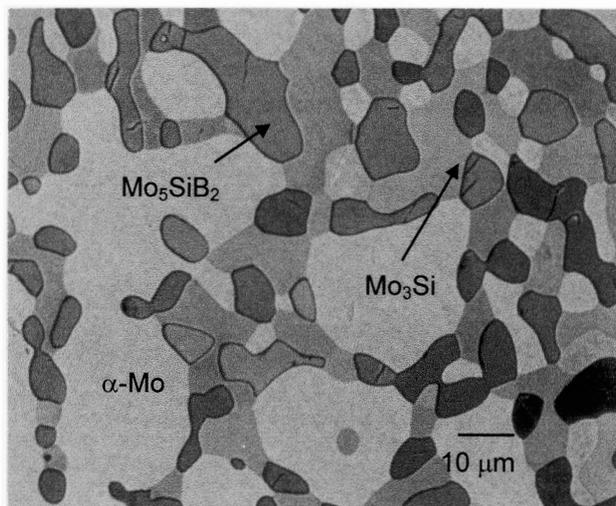


Figure 1: Scanning electron micrograph of the Mo-12Si-8.5B (at.%) alloy, showing α -Mo particles in the Mo₃Si/Mo₅SiB₂ matrix (etched with Murakami’s reagent).

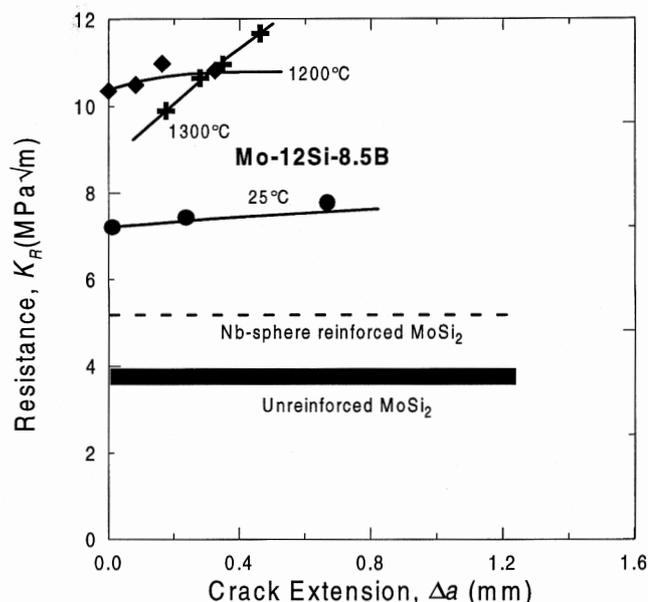


Figure 2: Fracture toughness behavior, in the form of $K_R(\Delta a)$ crack-growth resistance curves, for Mo-12Si-8.5B alloy both at ambient and elevated temperatures, as compared to published results [4,14] on MoSi₂ reinforced with Nb spheres.

Prior to data collection, samples were fatigue precracked for a few millimeters beyond this notch. Owing to the brittleness of the material, the initiation of the precrack was one of the most critical procedures in the test. In the current work, crack initiation was facilitated using a half-chevron shaped notch followed by razor notching using extra keen single edge blades with the thickness of 230 μ m. For room temperature testing, crack lengths were continuously monitored using unloading elastic-compliance measurements with a 350- Ω strain gauge attached to the back-face of the specimen [11]. At elevated temperatures, an electrical potential-drop technique was used to similarly monitor crack lengths. More details on this technique are given in refs. [12,13]. The resistance curve (R-curve) was measured by loading specimens to failure under monotonically increasing loads (displacement control). During such tests, crack lengths were periodically monitored using the same procedures (unloading back-face strain compliance at room temperature, electrical potential methods at high temperatures); unloading excursions were limited to less than 10% of the current load. Following precracking, specimens were cycled for ~24 hr at the ΔK_{TH} threshold, where no discernable crack growth occurs; this procedure was intended to minimize the effect of any pre-existing crack-tip shielding on the subsequently measured initiation toughness, K_0 . Since the latter tests all involve sharp cracks, measured toughness values may be smaller than values obtained from other methods that rely on a machined notch as the initial crack [10]. Data are presented in terms of crack-growth resistance, K_R , plotted as a function of the crack extension, Δa . Fatigue and fracture morphologies were examined in a scanning electron microscope and from crack-path profiles, obtained by

metallographic sectioning at the specimen mid-thickness. Measurements of the size and proportion of cracked and decohered α -Mo particles involved in crack advance were carried out using a direct-counting technique on both fracture surfaces and crack path profiles.

Results and Discussion

Resistance-Curve Behavior

Measurements of the fracture toughness and R-curve behavior indicate relatively large crack-initiation toughnesses in Mo-12Si-8.5B (Fig. 2). Compared to a K_c value of ~ 3 to 4 MPa \sqrt{m} in monolithic MoSi₂ [4], the initiation toughness in Mo-12Si-8.5B at room temperature is ~ 7.2 MPa \sqrt{m} , i.e., over 70% higher. However, most of the toughening appears to be intrinsic, i.e., not involving crack-tip shielding, as the subsequent R-curve is very shallow.

Mechanistically, metallographic observations show only minimal interaction between the α -Mo particles and the crack path at ambient temperatures (Fig. 3a); indeed, somewhat surprisingly, the Mo particles do not appear to provide any appreciable impedance to crack advance. The crack path is primarily confined to the matrix and the Mo/matrix interface. From direct-counting techniques, approximately 50% of the Mo particles (which in total comprise 38 vol.% of the microstructure) cracked through the particles, the remainder failed along the interface. Specifically, the crack tended to circumvent the relatively small (less than ~ 5 μ m) Mo particles with spherical shape and to propagate through them when they were relatively large with elongated shape. Of note is the fact that there is little evidence of plastic stretching as the Mo phase is traversed by the crack; this is consistent with the minimal crack-growth resistance associated with crack extension on the R-curve (Fig. 2).

At elevated temperatures, the intrinsic toughness of the Mo-12Si-8.5B alloy is significantly increased, to over 10 MPa \sqrt{m} at 1200°C, again with very shallow R-curves, although at 1300°C, the R-curve does become somewhat steeper. As shown in Fig. 2, the crack-growth resistance at 1300°C steadily increased over the first ~ 400 μ m of crack extension, from an initial value of $K_0 \sim 9$ MPa \sqrt{m} to a maximum value of $K_c \sim 11.8$ MPa \sqrt{m} . The presence of some degree of crack-growth toughening at this temperature is consistent with metallographic observations (Fig. 3b) which do show evidence of crack bridging by unbroken α -Mo particles in the crack wake. However, as discussed below, also apparent is that the ductile-particle bridging additionally occurs within an extensive network of microcracking parallel to the main crack; indeed, the microcracks all appear to be arrested at the α -Mo regions, presumably because of the increased ductility of the Mo at this temperature.

Fatigue-Crack Growth Behavior

The variation in fatigue-crack propagation rates with the applied stress-intensity range for the Mo-12Si-8.5B alloy is shown in Fig. 4; results are plotted for ambient and elevated (1200° and 1300°C) temperatures and are compared with previous results on monolithic and composite MoSi₂ [4,14]. It is apparent that the

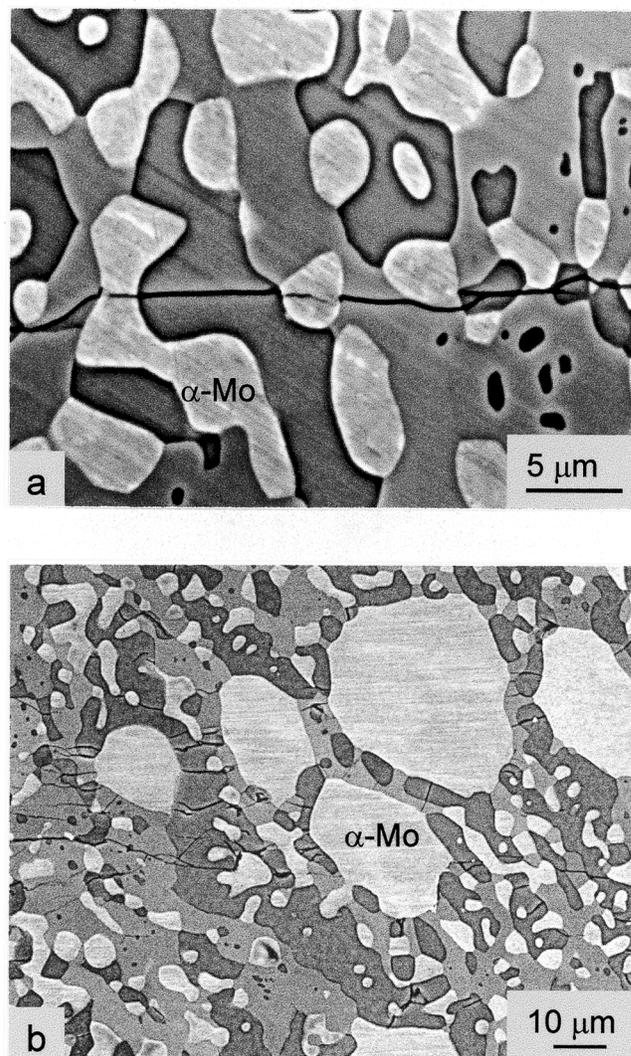


Figure 3: Scanning electron micrographs of crack paths under monotonic loading in the Mo-12Si-8.5B alloy, showing the interaction of the crack with the microstructure, at (a) ambient (25°C) and (b) elevated (1300°C) temperatures. The direction of crack growth is from left to right.

fatigue-crack growth properties of this alloy are superior to that of monolithic MoSi₂; indeed, at 25°C, the ΔK_{TH} threshold in Mo-12Si-8.5B of ~ 5 MPa \sqrt{m} is significantly larger than the fracture toughness of MoSi₂. Moreover, threshold values are even higher at elevated temperatures, rising to over 7 MPa \sqrt{m} above 1200°C. Characteristic of brittle materials at low homologous temperatures [15], crack-growth rates in Mo-12Si-8.5B exhibit a marked sensitivity to the stress intensity. In terms of the Paris power-law relationship, $da/dN = C\Delta K^m$ (where C and m are scaling constants), the Paris exponents are $m \sim 60$ at 25°C and 55 at 1200°C. This implies that this material is essentially not susceptible to premature failure by fatigue, particularly at the lower temperatures. There are good mechanistic reasons for this. Cyclic fatigue in brittle materials, e.g., ceramics and

intermetallics, results from a conceptually different mechanism to that of the well known metal fatigue; specifically it arises from a progressive (cycle-dependent) degradation in extrinsic (R-curve) toughening behind the crack tip [15]. Except for a limited extent at 1300°C, the Mo-12Si-8.5B alloy is toughened primarily by intrinsic mechanisms, as is apparent by the comparatively high initiation toughnesses and relatively flat R-curves (Fig. 2). Thus, since there is only limited extrinsic toughening to degrade, this alloy shows only minimal susceptibility to fatigue failure. The cyclic fatigue resistance of the Mo-12Si-8.5B alloy is further improved with increase in temperature up to 1300°C. Specifically, the ΔK_{TH} fatigue threshold was increased, by ~50% compared to room temperature, to ~7.5 MPa \sqrt{m} . However, the development of some degree of extrinsic toughening at the temperature, due to crack bridging by the α -Mo phase, does lead to a marginally increased susceptibility to fatigue, i.e., the Paris exponent is reduced somewhat to $m \sim 44$. No appreciable evidence of creep mechanisms, e.g., in the form of cavitation damage, could be found at 1300°C.

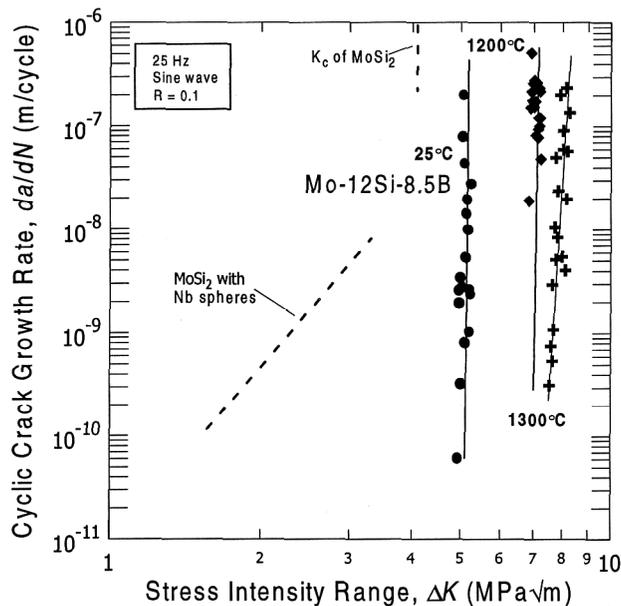


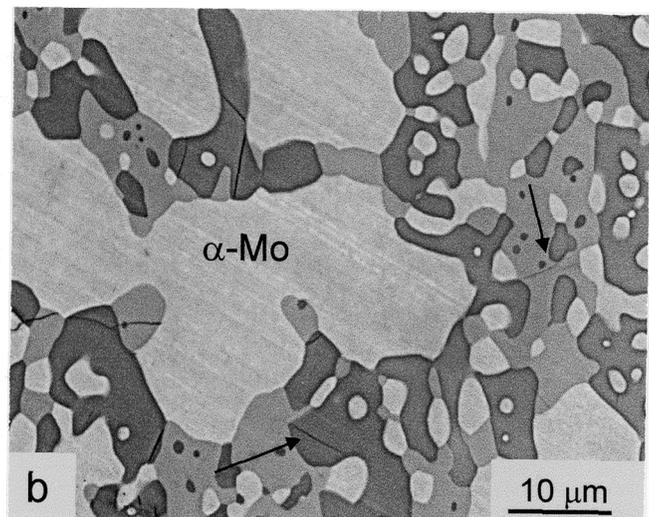
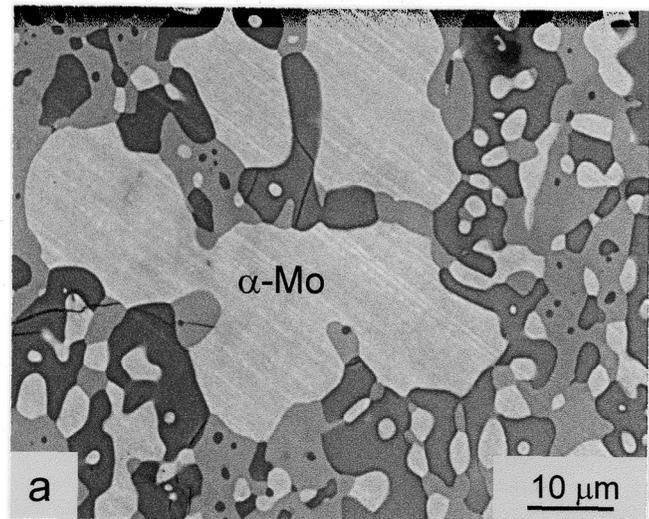
Figure 4: Cyclic fatigue-crack propagation data of Mo-12Si-8.5B alloy as a function of applied ΔK at 25°C, 1200°C, and 1300°C, respectively, compared to published results [4,14] on monolithic MoSi₂ and MoSi₂ reinforced with Nb spheres.

Toughening Mechanisms at Ambient Temperatures

The toughening of brittle solids through the inclusion of ductile phase is generally accomplished extrinsically, i.e., through the development of crack-tip shielding from crack deflection and/or crack bridging by intact ductile particles in the crack wake [e.g., 15-17]; such mechanisms invariably lead to rising R-curve behavior (crack-growth toughening) but can result in susceptibility to fatigue failure as they have a tendency to degrade under cyclic loading [15]. However, if the crack can be arrested at the ductile phase such that it must renucleate on the other side, the consequent crack trapping acts to toughen the material intrinsically. This tends to enhance the crack-initiation toughness;

moreover, it is an equally effective toughening mechanism under cyclic loads [15,18].

In the current Mo-12Si-8.5B alloy, Figs. 5a-d show the interaction of the α -Mo phase with the main crack during crack extension at ambient temperature under monotonic loading. Microcracks can be seen to form around the crack tip as the main crack is arrested at a Mo particle; further microcrack formation then occurs as the crack renucleates on the far side of the particle. Such crack trapping accompanied by microcracking appears to provide the main source of (intrinsic) toughening at lower temperatures. However, as the Mo particles do not remain unbroken in the crack wake (Fig. 3), presumably because of the limited ductility of Mo at 25°C¹, there is little crack-growth toughening due to the absence of significant crack bridging. Accordingly, the R-curve is relatively shallow and susceptibility



¹ Depending on purity, the ductile-brittle transition temperature of molybdenum is of the order of ~50° to 500°C [19,20].

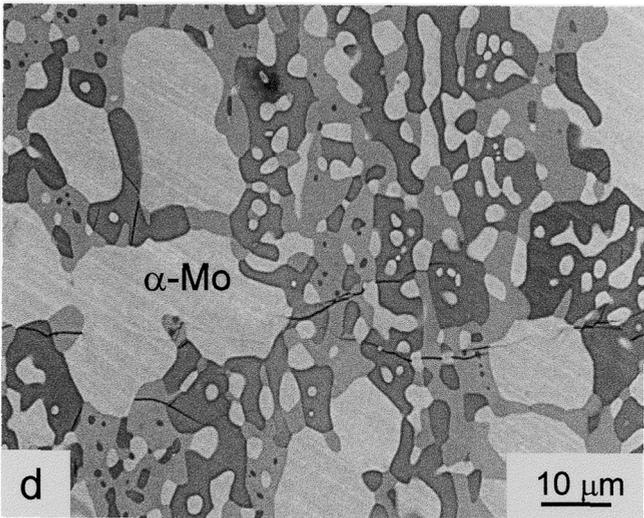
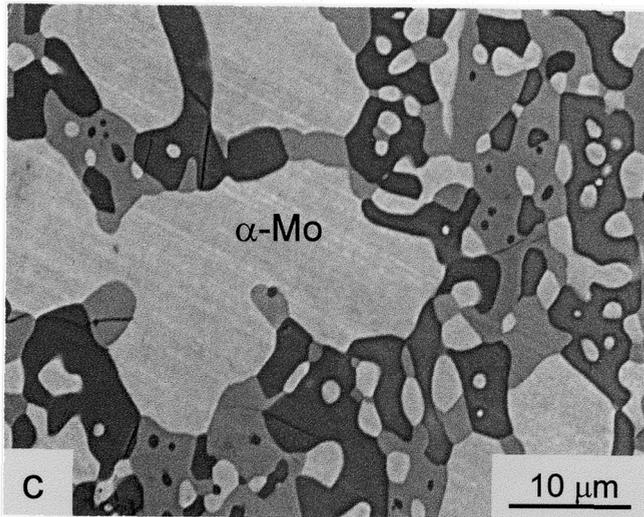


Figure 5: *In situ* scanning electron micrographs illustrating the development of microcracking ahead of the crack tip during the extension by fatigue of the main crack. Figures show (a) the initial fatigue precrack, (b) microcrack formation in the matrix ahead of the crack tip (indicated by arrows), (c) opening up of the main crack and surrounding microcracks, and (d) propagation of the main crack through α -Mo particles. The direction of crack growth is from left to right.

to fatigue is minimal. The failure of the Mo phase is shown in Fig. 6; fracture at room temperature is quite brittle (Fig. 6a), as reported in refs. [21,22], whereas at 1300°C, the Mo particles debond from the $\text{Mo}_3\text{Si}/\text{Mo}_5\text{SiB}_2$ matrix with significant amounts of plastic stretching (Fig. 6b). As discussed below, such increased ductility of the Mo particles does result in some degree of wake bridging in the Mo-12Si-8.5 alloy at elevated temperatures.

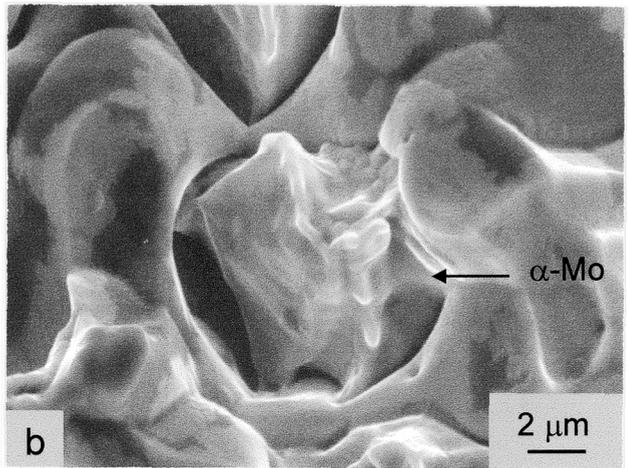
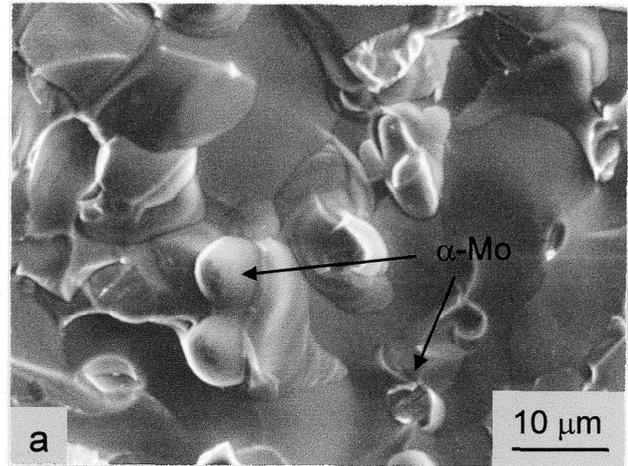


Figure 6: Scanning electron micrographs of the fracture surfaces in the Mo-12Si-8.5B alloy which failed in a brittle manner, showing (a) no evidence of plastic deformation of Mo phase at ambient temperature, and (b) significant amount of plastic stretching and debonding of the Mo phase from the brittle $\text{Mo}_3\text{Si}/\text{Mo}_5\text{SiB}_2$ matrix at 1300°C.

Thus, based on *in situ* observations of the crack/ α -Mo interactions (Fig. 5), crack trapping appears to be the dominant toughening mechanism in Mo-12Si-8.5B at ambient temperatures. The process involves crack arrest at an α -Mo particle, subsequent microcrack ahead of the crack tip and, with increasing stress intensity, renucleation across the particle achieved by the remainder of the crack bowing out between the pinning regions. The extent of toughening can be estimated in terms of the relative toughness of the “composite”, K_c^c , and matrix, K_c^m [23]:

$$\frac{K_c^c}{K_c^m} = \left\{ 1 + \frac{2r}{l} \left[\left(\frac{K_c^p}{K_c^m} \right)^2 - 1 \right] \right\}^{1/2} \quad (1)$$

where r is the characteristic dimension of the trapping phase, l is the average spacing (not necessarily the particle spacing, but the

distance between the particles where the crack is trapped), and K_c^p is their toughness. Using a fracture toughness for Mo at 25°C of 15 MPa√m [16,24] and for the matrix of 3.5 MPa√m [10], and an average value r/l of -0.2 (based on crack profile measurements), Eq. 1 predicts a toughness due to crack trapping of ~9.8 MPa√m, which, considering the uncertainties in the toughness values², is reasonably close to the experimentally measured values.

Toughening Mechanisms at Elevated Temperatures

Ductile-phase toughening: As noted above, the increased ductility of the α -Mo phase at elevated temperatures promotes some degree of ductile-phase bridging (Fig. 3b), which at 1300°C results in a rising R-curve. Quantitatively, the magnitude of such toughening can be estimated from the increase in energy associated with particle deformation and failure in the wake of the crack [25]. Assuming that small-scale bridging conditions apply, i.e., the bridging zone is small compared to crack length and specimen dimensions, the steady-state toughness can be determined from the dimensionless work of rupture of the reinforcement, or the area under the normalized stress [$\sigma(u)$]-

displacement [u] function, as $\chi = \int_0^{u^*} (\sigma(u)du/\sigma_0 r)$, where σ_0 is the yield strength of the ductile phase, and u^* is the critical crack-opening displacement for its fracture [25,26]. The corresponding steady-state toughening, K_{ssb} , is then given by:

$$K_{ssb} = \sqrt{K_t^2 + f E' \sigma_0 r \chi} \quad (2)$$

where K_t is approximately the matrix toughness, E' is the plane-strain elastic modulus of the "composite", and f is the volume fraction of bridging phase. Taking values at 1300°C for E' for Mo-12Si-8.5B of ~179 GPa and σ_0 for α -Mo of ~103 MPa [9,10,14], with a volume fraction of α -Mo of $f \sim 0.38$ with $r \sim 5 \mu\text{m}$, Eq. 2 predicts a value of K_{ssb} of ~10.8 MPa√m, assuming a matrix toughness of $K_t \sim 3.5 \text{ MPa}\sqrt{\text{m}}$ [10] and an estimated value of χ of 3, based on the tensile properties of Mo at 1300°C [17,27]. Although only a rough estimate, the predicted toughness is comparable to the experimentally measured value of 11.7 MPa√m at 1300°C.

Microcracking toughening: The other potential source of toughening in Mo-12Si-8.5B at elevated temperatures arises from microcracking. This can be seen in Figs. 3b as a zone of microcracks, arrested between α -Mo particles, in layers parallel to the main crack. Most of the microcracks are formed in Mo_5SiB_2 phase (Fig. 7), presumably because of the possible anisotropy in its thermal expansion resulting from its tetragonal crystal structure (both Mo and Mo_3Si are cubic).

The formation of such a zone of microcracks around the crack tip can be considered as analogous to the crack-tip plastic zone in metals, which dissipates energy through work done in the opening

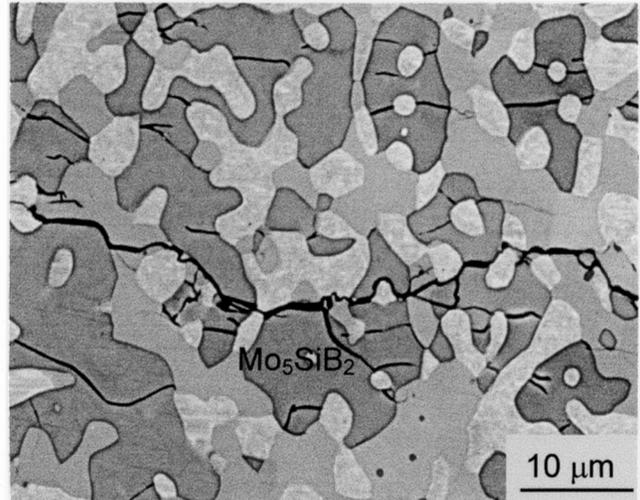


Figure 7: Development of parallel microcracks around the crack tip in the Mo-12Si-8.5B alloy during cyclic fatigue-crack propagation at 1300°C. The crack growth direction is from left to right.

and sliding displacements involved in microcracking and through creation of new surfaces [28]. In addition, the microcracks increase the compliance of the solid and can act as a mechanism of extrinsic toughening by shielding the crack tip from the remote stresses [29]. Controlled microcracks can be formed most effectively by a dispersion of a second phase, where tensile stresses develop around this phase when its thermal expansion coefficient is lower than that of the matrix [30,31]. As the coefficient of thermal expansion of Mo at 1300°C ($6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [19]) is lower than that of Mo_5SiB_2 ($8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [32]), it would be expected that the microcracking should form in the latter phase, and be parallel to the main crack, i.e., perpendicular to the applied tensile stresses. This orientation of microcracking is particularly effective in promoting toughening, as microcracks located parallel to the main crack can more easily extend and coalesce within the process zone, and hence are more effective in absorbing energy before the major crack can propagate [30].

In summary, it has been shown that the boron-modified molybdenum silicide alloy, Mo-12Si-8.5B, can be processed to be considerably tougher and more fatigue resistant than monolithic MoSi_2 alloys; moreover, its crack-growth resistance further improves with increase in temperature up to 1300°C. Despite such significant toughening, which in large part is due to the presence of the primary α -Mo phase, it is this same microstructural constituent that results in a lower oxidation resistance compared to MoSi_2 . Clearly, if molybdenum silicides are ever to be seriously contemplated as ultrahigh temperature structural materials, alloys displaying both low-temperature toughness and high temperature strength/oxidation resistance will still need to be developed.

Conclusions

The ambient to elevated temperature fracture and fatigue-crack propagation behavior of a boron-modified, molybdenum silicide based alloy, Mo-12Si-8.5B (at.%), has been examined at 25° to 1300°C with the aim of discerning the salient mechanisms

² Small amounts of interstitial impurities, such as oxygen, are known to severely embrittle Mo to below 5% elongation at ambient temperatures [24].

responsible for crack-growth resistance. Based on this work, the following conclusions can be made:

1. Compared to a fracture toughness of 3 to 4 MPa \sqrt{m} in monolithic MoSi₂ alloy, Mo-12Si-8.5B displays a K_{IC} of \sim 7 MPa \sqrt{m} at ambient temperatures, which rises to over 10 MPa \sqrt{m} at 1200°C. Over this temperature range, however, the associated R-curves are relatively flat, inferring that such toughening is primarily intrinsic in nature, i.e., affecting the crack-initiation toughness. Mechanistic studies indicate that microcracking and extensive crack trapping by the primary α -Mo phase are the principal mechanisms of toughening; however, due to the limited ductility of the Mo at these temperatures, the Mo phase rarely remains unbroken in the crack wake such that crack-tip shielding by ductile-phase bridging is minimal.

2. At 1300°C, conversely, some degree of ductile-phase bridging is evident, due to the presence of uncracked α -Mo regions in the crack wake; in addition, extensive microcracking (primarily in Mo₃SiB₂ phase) can be seen in the form of a network of arrested cracks parallel to the main crack. Since the former mechanism is extrinsic in nature, i.e., affecting the crack-growth toughness, the alloy displays rising R-curve behavior at this temperature, with a maximum toughness of 11.8 MPa \sqrt{m}

3. The fatigue-crack growth resistance of the Mo-12Si-8.5B alloy at ambient temperatures is also superior to that of monolithic MoSi₂; indeed, its ΔK_{TH} fatigue threshold value of \sim 5 MPa \sqrt{m} is significantly larger than the fracture toughness of MoSi₂. ΔK_{TH} thresholds are further enhanced at elevated temperatures, rising to 7 to 7.5 MPa \sqrt{m} at 1200° to 1300°C. Due to the minimal role of extrinsic toughening (except at 1300°C), Paris power-law exponents are extremely high, i.e., $m \sim$ 44 to 60, such that the Mo-12Si-8.5B alloy can be considered to be only marginally susceptible to premature failure by fatigue at temperatures up to 1200°C.

Acknowledgements

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