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**FRACTURE AND FATIGUE PROPERTIES OF  
Mo-Mo<sub>3</sub>Si-Mo<sub>5</sub>SiB<sub>2</sub> REFRACTORY INTERMETALLIC ALLOYS  
AT AMBIENT TO ELEVATED TEMPERATURES (25°-1300°C)**

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# ON THE FRACTURE AND FATIGUE PROPERTIES OF Mo-Mo<sub>3</sub>Si-Mo<sub>5</sub>SiB<sub>2</sub> REFRACTORY INTERMETALLIC ALLOYS AT AMBIENT TO ELEVATED TEMPERATURES (25°-1300°C)

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## Abstract

The need for structural materials with high-temperature strength and oxidation resistance coupled with adequate lower-temperature toughness for potential use at temperatures above ~1000°C has remained a persistent challenge in materials science. In this work, one promising class of intermetallic alloys is examined, namely boron-containing molybdenum silicides, with compositions in the range Mo (bal), 12-17 at.%Si, 8.5 at.%B, processed using both ingot (I/M) and powder (P/M) metallurgy methods. Specifically, the oxidation (“pestring”), fracture toughness and fatigue-crack propagation resistance of four such alloys, which consisted of ~21 to 38 vol.%  $\alpha$ -Mo phase in an intermetallic matrix of Mo<sub>3</sub>Si and Mo<sub>5</sub>SiB<sub>2</sub> (T<sub>2</sub>), were characterized at temperatures between 25° and 1300°C. The boron additions were found to confer superior “pest” resistance (at 400° to 900°C) as compared to unmodified molybdenum silicides, such as Mo<sub>5</sub>Si<sub>3</sub>. Moreover, although the fracture and fatigue properties of the finer-scale P/M alloys were only marginally better than those of MoSi<sub>2</sub>, for the I/M processed microstructures with coarse distributions of the  $\alpha$ -Mo phase, fracture toughness properties were far superior, rising from values above 7 MPa√m at ambient temperatures to almost 12 MPa√m at 1300°C. Similarly, the fatigue-crack propagation resistance was significantly better than that of MoSi<sub>2</sub>, with fatigue threshold values roughly 70% of the toughness, i.e., rising from over 5 MPa√m at 25°C to ~8 MPa√m at 1300°C. These results, in particular that the toughness and cyclic crack-growth resistance actually increased with increasing temperature, are discussed in terms of the salient mechanisms of toughening in Mo-Si-B alloys and the specific role of microstructure.

## I. INTRODUCTION

In the search for higher temperature structural materials to replace nickel-based superalloys for future propulsion systems, transition-metal silicides have received considerable recent interest [e.g.,1-7]. These alloys constitute a unique class of ultrahigh-temperature intermetallic materials, with high melting points (molybdenum and titanium silicides have melting points in excess of 2000°C) and the capability of forming protective silicon oxide films for enhanced oxidation resistance at elevated temperatures in hostile environments. In addition, specific silicides, such as  $\text{Mo}_5\text{Si}_3$  ( $T_1$ ), have excellent creep resistance at temperatures as high as 1400°C [2,3]. Despite these advantages, most refractory silicides invariably display very poor fracture toughness at low temperatures [4] and can be susceptible to oxidation problems (“pest” reactions<sup>1</sup>) at temperatures below ~1000°C [8-10].

A potential solution to these problems may be provided by the boron-modified molybdenum silicide system [11]. These alloys generally consist of thermodynamically stable two-phase mixtures of Mo and  $\text{Mo}_5\text{SiB}_2$  ( $T_2$ ) or three-phase mixtures of Mo,  $\text{Mo}_5\text{SiB}_2$  and  $\text{Mo}_3\text{Si}$ , have high melting temperatures above ~2000°C, improved low-temperature fracture toughness properties (compared to  $\text{MoSi}_2$ ) [3,7], and excellent oxidation resistance that increases with increasing boron content [12-18]. Indeed, in contrast to  $\text{MoSi}_2$  and  $\text{Mo}_5\text{Si}_3$ , which are very prone to pest reactions [10,12,14], tertiary Mo-Si-B alloys have a far reduced susceptibility to such intermediate temperature oxidation due to the formation of a protective borosilicate layer [12-14,16-18]. However, as the compositions that promote such oxidation resistance, i.e., higher B and Si, may not be the ones that promote toughness, i.e., higher Mo, optimization of these alloys requires a trade-off between crack growth and oxidation resistance. Although several recent studies have focused on the oxidation and pesting properties of Mo-Si-B alloys [8-10,11-18], few studies have been devoted to their fracture and fatigue properties, particularly at elevated temperatures above 1000°C.

Accordingly, in the current work, several boron-doped molybdenum silicide alloys with varying chemistries and microstructures are examined with respect to their fracture toughness and fatigue-crack growth behavior at ambient and elevated temperatures up to 1300°C. These alloys, which all consisted of  $\alpha$ -Mo and the intermetallic phases  $\text{Mo}_3\text{Si}$ , and  $\text{Mo}_5\text{SiB}_2$ , are based on the composition Mo-12Si-8.5B

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<sup>1</sup> The pest reaction, i.e., accelerated oxidation at intermediate temperatures, is generic to all forms of molybdenum silicides. For example,  $\text{MoSi}_2$  is prone to pest reaction in air between 300° and 600°C [8,9] whereas monolithic  $\text{Mo}_5\text{Si}_3$  exhibits severe pest reaction at 800°C [12,14].

(at.%), but some with higher Si and lower Mo concentrations for oxidation resistance, and another with Nb additions [3] for solid-solution strengthening of the  $\alpha$ -Mo and improved creep strength. Since the coarseness of microstructure can have a marked influence on the fracture and fatigue properties, both ingot (I/M) and powder metallurgy (P/M) processing was employed to significantly vary the characteristic microstructural dimensions.

Due to the extreme brittleness of refractory silicides, principal emphasis is given to the understanding of the effect of microstructure on toughening behavior as this is clearly a limiting feature in the design of Mo-Si-B alloys with acceptable properties. Particular attention is given to the morphology and composition of the individual phases, especially the  $\alpha$ -Mo phase, as this has been recently shown to play a central role in determining fracture properties of alloys containing the  $\alpha$ -Mo,  $\text{Mo}_3\text{Si}$ , and  $\text{Mo}_5\text{SiB}_2$  phases [7]. In the present work, it is found that mechanistically, crack trapping and ductile-phase bridging by the  $\alpha$ -Mo phase and microcracking within the  $\text{Mo}_5\text{SiB}_2$  phase provide the major contributions to crack-growth resistance, with the coarser-grained I/M Mo-12Si-8.5B alloy having the optimal crack-growth properties with a reduced susceptibility to lower temperature pest reactions than unmodified molybdenum silicides.

## II. EXPERIMENTAL PROCEDURES

### A. Processing and Microstructure

Four alloys, of composition (in at.%) Mo-12Si-8.5B (termed alloy IM1), Mo-16.8Si-8.4B (alloys PM1 and PM2), and Mo-12Si-10Nb-8.5B (alloy IM2), were prepared from elemental Mo, Si, B, and Nb, which were, respectively, 99.95, 99.99, 99.5, and 99.8 wt.% pure. Alloys IM1 and IM2 were directly prepared by arc-melting ~500 g of the starting materials into a water-cooled 25 mm diameter copper mold; the castings were then homogenized by annealing *in vacuo* for 24 hr at 1600°C. As noted above, Nb was added as a solid solution strengthener to alloy IM2 to harden the  $\alpha$ -Mo phase.

Alloys PM1 and PM2, conversely, were processed using powder-metallurgy methods. The rationale for this was two-fold: (i) to improve oxidation resistance by reducing the  $\alpha$ -Mo volume fraction through increases in the Si content, which can cause severe cracking during melting and casting in I/M processing, and (ii) to discern how much the fracture toughness is compromised by such reductions in the Mo content. Alloy PM1 was prepared by first arc-casting several 500 g buttons with the

composition Mo-16.8Si-8.4B; the resulting ingots were then crushed into  $-60/+230$  mesh (63 to 250  $\mu\text{m}$ ) powder. The powder was filled into a Nb hot-isostatic pressing (HIP) can, which was sealed by electron beam welding, consolidated in argon at 1600°C and 200 MPa for 2 hr, and subsequently annealed *in vacuo* for 24 hr at 1600°C. Alloy PM2 was prepared by arc-casting several 500 g buttons with the composition Mo-20Si-10B, which were crushed into  $-100/+270$  mesh (53 to 150  $\mu\text{m}$ ) powder. The powder was then mixed with an appropriate quantity of 2-8  $\mu\text{m}$  Mo powder to give a nominal composition Mo-16.8-8.4B. Because of a leak in the Nb can, initial HIPing of the powder mixture was not successful; however, hot pressing for 2 hr in a graphite die *in vacuo* at 1800°C at 35 MPa pressure resulted in almost complete consolidation. The hot-pressed material was subsequently containerless HIPed and annealed in the same way as alloy PM1 (Table I). Further details on the processing and microstructure characterization of these materials are reported elsewhere [5-7]; a general summary of the powder processing of silicides can be found in ref. [19].

**Table I: Composition of Mo-Si-B Alloys Examined**

<b>Alloy</b>	<b>Composition (at.%)</b>	<b>Processing</b>
<b>IM 1</b>	Mo-12Si-8.5B	Ingot Metallurgy, arc melting and casting
<b>IM 2</b>	Mo-12Si-10Nb-8.5B	Ingot Metallurgy, arc melting and casting
<b>PM 1</b>	Mo-16.8Si-8.4B	Powder Metallurgy with Mo-16.8Si-8.4B
<b>PM 2</b>	Mo-16.8Si-8.4B	Powder Metallurgy with Mo-20Si-10B and Mo

### B. Cyclic Fatigue Testing

Cyclic fatigue-crack growth behavior in the Mo-12Si-8.5B alloys was examined both at ambient temperature in a controlled room-air environment and elevated temperatures (800°-1300°C) in flowing gaseous argon. Testing was conducted under tension-tension loading using  $\sim 2.8$  mm thick, disk-shaped compact-tension DC(T) specimens (of width  $\sim 18$  mm), containing “large” ( $>3$  mm) through-thickness cracks. Specimens were cycled under stress-intensity control on computer-controlled servo-hydraulic testing machines at a load ratio (ratio of minimum to maximum loads) of  $R = 0.1$  with a test frequency of 25 Hz (sine wave). Procedures essentially conform to ASTM Standard E647 [20], although modified for the testing of brittle materials [21]. Crack-growth rates,  $da/dN$ , were obtained over the range  $\sim 10^{-11}$  to  $10^{-5}$  m/cycle under both  $K$ -decreasing and  $K$ -increasing conditions, with a normalized  $K$ -gradient of

$\pm 0.1 \text{ mm}^{-1}$  [20]. Data are presented in terms of the growth rate per cycle as a function of applied stress-intensity range, given by the difference in the maximum and minimum stress intensities during the cycle ( $\Delta K = K_{\max} - K_{\min}$ ). Fatigue thresholds,  $\Delta K_{\text{th}}$  and  $K_{\max, \text{th}}$ , below which large cracks are presumed to grow at vanishingly small rates, were defined as the maximum value of the appropriate stress intensity at which growth rates did not exceed  $10^{-11} \text{ m/cycle}$ .

Prior to data collection, samples were fatigue pre-cracked at room temperature for at least one millimeter beyond the notch. Pre-cracking was facilitated using a half-chevron shaped notch that was sharpened using a razor micro-notching technique. Further details are given in ref. [7].

For room temperature testing, crack lengths were continuously monitored *in situ* using unloading elastic compliance based on the back-face strain; measurements were made with a 350- $\Omega$  back-face strain gauge and utilized the calibrations for the DC(T) sample given in ref. [22]. At elevated temperatures between 800° and 1300°C, electrical potential-drop methods were alternatively used to monitor crack lengths [23,24]. Specifically, a constant direct current of  $\sim 2 \text{ A}$  was applied to the sample, such that an initial amplified output potential of  $\sim 0.4\text{-}0.6 \text{ V}$  was developed across the starter crack. With crack extension, subsequent changes in output potential were normalized by the initial potential, and then continuously monitored to permit *in situ* monitoring of the crack length using the potential calibrations derived in ref. [22]. Full details of this application of electrical-potential techniques to crack length monitoring at temperatures up to 1300°C are presented elsewhere [23].

### C. Resistance-Curve Measurements

Fracture toughness behavior was evaluated under plane-strain conditions by monotonically loading fatigue-precracked, disk-shaped compact-tension DC(T) specimens to failure. During such tests, crack lengths were periodically monitored using the same elastic unloading compliance (at 25°C) and electrical-potential (at 800°-1300°C) methods described above, although unloading excursions were limited to less than 10% of the current load. Following pre-cracking, specimens were cycled for  $\sim 24 \text{ hr}$  at the  $\Delta K_{\text{TH}}$  threshold (where there is no discernable crack growth) in an attempt to remove any possible crack bridging in the wake of the pre-crack. The resistance curve (R-curve) behavior was then evaluated by measuring the crack-growth resistance,  $K_{\text{R}}$ , as a function of crack extension,  $\Delta a$ .

### D. Metallography and Fractography

Fatigue and fracture surfaces were imaged in a scanning electron microscope (SEM). Specimens were prepared by mechanical polishing, followed by etching in Murakami's reagent (aqueous solution of potassium ferricyanide and sodium hydroxide). This etchant selectively attacks  $\text{Mo}_5\text{SiB}_2$  ( $T_2$ ) and hence can be used to differentiate between the  $T_2$  and  $\text{Mo}_3\text{Si}$  phases, which have nearly the same back-scattered electron contrast. These phases were identified both by energy dispersive spectroscopy (EDS, Noran 5502) and powder x-ray diffraction (XRD, Siemens Diffraktometer). In addition, crack-path profiles were obtained by examining polished and etched metallographic sections cut perpendicular to the fracture surfaces.



#### D. Oxidation/Pesting Behavior of Mo-Si-B Alloy

In order to assess the oxidation resistance of the Mo-Si-B alloy, particularly at intermediate temperatures (400° to 900°C) where pest reactions can occur, oxidation tests were carried out on the alloy IM1. Small coupons measuring ~10 x 10 x 1 mm were sectioned from HIPed samples, polished in successive steps to a 1  $\mu\text{m}$  finish, ultrasonically cleaned in water, and then rinsed successively in ethanol and acetone prior to drying in air. The initial size and weight of each coupon were carefully measured before being placed in high-purity alumina boats in such a way as to minimize contact. Oxidation tests involved exposure for a fixed length of time at a constant temperature in an air furnace, with coupons they were inserted into the furnace chamber 2 hr after the desired temperature had been reached in order to purge the chamber with air prior to each run. Coupons were then periodically weighed to observe the transient weight change and to determine isothermal oxidation rates. The oxidation resistance was estimated by dividing the weight change of the coupons after exposure by their surface area. Oxidation scales and phases after exposure were evaluated using x-ray diffraction and energy dispersive spectroscopy.

### III. RESULTS

#### A. Microstructure

Microstructures and particle size distributions of  $\alpha$ -Mo phase in the four boron-modified molybdenum silicide alloys developed for the present study are shown, respectively, in Fig. 1 and Table 2. All alloy microstructures consist of three phases:  $\alpha$ -Mo (bcc structure),  $\text{Mo}_3\text{Si}$  (cubic A15) and  $\text{Mo}_5\text{SiB}_2$  ( $T_2$ ) (tetragonal D8<sub>1</sub>). The I/M alloys consist of ~38 vol.% of  $\alpha$ -Mo with roughly 30 vol.% of each of the two intermetallic phases; the P/M alloys, conversely, contain a significantly lower  $\alpha$ -Mo volume fraction (~21%). Specifically, the differences in the four alloys lie in the volume fraction, size and distribution of the  $\alpha$ -Mo, especially with respect to the extent of clustering, which is most prevalent in the I/M alloys (Table 2).

- IM1 alloy: This Mo-12Si-8.5B alloy has the coarsest microstructure, with the largest average  $\alpha$ -Mo particle size of ~10  $\mu\text{m}$  (range from ~0.5 to 100  $\mu\text{m}$ ) within a brittle intermetallic  $\text{Mo}_3\text{Si}/\text{Mo}_5\text{SiB}_2$  matrix. The  $\alpha$ -Mo generally exists as a discrete and discontinuous phase, as in all four alloys; however, in the IM1 alloy, there is the largest number of large (> 30  $\mu\text{m}$ )  $\alpha$ -Mo particles which often form semi-continuous Mo phase regions (Fig. 1a).

- IM2 alloy: Despite the difference in composition due to the addition of 10 at.% Nb,<sup>2</sup> the microstructure of this Mo-12Si-10Nb-8.5B alloy (Fig. 1d) is quite similar to that of IM1. However, the “semi-continuity” of the Mo phase distribution is far less in evidence and the average size of  $\alpha$ -Mo phase is somewhat smaller ( $\sim 7 \mu\text{m}$ ). Indeed, the less continuous distribution of  $\alpha$ -Mo phase and its smaller average size is reasoned to be a prime reason for its lower fracture toughness compared to that of alloy IM1, although the Nb additions (which harden the Mo phase) may also lower its toughness.
- PM1 and PM2 alloys: Both these alloys have nominally identical compositions (Mo-16.8Si-8.4B) despite being processed by different routes; their respective microstructures are shown in Figs. 1b and 1c. They have significantly finer microstructures than the corresponding I/M alloys, with a lower  $\alpha$ -Mo content. Alloy PM1 consists of a uniform distribution of fine  $\alpha$ -Mo particles (average size  $\sim 2 \mu\text{m}$ ) within a brittle  $\text{Mo}_3\text{Si}/\text{Mo}_5\text{SiB}_2$  matrix, with little evidence of clustering (standard deviation,  $2.03 \mu\text{m}$ ). Alloy PM2, obtained by HIPing crushed Mo-20Si-10B particles with fine Mo powders, displays an extreme distribution of the Mo phase, consisting of either small ( $\sim 1 \mu\text{m}$ ) or large ( $\sim 50 - 60 \mu\text{m}$ ) particles with an average size of  $\sim 4.41 \mu\text{m}$ . The finer  $\alpha$ -Mo particles are relatively equiaxed in shape and have a fairly periodic distribution in the  $\text{Mo}_3\text{Si}/\text{Mo}_5\text{SiB}_2$  matrix, whereas the larger particles tend to be elongated (aspect ratio  $\sim 5$  to  $10$ ) and are more randomly distributed.

**Table II:  $\alpha$ -Mo Particle Size Distributions**

<b>Alloy</b>	<b>Volume fraction of <math>\alpha</math>-Mo phase (%)</b>	<b>Average size of <math>\alpha</math>-Mo phase (<math>\mu\text{m}</math>)</b>	<b>Standard deviation (<math>\mu\text{m}</math>)</b>	<b>Maximum size (<math>\mu\text{m}</math>)</b>	<b>Minimum size (<math>\mu\text{m}</math>)</b>
<b>IM1</b>	38	10.43	16.37	100	0.5
<b>IM2</b>	38	6.99	10.83	50	0.5
<b>PM1</b>	21	2.14	2.03	8	0.5
<b>PM2</b>	21	4.41	11.21	60*	0.5

\*As the largest  $\alpha$ -Mo particles in the PM2 microstructure have an elongated shape with aspect ratios between  $\sim 5$  to  $10$ , the diameter of the maximum particle is defined as an average of the largest and the smallest diameters.

<sup>2</sup> Essentially, Nb dissolves in all three phases ( $\alpha$ -Mo,  $\text{Mo}_3\text{Si}$ , and  $\text{Mo}_5\text{SiB}_2$ ), which leads to an increase in their lattice parameters as Nb has a larger atomic radius than Mo for which it substitutes [3].

## B. “Pest” Reaction

Molybdenum silicide alloys are known to be susceptible to oxidation (or “pestering” [2,8,12,14,15]) at intermediate temperatures (~300 to 800°C), which results from a competition between the formation and volatilization of the MoO<sub>3</sub>, which begins at lower temperatures, with the formation of a continuous protective passivating SiO<sub>2</sub> layer at higher temperatures. The pest problem generally arises at the lower temperatures as the protective oxide layers which form there have insufficient fluidity to effectively cover microcracks created by the large dilation associated with the oxide formation. This problem is generic to all forms of molybdenum silicides [14-18], and is typically characterized by a brief initial period of fairly rapid weight gain, an intermediate period of several hours of duration where the weight changes little with time, and finally a period of accelerating rate of weight loss.

Since MoSi<sub>2</sub> is highly susceptible to pestering at ~300 to 600°C (the bulk material can be completely reduced to powder after less than 100 hr exposure in air [8,9,12]), the oxidation properties of the current IM1 alloy were examined between 400° and 900°C. Results are shown in Fig. 2 for 50 hr exposures in air, and are compared to those for monolithic Mo<sub>5</sub>Si<sub>3</sub> at 800°C [12]. It is apparent that compared to Mo<sub>5</sub>Si<sub>3</sub>, the kinetics of the pest reaction in the Mo-Si-B alloy was significantly slowed down at these temperatures.

Specifically, oxidation rates were negligible at 400° to 600°C as samples showed no change in weight or appearance. The formation of the MoO<sub>3</sub> scale in this alloy is negligible below 600°C; indeed, x-ray diffraction studies did not reveal any molybdenum or silicon oxide scales either at 400° or 500°C, except for a thin white surface layer of MoO<sub>3</sub> at 600°C. At 700°C, MoO<sub>3</sub> was also detected, and the small, but finite, measured weight loss, coupled with some degree of shape change (inset, Fig. 2), at this temperature can be attributed to the onset of MoO<sub>3</sub> evaporation. At 800°C, the largest weight loss was seen with some degree of distortion and delamination of the specimen (inset, Fig. 2), due to the sublimation of the MoO<sub>3</sub> which becomes significant above ~750°C [14,16]. However, the weight change was not large as compared to Mo<sub>5</sub>Si<sub>3</sub>, due to the formation of a nearly continuous layer of borosilicate glass (B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>) at ~800°C which provides a degree of protection that increases with increasing temperature. As this B-containing silica glass exhibits a lower viscosity than silica itself, with a higher diffusion rate for oxygen, it can form more rapidly and flow into cracks and voids on the alloy surface to provide greater oxidation protection [13,25]. This is particularly apparent at 900°C where the large surface pores caused by severe volatilization of MoO<sub>3</sub> were covered by a liquid-like borosilicate

glass layer (inset, Fig. 2). This resulted in an improved oxidation protection with the weight change at 900°C lower than either at 700° or 800°C. X-ray diffraction analysis also revealed the presence of the MoO<sub>2</sub> phase on the surfaces at 900°C.

These results suggest that Mo-Si-B alloys possess a better pesting resistance as compared to non B-containing molybdenum silicides, due to minimal MoO<sub>3</sub> formation below ~700°C and protection by the B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> scale above ~800°C. However, the oxidation resistance of these alloys at and just below 800°C is still of some concern with weight losses that are not insignificant. Moreover, the pesting resistance can be quite sensitive to small variations in temperature, and such factors as the local composition, the degree of pre-existing pores or cracks, etc., can cause of changes in the oxidation behavior. In addition, at very high temperatures above ~1500°C, the viscosity of the borosilicate glass can decrease so much that dripping of the scale takes place; this naturally leads to the protection capability of the glass to be considerably diminished [13]. Clearly, the oxidation resistance of these alloys is far from optimized and does require further study.

### C. *Fracture Toughness Behavior*

The fracture toughness properties of the four Mo-Si-B alloys were determined at temperatures between ambient and 1300°C in terms of their resistance-curve behavior. From the results, which are plotted in Fig. 3, several points are worthy of note:

- Both I/M alloys displayed some degree of rising R-curve behavior at all temperatures with subcritical crack growth extending for ~200 to 800 μm; this effect is relatively minor, however, at 25°C. Such R-curve behavior is not shown by either of the P/M alloys, which failed catastrophically with little or no subcritical crack growth once the stress intensity exceeded the crack-initiation toughness,  $K_0 = K_{Ic}$ . The latter behavior is characteristic of monolithic MoSi<sub>2</sub> and Nb-particulate reinforced MoSi<sub>2</sub> [4].
- With the exception of the PM1 alloy, all Mo-Si-B alloys displayed at least a 50% higher fracture toughness than MoSi<sub>2</sub> [4] at ambient temperatures. The I/M alloys were significantly tougher than the P/M alloys, consistent with their higher α-Mo volume fraction and larger α-Mo particle size.
- The highest toughness was shown by the IM1 alloy, which had a crack-initiation toughness at 25°C of  $K_0 \sim 7.2 \text{ MPa}\sqrt{\text{m}}$ , rising over ~800 μm of crack extension to a steady-state (plateau) toughness of  $K_{ss} \sim 7.8 \text{ MPa}\sqrt{\text{m}}$ , i.e., some ~80 to 95% higher than that for monolithic MoSi<sub>2</sub> (where  $K_{Ic} \sim 4$

MPa√m). In comparison, the finer-grained IM2 alloy had ~13% lower toughness than IM1 at 25°C, with crack initiation and steady-state values of 6.3 and 6.7 MPa√m, respectively.

- Both P/M alloys were considerably more brittle. The PM2 alloy fractured catastrophically at crack initiation at  $K_{Ic} = 5.7$  MPa√m. The PM1 alloy was so brittle that it could not even be fatigue-precracked (at 25 or 1300°C). Based on crack initiation from a sharpened razor-micronotch, an over-estimate of  $K_{Ic}$  was measured at 4.3 MPa√m, consistent with an approximate indentation toughness measurement of 4.1 MPa√m; these values are essentially the same as that of unreinforced molybdenum disilicide.
- With increasing temperature, the fracture toughness of all four Mo-Si-B alloys increased. At 1300°C, the two P/M alloys displayed  $K_{Ic}$  values of 7.5 – 8.1 MPa√m, nearly twice the room temperature toughness. The IM1 alloy, however, had a toughness exceeding 10 MPa√m at 800° and 1200°C, whereas at 1300°C, a steeply rising R-curve was seen with the toughness increasing from an initial value of  $K_0 \sim 9.7$  MPa√m at crack initiation to a steady-state value of  $K_{ss} \sim 11.7$  MPa√m after ~400 μm of crack extension.

Specific crack-initiation and steady-state toughness values for all alloys are listed in Table III.

**Table III: Fatigue Toughness and Fatigue Threshold ( $R = 0.1$ ) Values**

Alloy	Temperature (°C)	Initiation Toughness, $K_0$ (MPa√m)	Steady-State Toughness, $K_0$ (MPa√m)	Fatigue Threshold $\Delta K_{th}$ (MPa√m)	Fatigue Threshold $K_{max,th}$ (MPa√m)
<b>IM1</b>	25°	7.2	7.8	4.9	5.4
	800°	9.9	10.4	6.6	7.3
	1200°	10.4	11.0	6.8	7.6
	1300°	9.7	11.7	7.5	8.3
<b>PM1</b>	25°	4.1	(4.1)	*	4.1
	1300°	8.1	(8.1)	-	8.1
<b>PM2</b>	25°	5.7	(5.7)	4.7	5.2
	1300°	7.5	7.7	-	-
<b>IM2</b>	25°	6.3	6.7	3.7	4.1
<b>MoSi<sub>2</sub><sup>#</sup></b>	25°	~4.0	(~4.0)	*	~4.0

<b>MoSi<sub>2</sub>/Nb<sub>p</sub><sup>#</sup></b>	25°	5.2	(5.2)	~2.0	~2.2
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\* No fatigue-crack growth is detected; samples fail catastrophically when  $K_{\max} \sim K_0$ .

<sup>#</sup> Prior results from refs. [4].

Fig. 4 shows scanning electron micrographs of the corresponding fracture surfaces for the IM1, PM1 and PM2 alloys. It is apparent that the fractures at 25°C are all predominantly brittle and transgranular in nature. The fracture surface of the lowest toughness PM1 alloy is particularly flat, shiny and “brittle-like” in appearance (Fig. 4b). Fracture at ambient temperatures is associated with crack trapping by the larger (>30 μm) α-Mo-particles (Fig. 5). Crack paths (Fig. 6) tend to be predominantly confined to the intermetallic matrix and the Mo/matrix interfaces, with the crack tending to circumvent or crack many of the smaller (≤10 μm) spherical particles and eventually fracturing through the larger (>30 μm) elongated ones. There is little evidence of plastic stretching in the Mo phase. Indeed, the “particle-like” features on the fracture surfaces (Fig. 4) are associated with the smaller α-Mo regions; they show few signs of interaction with the brittle fracture of the intermetallic matrix, and show little evidence of plastic deformation prior to failure (Fig. 4a). There is evidence of some of the larger α-Mo particles remaining unbroken in the crack wake, but the fact that so little deformation of the Mo phase occurs when it breaks limits the degree of ductile-phase toughening. A typical crack/particle interaction in the coarser-grained IM1 alloy at 25°C involves the main crack first being trapped by a large (~ 30 μm) α-Mo region (Fig. 5). With increasing applied stress, several microcracks form around the main crack and open up as the main crack moves on leaving the Mo phase unbroken in the crack wake; the main crack is then arrested at the next large α-Mo region and the process repeats itself (Fig. 6).

At elevated temperatures (800°–1300°C), however, above the ductile-brittle transition temperature of molybdenum<sup>3</sup>, a significant amount of stretching and debonding of the α-Mo phase from the Mo<sub>3</sub>Si/Mo<sub>5</sub>SiB<sub>2</sub> matrix can be seen prior to failure of the Mo particles (Fig. 4d). In the coarser-grained I/M alloys, this results in significantly increased toughening, primarily from crack bridging by unbroken α-Mo particles in the crack wake (Fig. 7). In addition, there is evidence of extensive microcracking, parallel to the main crack tip. Such microcracking is predominantly contained in the Mo<sub>5</sub>SiB<sub>2</sub> phase and invariably arrests at the α-Mo, presumably because of the higher ductility of molybdenum at these temperatures.

<sup>3</sup> Depending upon purity and processing history, the ductile-brittle transition temperature of molybdenum is between ~50° and 500°C [26,27].

#### D. Fatigue-Crack Propagation Behavior

The variation in the cyclic fatigue-crack propagation rates,  $da/dN$ , with the maximum and alternating stress intensities,  $K_{\max}$  and  $\Delta K$ , respectively, at  $R = 0.1$  for Mo-Si-B alloys IM1, IM2 and PM2 at 25°C and alloy IM1 at 800° to 1300°C is shown in Fig. 8; fatigue threshold values are listed in Table III. Corresponding stable fatigue-crack growth in alloy PM1 could not be obtained as samples failed catastrophically at  $\Delta K \sim 4 \text{ MPa}\sqrt{\text{m}}$  after less than 30  $\mu\text{m}$  of apparent crack extension. Results for the Mo-Si-B alloys, which span growth rates from  $<10^{-10}$  to  $10^{-6}$  m/cycle, are compared in Fig. 8 with previous data on the monolithic  $\text{MoSi}_2$  and the  $\text{MoSi}_2$  reinforced with Nb spheres [4].

At ambient temperatures, the optimal resistance to fatigue-crack growth, in the form of the highest  $\Delta K_{\text{th}}$  or  $K_{\max,\text{th}}$  fatigue thresholds, was found in the coarser-grained IM1 alloy; the somewhat finer-scale IM2 alloy had an approximately 30% lower threshold. Despite its lower toughness, the PM2 alloy showed a room temperature threshold close to that of the IM1 alloy; compliance measurements suggested that this anisotropic microstructure, with large elongated  $\alpha$ -Mo particles, was somewhat more effective in promoting crack deflection and (roughness-induced) crack closure. In general though, higher toughness equated to improved fatigue resistance, with the  $K_{\max,\text{th}}$  threshold being on the order of  $0.7 K_{\text{ss}}$  in the I/M alloys and  $\sim K_0$  in the P/M alloys (which essentially displayed a minimal sensitivity to fatigue).

With increase in temperature, resistance to fatigue-crack propagation was enhanced, at least in the IM1, PM1 and PM2 alloys that were evaluated. Fatigue thresholds,  $\Delta K_{\text{th}}$ , in IM1 were increased from  $\sim 5 \text{ MPa}\sqrt{\text{m}}$  at 25°C to over  $7 \text{ MPa}\sqrt{\text{m}}$  at 1200° to 1300°C. Indeed, it is apparent that both toughness and fatigue resistance are increased with increasing temperature in these alloys (Fig. 9).

Similar to most brittle ceramics and intermetallics, however, cyclic crack-growth rates in these alloys was strongly dependent upon  $\Delta K$  (or more precisely with the prime dependency on  $K_{\max}$ ) and displayed steep, linear, growth-rate curves [28,29]. In terms of a Paris power-law expression,  $da/dN \propto \Delta K^m$ , the exponent,  $m$ , for these alloys was extremely high and comparable to those measured in untoughened ceramics, where  $m$  can be as high as 50 or more [30]. Due to improved ductility, the value of this exponent decreased with temperature: at 25°C,  $m \sim 60$ , between 800° and 1200°C, it is  $\sim 55$ , and at 1300°C, it drops to  $\sim 44$ .

Crack-particle interactions in the Mo-Si-B alloys under cyclic loading were observed to be quite similar to those under monotonic loading. In general, fatigue cracks at ambient temperatures tended to propagate through, or around, the smaller ( $<10\ \mu\text{m}$ )  $\alpha$ -Mo particles and arrest at the larger ones. However, at increasing temperatures, only limited ductile-phase bridging by the  $\alpha$ -Mo phase was detected, although extensive microcracking in the  $\text{Mo}_5\text{SiB}_2$  regions was again seen parallel to the main crack path.

#### IV. DISCUSSION

On the basis of several recent studies [e.g., 1-3,7,11-18], boron-containing molybdenum silicide alloys appear offer good potential for future very high temperature structural alloys. Of these, alloys containing  $\text{Mo}_3\text{Si}$  and T2, with  $\alpha$ -Mo to promote ductile-phase toughening and boron to promote resistance to intermediate temperature oxidation (pestring), appear to be stable and superior to  $\text{MoSi}_2$  and  $\text{Mo}_5\text{Si}_3$ , both in terms of pestring resistance and low-temperature toughness properties. In the present work, alloys based on the nominal composition (in at.%) Mo-12-17Si-8.5B, comprising  $\sim 21$ -38 vol.%  $\alpha$ -Mo within an intermetallic matrix of  $\text{Mo}_3\text{Si}$  and  $\text{Mo}_5\text{SiB}_2$ , have been shown (i) to be more resistant to pestring than Mo-Si alloys primarily due to the formation of a low-viscosity protective scale of borosilicate glass (see also [12-18]), and (ii) to provide much improved fracture toughness and crack-growth resistance compared to  $\text{MoSi}_2$ . Moreover, what is perhaps most impressive about these alloys is that their toughness and crack-growth resistance appear to improve with increase in temperature up to  $1300^\circ\text{C}$ .

*It is important to note, however, that the superior fracture toughness (and fatigue) properties are only realized with specific microstructures.* Although the coarse-grained I/M alloy, IM1, which develops an ambient-temperature toughness that is almost double that of unreinforced  $\text{MoSi}_2$ , the much finer-grained P/M microstructure, PM1, which contains  $\sim 50\%$  lower  $\alpha$ -Mo volume fraction, has a toughness of only  $4\ \text{MPa}\sqrt{\text{m}}$ , which is no better than  $\text{MoSi}_2$ .

Below we examine the various toughening mechanisms involved, the influence of microstructure in promoting these mechanisms, and their comparative effect on resistance to fatigue-crack propagation, at both ambient and elevated temperatures.

##### A. Toughening Mechanisms



The toughening of a brittle matrix with a ductile phase can be achieved through *extrinsic* toughening mechanisms such as ductile-phase bridging and microcracking [29]. These mechanisms can impede crack growth through a process of crack-tip shielding in the crack wake, which acts to “shield” the crack tip from the full applied driving force; as such, they promote *crack-growth toughness* in the form of a rising R-curve. Crack trapping, where the main crack is impeded by the presence of a particle or phase and must renucleate across this entity, is an *intrinsic* toughening mechanism which, conversely, tends to enhance the *crack-initiation toughness*. In addition to their effect on the R-curve, which is shown schematically in Fig. 10, these classes of toughening mechanisms have other important distinctions, notably that intrinsic mechanisms are equally effective under fatigue loading, whereas extrinsic mechanisms tend to degrade under cyclic loads. Indeed, there is ample evidence that ductile-phase bridging in an intermetallic matrix is relatively ineffective under cyclic loading as the ductile bridges tend to fail prematurely by fatigue [4,29,31-33].

In the current work, fractographic and crack-path observations imply that these are the three primary toughening mechanisms in Mo-Si-B alloys, specifically:

- crack trapping, principally by the  $\alpha$ -Mo phase at ambient temperatures
- additional ductile-phase bridging, again by the  $\alpha$ -Mo phase, at elevated temperatures, and
- microcracking, within the  $\text{Mo}_5\text{SiB}_2$  phase, exclusively at elevated temperatures.

Of the four alloys tested at 25°C, the coarsest-scale I/M alloy, IM1, exhibits the highest initiation toughness ( $\sim 7.2 \text{ MPa}\sqrt{\text{m}}$ ), followed by IM2 ( $\sim 6.3 \text{ MPa}\sqrt{\text{m}}$ ); the finer-scale P/M alloys, with their lower  $\alpha$ -Mo content, show the lowest toughnesses, i.e.,  $\sim 5.7 \text{ MPa}\sqrt{\text{m}}$  for alloy PM2 and  $\sim 4.1 \text{ MPa}\sqrt{\text{m}}$  for alloy PM1. This same ranking applies at elevated temperatures and is true for both the initiation and steady-state toughness values. This implies that the alloys with a higher fraction of large  $\alpha$ -Mo particles, and hence the smaller “effective” inter-particle spacing, exhibit higher fracture toughness than those with low volume fractions and finer  $\alpha$ -Mo particles. Indeed, microstructural observations clearly show how cracks are locally arrested at the larger Mo regions, typically greater than  $\sim 30 \mu\text{m}$ , as opposed to propagating through, or around, the smaller ones (Fig. 5). Moreover, compared to the IM2 alloy which displays the second coarsest distribution of  $\alpha$ -Mo, the IM1 microstructure has the larger degree of clustering of the  $\alpha$ -Mo phase, which results in semi-continuous Mo regions (Fig. 1a). Since this increases the probability of the crack intercepting the ductile phase, such coarse, semi-continuous Mo regions significantly enhance the effectiveness of both the crack trapping and ductile-phase bridging

mechanisms. Indeed, compared to the PM1, which is the most brittle, and the finest-scale, of the four alloys, the IM1 alloy has a factor of five times larger average size of  $\alpha$ -Mo particles (Table II).

### 1. Crack trapping

Crack trapping is a common toughening mechanism for brittle materials reinforced with ductile phases [34,35]. As an intrinsic toughening process, it does not result in a rising R-curve due to the absence of process zone, but instead acts to enhance the crack-initiation toughness; furthermore, it is effective in fatigue. Both characteristics are shown by the alloys in the present study (Figs. 3 and 8).

Such trapping appears to be the dominant toughening mechanism in Mo-Si-B alloys at 25°C, although it is still active at elevated temperatures. At such ambient temperatures, the toughening effect of the crack bridging by the intact ductile particles appears to be comparatively minor, presumably due to the limited ductility of Mo at 25°C [26,27]; this results in the Mo-Si-B alloys displaying relatively shallow R-curves at lower temperatures, as shown in Fig. 3.

As noted above, the trapping process involves crack arrest primarily at the larger  $\alpha$ -Mo particles, subsequent microcrack formation ahead of the crack tip, and renucleation of the crack across the particle, either by bowing out between the pinning regions or propagating through the particle (Fig. 6). The increase in crack-initiation toughness,  $K_o$ , with increasing volume fraction, size and changing morphology of the  $\alpha$ -Mo phase is consistent with this mechanism, as shown by the ambient-temperature  $K_o$  data for the four alloys in Fig. 3; it is further consistent with theoretical models. In terms of the Bower and Ortiz model [34] for a composite of crack-trapping particles embedded in a matrix, the crack-initiation toughness of the “composite”,  $K_o^{trap}$ , can be expressed in terms of the relative toughness of the matrix,  $K_c^m$ , and the particles,  $K_c^p$ , as:

$$K_o^{trap} \approx K_c^m \left\{ 1 + \frac{2r}{l} \left[ \left( \frac{K_c^p}{K_c^m} \right)^2 - 1 \right] \right\}^{1/2}, \quad (1)$$

where  $r$  is the characteristic dimension of the trapping particles, and  $l$  is their average spacing. From this expression, it is immediately apparent that as the size,  $r$ , of  $\alpha$ -Mo regions increase (and correspondingly their spacing,  $l$ , decreases), the crack-trapping mechanism becomes more effective resulting in a higher initiation toughness, as shown by the results in Fig. 3. Quantitatively, using a fracture toughness for Mo at 25°C of 15 MPa $\sqrt{m}$  [36,37] and for the Mo<sub>3</sub>Si/Mo<sub>5</sub>SiB<sub>2</sub> matrix of 3.5 MPa $\sqrt{m}$  [6], and average values (based on crack profile measurements) of  $r/l$  ranging from  $\sim 0.2$  (for

alloy IM1) to 0 (for alloy PM1), estimates of the ambient-temperature crack-initiation toughness were calculated from Eq. 1 and are listed in Table IV. Despite the uncertainties involved<sup>4</sup>, the predicted  $K_0$  toughnesses due solely to crack trapping are reasonably close to the experimentally measured values, and exactly reflect the ranking of the alloys.

**Table IV: Crack-Initiation Toughness Predictions Based on Crack Trapping**

Alloy	$r$ , Characteristic dimension ( $\mu\text{m}$ )	$l$ , Effective spacing <sup>a</sup> ( $\mu\text{m}$ )	$2r/l$	Calculated $K_0$ toughness ( $\text{MPa}\sqrt{\text{m}}$ )	Experimental $K_0$ toughness ( $\text{MPa}\sqrt{\text{m}}$ )
IM1	10.43	50	0.42	9.8	7.2
IM2	6.99	50	0.14	6.5	6.3
PM1	2.14	$\infty$	0	3.5	4.1 <sup>b</sup>
PM2	4.41	50	0.09	5.6	5.7

<sup>a</sup> Effective spacing,  $l$ , is defined as an average distance between the large (trapping)  $\alpha$ -Mo particles ( $\geq 20 - 30 \mu\text{m}$ ).

<sup>b</sup> This represents an indentation toughness, which is used instead of the more conventional techniques due to the extreme brittleness of alloy PM1.

Although Eq. 1 does not take into account the shape of  $\alpha$ -Mo particles, it was apparent from crack profiles showing the crack/ $\alpha$ -Mo particle interactions that crack trapping was more effective at irregular, rather than spherically, shaped particles. This observation is consistent with previous studies on  $\text{MoSi}_2$ , where composite alloys reinforced with Nb wires exhibited far higher toughnesses than those containing Nb particulate [32].

## 2. Ductile-phase bridging

Due to crack trapping by the larger  $\alpha$ -Mo regions, there is some degree of crack bridging by intact Mo regions in the crack wake at ambient temperatures; however, because of the low ductility of Mo at these temperatures, this mechanism is not particularly effective, as evidenced by the relatively flat R-curves at 25°C. Indeed, the limited effect of ductile-phase bridging at low temperatures is not unusual where “semi-ductile” refractory metals such as Mo, V, Cr, or W are selected as bridging phases, simply because of their minimal ductility at these temperatures [38]. However, with the increased ductility of the metal phase, this extrinsic toughening mechanism appears to be far more effective at elevated

<sup>4</sup>The precise toughness of the  $\alpha$ -Mo phase is difficult to assess as small amounts of interstitial impurities, such as oxygen, can severely embrittle molybdenum at ambient temperatures [37].

temperatures (Fig. 7) and results in more pronounced R-curve behavior, as is particularly apparent for the IM1 alloy at 1300°C (Fig. 3).

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 [39]. 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  $\chi = \int_0^{u^*} (\sigma(u) du / \sigma_o r)$ , where  $\sigma_o$  is the yield strength of the ductile phase, and  $u^*$  is the critical crack-opening displacement for its fracture [39,40]. The corresponding steady-state toughening,  $K_{ss}^{br}$ , is then given by:

$$K_{ss}^{br} \approx \sqrt{(K_o^m)^2 + f_b E' \sigma_o r \chi} \quad , \quad (2)$$

where  $K_o^m$  is effectively the crack-initiation toughness of the matrix,  $E'$  is the plane-strain elastic modulus of the “composite”, and  $f_b$  is the volume fraction of bridging phase. Considering the IM1 alloy, taking values at 1300°C for  $E'$  for Mo-12Si-8.5B of  $\sim 179$  GPa and  $\sigma_o$  for  $\alpha$ -Mo of  $\sim 103$  MPa [5,6,32], with a volume fraction of  $\alpha$ -Mo of  $f \sim 0.38$  with  $r \sim 5$   $\mu\text{m}$ , Eq. 2 predicts a value of the steady-state toughness due solely to bridging in alloy IM1 of  $K_{ss}^{br} \sim 10.8$  MPa $\sqrt{\text{m}}$ , assuming a matrix toughness of  $K_o^m \sim 3.5$  MPa $\sqrt{\text{m}}$  [6] and an estimated value of  $\chi$  of 3, based on the tensile properties of Mo at 1300°C [41,42]. Although only a rough estimate, the predicted toughness is comparable to the experimentally measured  $K_{ss}$  value of  $\sim 11.7$  MPa $\sqrt{\text{m}}$  at 1300°C.

### 3. Microcracking toughening

An additional source of toughening in Mo-Si-B alloys can arise at elevated temperatures from microcracking. This can be seen in Fig. 7 as microcracks zone of significant dimensions ( $\sim 400$   $\mu\text{m}$ ), arrested between  $\alpha$ -Mo regions, in layers parallel to the main crack path. Most of the microcracks formed in the  $\text{Mo}_5\text{SiB}_2$  phase, presumably because of its higher thermal expansion, i.e., 8 ppm/K, as compared to Mo and  $\text{Mo}_3\text{Si}$  (5.9 and 6.0 ppm/K, respectively) [43], and its tetragonal crystal structure (both Mo and  $\text{Mo}_3\text{Si}$  are cubic).

The formation of such a zone of microcracks around the crack tip can be considered to dissipate energy through work done in the opening and sliding displacements involved in microcracking and

through creation of new surfaces [44-51]. 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 [45]. 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 [46,47]. As the coefficient of thermal expansion of Mo at 1300°C ( $6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  [26]) is lower than that of  $\text{Mo}_5\text{SiB}_2$  ( $8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  [52]), 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 [46].

Microcrack toughening has been modeled in terms of (i) the volume displaced by the microcracks and (ii) the resulting reduction in the elastic modulus within the process zone. The dilatation in the vicinity of the crack tip introduces a nonlinear stress-strain response, which on unloading results in closure forces on the crack wake [53]. The increase in toughness at steady-state can then be estimated in terms of the closure stress intensity for such dilatational toughening [49,53] and the modulus reduction [45,54] as:

$$\Delta K_{ss}^{mic} \approx 0.22 \varepsilon E' f_m h^{1/2} + \beta f_m K_o^m . \quad (3)$$

The first term in Eq. 3 represents the dilatation toughening, where  $E' = E$ , Young's modulus, in plane stress, and  $E/(1 - \nu^2)$  in plane strain ( $\nu$  is Poisson's ratio),  $f_m$  is the volume fraction of microcracks,  $\varepsilon$  is the dilatational strain, and  $h$  is the height of microcrack zone. The second term represents the compliance toughening, where  $\beta$  is a parameter ( $\sim 1.2$  [54]) that depends on Poisson's ratio and the (untoughened) matrix toughness ( $K_o^m \sim 3.5 \text{ MPa}\sqrt{\text{m}}$  [3]). For the IM1 alloy at 1300°C, direct measurements of crack profiles gave approximate values for the volume fraction of microcracks in the microcracking zone as  $f_m \sim 0.15$ , the height of this zone as  $h \sim 20 \text{ }\mu\text{m}$ , and the residual volumetric strain as  $\varepsilon \sim 0.06$ . Estimates of the maximum microcrack toughening at 1300°C yield an increase in  $K_{ss}$  of  $\sim 2 \text{ MPa}\sqrt{\text{m}}$  due to dilatation toughening and a further  $\sim 1 \text{ MPa}\sqrt{\text{m}}$  from the compliance change.

Although comparatively minor compared to crack trapping and bridging, it can be seen that microcracking does have the potential to further increase the R-curve toughening by up to  $\sim 3 \text{ MPa}\sqrt{\text{m}}$ , which is roughly consistent with experimental findings (Fig. 3).

## B. Fatigue-Crack Propagation

Characteristic of many brittle intermetallic and ceramic materials [29], fatigue-crack propagation in the Mo-Si-B alloys is extremely sensitive to the applied stress intensities (Fig. 8), i.e., to the stresses and crack size, which results in very high exponent  $m$  values in the Paris law relationship. Despite these high values, resistance to fatigue-crack growth in terms of the specific fatigue thresholds (Table III) is in general far larger in the present boron-doped molybdenum silicides than in monolithic MoSi<sub>2</sub> (which simply fails catastrophically at  $K_{Ic} \sim 4 \text{ MPa}\sqrt{\text{m}}$ ) or in MoSi<sub>2</sub> reinforced with Nb spheres (Nb<sub>p</sub>/MoSi<sub>2</sub>) [4]. However, similar to the fracture toughness behavior, these superior fatigue properties are not realized in all Mo-Si-B microstructures.

In general, the coarser microstructures with the higher  $\alpha$ -Mo content that develop the higher toughnesses display the better fatigue-crack growth resistance; specifically, in the I/M Mo-Si-B alloys,  $K_{\text{max,th}}$  thresholds are nominally 70% of the steady-state toughness values. Indeed at 25°C, the  $K_{\text{max,th}}$  threshold for the toughest alloy IM1 is over 5 MPa $\sqrt{\text{m}}$ , compared to  $\sim 2 \text{ MPa}\sqrt{\text{m}}$  in Nb<sub>p</sub>/MoSi<sub>2</sub> [4]. Moreover, akin to the toughness, the threshold values are even higher at elevated temperatures, rising in the IM1 alloy to over 8 MPa $\sqrt{\text{m}}$  at 1300°C. This results from the coupled nature of the fracture toughness and fatigue-crack growth properties in brittle solids such as molybdenum silicides. As noted above, the toughness is increased at elevated temperatures primarily due to the improved high temperature ductility of  $\alpha$ -Mo phase, which results in the onset of additional (extrinsic) toughening mechanisms, namely microcracking and more significantly ductile-phase bridging. However, due to premature fatigue of the bridging  $\alpha$ -Mo particles in the crack wake, the latter mechanism appears to degrade under cyclic loading leading to subcritical crack growth at lower applied  $K$  levels, similar to behavior reported for ductile-phase toughened MoSi<sub>2</sub>,  $\gamma$ -TiAl and Nb<sub>3</sub>Al intermetallics [31-33]. It is likely that except for crack growth in the Mo regions at temperatures above ambient, fatigue-crack growth in these alloys occurs, as in most brittle solids [29], primarily by the cyclic-loading induced suppression of extrinsic toughening in the crack wake, with the actual crack advance mechanism being essentially identical to that under monotonic loads. Such a mechanism is totally consistent with the lack of any significant change in the fracture morphology under monotonic and cyclic loading, and more importantly with the extremely high sensitivity of growth rates to the applied stress intensities, i.e., to very high  $m$  exponents.

In light of this large dependency on applied stress intensities, the use of these intermetallics and for safety-critical structural applications subject to cyclic loading will increasingly require reliable in-service fatigue lifetime prediction. The extremely high  $m$  values are actually indicative of a minimal susceptibility to fatigue failure; however, they do imply that the cycles or time to failure will be extremely sensitivity to crack size and the applied stress. For this reason, the use of traditional damage-tolerant approaches for lifetime prediction, which rely on the integration of  $(da/dN)/K$  curves to estimate the time for a presumed initial crack to grow to failure, may prove difficult to utilize in practice [30]. However, since subcritical crack growth under cyclic loading can definitely occur in these alloys, a more reasonable basis for design with these materials would appear to be through the use of the  $K_{\max,TH}$  (or  $\Delta K_{TH}$ ) fatigue threshold, which in these alloys is typically  $\sim 70$  to  $100\%$  of the highest toughness on the R-curve; indeed, in the limit,  $K_{\max,TH} \rightarrow K_0$ . In this regard, it is pertinent to note in conclusion that the threshold values measured in this work for the tougher I/M alloys are certainly comparable at ambient temperatures with many metallic alloys, but are far superior to any metallic material at temperatures above  $1000^\circ\text{C}$ .

## V. CONCLUSIONS

Based on a study, at ambient to elevated temperatures ( $25^\circ$  to  $1300^\circ\text{C}$ ), of the fracture toughness, fatigue-crack propagation and “pecking” properties of a range of I/M and P/M boron-containing molybdenum silicide (Mo/12-17at.%Si/8.5at.%B) alloys, comprising  $\sim 21$  to  $38$  vol.%  $\alpha$ -Mo phase in an intermetallic matrix of  $\text{Mo}_3\text{Si}$  and  $\text{Mo}_5\text{SiB}_2$  ( $T_2$ ), the following conclusions can be made:

1. Boron-modified molybdenum silicide alloys display an improved “pest” resistance at  $400^\circ$  to  $900^\circ\text{C}$  as compared to unmodified molybdenum silicides, such as  $\text{Mo}_5\text{Si}_3$ , although the weight losses at  $\sim 800^\circ\text{C}$  are still of some concern. The improved pest resistance compared to  $\text{Mo}_5\text{Si}_3$ , however, results from the formation of a semi-protective layer of borosilicate glass ( $\text{B}_2\text{O}_3/\text{SiO}_2$ ), which (i) provides a degree of protection that increases with increasing temperature, and (ii) has sufficient fluidity (compared to  $\text{SiO}_2$ ) at lower temperatures to flow into cracks and voids to protect the alloy surface.
2. In their ingot-metallurgy processed form, these Mo-Si-B alloys, which contain a higher volume fraction of relatively ductile  $\alpha$ -Mo regions, provide a marked increase in the ambient to high temperature fracture toughness properties compared to conventional monolithic molybdenum silicides, such as  $\text{MoSi}_2$  or  $\text{Mo}_5\text{Si}_3$ . Fatigue-crack propagation resistance between  $25^\circ$  to  $1300^\circ\text{C}$  is

similarly improved. Indeed, both the fracture toughness and fatigue-crack propagation thresholds are actually increased with increasing temperature between 25° and 1300°C.

3. Corresponding powder-metallurgy processed Mo-Si-B alloys, which have considerably finer-scale microstructures with ~50% lower  $\alpha$ -Mo volume fraction, show far smaller improvements in their toughness and fatigue-crack propagation properties. Indeed, both alloys tested had, at best, only marginally better toughness properties than monolithic MoSi<sub>2</sub> (one was too brittle to fatigue).
4. The fracture toughness and fatigue-crack propagation thresholds for all Mo-Si-B alloys tested actually increased with increasing temperature between 25° and 1300°C.
5. Optimum toughness (and fatigue) properties were found with the coarser microstructures containing the high  $\alpha$ -Mo volume fractions with large (>30  $\mu$ m), “semi-continuous” regions of this phase. Such observations were consistent with the three primary toughening mechanisms identified for these alloys, namely crack trapping, ductile-phase bridging and microcracking.
6. At ambient temperatures, the principal toughening mechanism appeared to be crack trapping by the larger (>30  $\mu$ m)  $\alpha$ -Mo particles. As such trapping requires renucleation of the main crack across the particle, this is an intrinsic toughening mechanism which acts to increase the crack-initiation toughness, consistent with experimental observations; consequently, only minimally rising R-curves were seen at 25°C. Microstructurally, the effect of this toughening mechanism was enhanced by increasing the volume fraction and size of the Mo particles.
7. At elevated temperatures, the principal toughening mechanism appeared to be ductile-phase bridging by the larger (>30  $\mu$ m)  $\alpha$ -Mo particles that remained unbroken in the crack wake. In principle, this mechanism is also active at lower temperatures, but the much lower ductility of the Mo phase severely limited its potency. As this is an extrinsic mechanism, rising R-curve behavior was observed at the higher temperatures; this became more apparent with increasing temperature owing to the increasing ductility of the Mo. Microstructurally, the effect of this toughening mechanism was also enhanced by increasing the volume fraction and size of the  $\alpha$ -Mo regions.
8. At elevated temperatures, additional toughening was provided by microcracking. This occurred primarily in the Mo<sub>5</sub>SiB<sub>2</sub> phase in the form of microcrack zones of significant dimensions (~400  $\mu$ m), arrested between  $\alpha$ -Mo regions, in layers parallel to the main crack path. The contribution to



the toughness here appeared to be associated with the dilatation associated with the microcrack formation, with a smaller contribution from the resulting change in compliance.

9. Based on metallographic observations, fatigue-crack propagation behavior in the tougher (I/M) Mo-Si-B alloys was reasoned to occur by the progressive degradation of the ductile-phase toughening under cyclic loading due to premature fatigue failure of the ductile, bridging phase. Nevertheless,  $K_{\max,th}$  thresholds were typically 70% of the maximum toughness values, and in the coarsest I/M alloy to be as high as 8 MPa $\sqrt{m}$  at 1300°C. These values, which are high even by metals standards, are far superior to those previously measured in unmodified monolithic molybdenum silicides.

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## LIST OF FIGURE CAPTIONS

Figure 1: Scanning electron micrographs of the microstructures in the Mo-Si-B alloys examined, showing (a) cast IM1 alloy, (b) PM1 alloy, processed by hipping crushed Mo-16.8Si-8.4B powders, (c) PM2 alloy, processed by hipping the mixture of crushed Mo-20Si-10B particles and Mo powders, and (d) cast IM2 alloy. (Etchant: Murakami's reagent).

Figure 2: Oxidation behavior of IM1 alloy (Mo-12Si-8.5B) in air at 700°, 800°, and 900°C, as compared to “pest reaction” in monolithic Mo<sub>5</sub>Si<sub>3</sub> at 800°C [12], showing weight change as a function of time at temperature. Insets show the surface appearance of the scale on test samples after ~50 hr exposure at the temperatures indicated.

Figure 3: Fracture toughness and R-curve behavior of Mo-Si-B alloys, showing crack-growth resistance,  $K_R$ , plotted as a function of crack extension,  $\Delta a$ , for the I/M and P/M alloys between 25 and 1300C. Results for the boron-modified molybdenum silicides are compared with previous data [4] on monolithic and Nb-particulate reinforced MoSi<sub>2</sub>.

Figure 4: Scanning electron micrographs of fracture surfaces in Mo-Si-B alloys (a) IM1 at 25°C, (b) PM1 at 25°C, (c) PM2 at 25°C, and (d) IM1 at 1300°C, under monotonic loading showing brittle transgranular fracture. Note the failure of the Mo particles in the IM1 alloy; little evidence of plastic deformation can be seen at ambient temperature (a), whereas significant plastic stretching and debonding is apparent at 1300°C (b). Fractographic features are nominally similar under cyclic loading.

Figure 5: The interaction of crack path with the microstructure in I/M Mo-Si-B alloy IM1 alloy, showing crack arrest at a large (~ 30 μm) α-Mo particle. Whereas the main crack readily propagates through, or around, the smaller Mo particles, the larger particles act as significant crack traps. Horizontal arrow represents direction of crack growth.

Figure 6: The interaction of crack path with microstructure in IM1 alloy at 25°C: at a  $\Delta K$  of ~7 MPa√m, crack advance was first arrested at the large α-Mo particle on the left-hand side of the micrograph (shown in Fig. 5). Following some degree of microcrack formation around the particle, the main crack propagated through the particle, and progressed some ~200 μm before being re-trapped at another large (>30 μm) α-Mo region. Horizontal arrow represents direction of crack growth.

Figure 7: The interaction of crack path with microstructure in IM1 alloy at 1300°C, showing ductile-phase bridging by the large α-Mo particles and extensive microcracking in the Mo<sub>5</sub>SiB<sub>2</sub> phase parallel to the main crack path. Horizontal arrow represents direction of crack growth.

Figure 8: Variation in cyclic fatigue-crack propagation rates,  $da/dN$ , as a function of the applied maximum,  $K_{\max}$ , and alternating,  $\Delta K$ , stress intensities, in the boron-modified molybdenum silicide alloys at a load ratio  $R$  of 0.1 between 25° and 1300°C. Shown for comparison are previous results [4] for Nb-particulate reinforced  $\text{MoSi}_2$ .

Figure 9: Results showing the increase in the  $K_{\max,th}$  fatigue threshold in Mo-B-Si alloy IM1 with increase in temperature, in comparison to the corresponding increase in fracture toughness, in terms of the crack initiation,  $K_0$ , and steady-state,  $K_{ss}$ , toughnesses on the R-curve. Previous data [4] for  $\text{MoSi}_2$  are shown for comparison.

Figure 10: Schematic illustration of the role of the different toughening mechanisms in Mo-Si-B alloys and their effect on resistance-curve behavior and the fracture toughness. Intrinsic toughening mechanisms, such as crack trapping, act primarily to enhance the crack-initiation toughness,  $K_0$ . Extrinsic mechanisms, such as ductile-phase toughening and microcracking, increase the crack-growth toughness and induce rising R-curve behavior.