

Fracture and fatigue resistance of Mo–Si–B alloys for ultrahigh-temperature structural applications

J.J. Kruzic^{a,b}, J.H. Schneibel^c, R.O. Ritchie^{a,b,*}

^a *Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

^b *Department of Materials Science and Engineering, University of California, 381 HMB, MC 1760, Berkeley, CA 94720, USA*

^c *Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

Received 3 October 2003; received in revised form 28 October 2003; accepted 3 November 2003

Abstract

Fracture and fatigue properties are examined for a series of Mo–Mo₃Si–Mo₅SiB₂ alloys, which utilize a continuous α -Mo matrix to achieve unprecedented room-temperature fracture resistance ($>20 \text{ MPa}\sqrt{\text{m}}$). Mechanistically, these properties are explained in terms of toughening by crack trapping and crack bridging by the more ductile α -Mo phase.

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Keywords: Fracture; Fatigue; Toughness; Molybdenum; Silicides

1. Introduction

For applications such as aerospace engines and power generation, future advancements are limited by the availability of higher-temperature structural materials. For example, single-crystal nickel-based superalloys have essentially reached their technological limit and are unsuitable for structural use above $\sim 1100 \text{ }^\circ\text{C}$ [1]. High melting-point ($>2000 \text{ }^\circ\text{C}$) materials, based on refractory metals such as molybdenum, represent a higher-temperature alternative but suffer from oxidation and creep problems. In this regard, molybdenum silicides and borosilicides have shown promise in improving the oxidation and creep resistance [2–4], leading to the development of two specific Mo–Si–B alloy systems by Akinc and coworkers [2–5] and Berczik [6,7]; however, the silicide compounds are brittle and provide little fracture resistance for most structural applications without significant additional toughening. In previous reports [8,9], we have described alloys containing molybdenum particles surrounded by the hard but brittle Mo₃Si and Mo₅SiB₂ (T2) intermetallic phases, which display definitive, but still small, improvements in

toughness relative to monolithic silicides. Clearly, the key to achieving high fracture resistance in these materials is in making more effective use of the relatively ductile molybdenum phase, not unlike nickel-base superalloys where high toughnesses are obtained with a similarly high fraction of intermetallic precipitates.

One promising approach is to design Mo–Si–B alloys where the intermetallic phases are completely surrounded by a continuous α -Mo matrix; higher toughness would be expected since incipient cracks are forced to interact with the locally tougher α -Mo. In this regard, a novel powder processing route has recently been developed to enable the production of such alloys [10]. Accordingly, the objective of the present paper is to present a first investigation into the fracture and fatigue properties of three Mo–Si–B alloys with continuous α -Mo phase, and to provide an initial description of the micromechanisms responsible for the enhanced toughening.

2. Materials and procedures

Ground powders of composition Mo–20Si–10B at%, were vacuum-annealed to remove silicon from the surface and leave an α -Mo coating on each particle. These surface-modified powders were then hot-isostatically pressed in evacuated Nb cans for 4 h at $1600 \text{ }^\circ\text{C}$ at 200

* Corresponding author. Address: Department of Materials Science and Engineering, University of California, 381 HMB, MC 1760, Berkeley, CA 94720, USA. Tel.: +1-510-486-5798; fax: +1-510-486-4881.

E-mail address: roritchie@lbl.gov (R.O. Ritchie).

MPa pressure. Three alloys were produced differing in volume fraction of the α -Mo matrix and coarseness of the intermetallic particles. These alloys contained Mo_3Si (cubic A15 structure) and Mo_5SiB_2 (tetragonal D8₁ structure) intermetallic phases within a continuous α -Mo matrix; alloys designated as “fine” and “medium” had 34 vol% α -Mo with initial powder sizes of ≤ 45 , 45–90 μm , respectively, while the “coarse” alloy had 49 vol% α -Mo and an initial powder size of 90–180 μm (Fig. 1). Tensile tests (strain rate $\sim 3.3 \times 10^{-3} \text{ s}^{-1}$) on the “coarse” alloy revealed brittle failure at 25 °C with a strength of 140 MPa; yield and tensile strengths at 1200 °C (in vacuo) were 336 and 354 MPa, respectively, with 1.8% elongation.

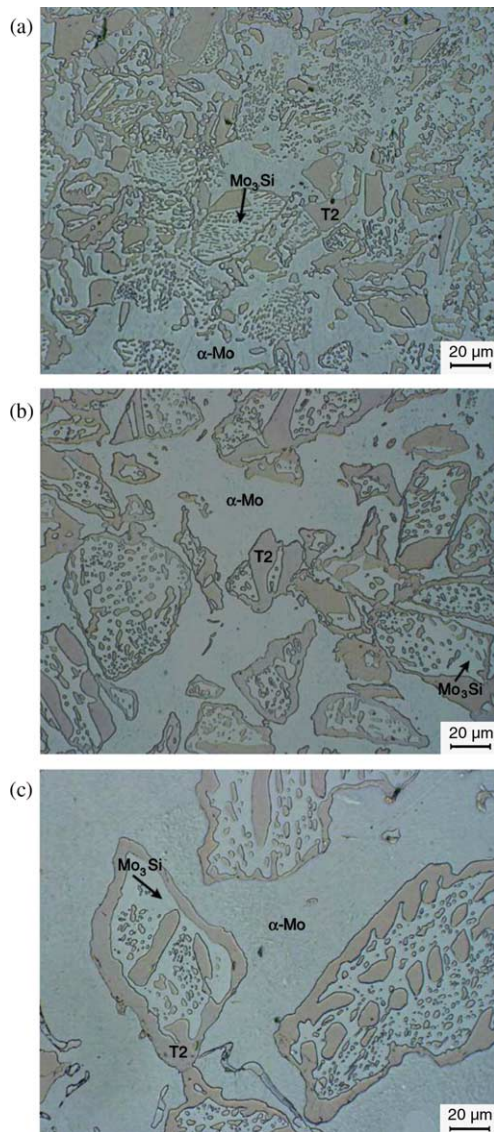


Fig. 1. Optical micrographs of the: (a) “fine”; (b) “medium”, and (c) “coarse” alloys, showing continuous α -Mo matrix with Mo_3Si and T2 (etched in Murakami’s reagent).

Resistance-curve (R-curve) fracture-toughness experiments were performed on disk-shaped, compact-tension DC(T) specimens (width 14 mm; thickness 3 mm) in general accordance with ASTM Standard E561. Specimens were pre-cracked by fatigue loading half-chevron notched specimens until pre-cracks had propagated beyond the half-chevron notch region, typically 300–600 μm in length. Samples were then loaded monotonically in displacement control at $\sim 1 \mu\text{m}/\text{min}$ until the onset of cracking. At 25 °C, periodic unloads (~ 10 –20% of peak load) were performed to measure the unloading back-face strain compliance, which was used to determine the crack length [11]. 1300 °C tests were conducted in a gettered argon environment using (direct-current) electrical potential-drop techniques to monitor crack length [12]. In specific instances, testing was paused to observe crack profiles by optical and scanning electron microscopy. R-curve tests were continued until catastrophic failure of the specimens occurred, at which point the test was concluded.

Fatigue-crack growth testing (25 Hz, sinusoidal waveform) was performed at 25 and 1300 °C in identical environments in general accordance with ASTM Standard E647 using computer-controlled servo-hydraulic testing machines at a load ratio R (ratio of minimum to maximum loads) of 0.1. Crack-growth rates, da/dN , were determined as a function of the stress-intensity range, ΔK , using continuous load-shedding to maintain a ΔK -gradient ($= 1/\Delta K [d\Delta K/da]$) of $\pm 0.08 \text{ mm}^{-1}$. ΔK_{TH} fatigue thresholds, operationally defined at a minimum growth rate of 10^{-10} – 10^{-11} m/cycle , were approached under decreasing ΔK conditions. Errors in crack-length measurements due to crack bridging were periodically evaluated by direct optical measurements of the crack size; readings were corrected by assuming that the error accumulated linearly with crack extension.

3. Results

3.1. Fracture toughness

R-curves for the three Mo– Mo_3Si –T2 alloys (Fig. 2) clearly indicate rising fracture toughness with crack extension. This effect is most dramatic for the “coarse” alloy, which had a peak room-temperature toughness of $21 \text{ MPa}\sqrt{\text{m}}$, i.e., up to seven times higher than that of monolithic molybdenum silicides (MoSi_2 , Mo_3Si), which have toughnesses of 3–4 $\text{MPa}\sqrt{\text{m}}$ [13,14]. The current alloys are also much tougher than Mo–Si–B alloys with discontinuous α -Mo phase, which displayed modest R-curve behavior with much lower peak toughness (~ 4.0 – $7.5 \text{ MPa}\sqrt{\text{m}}$) [8,9]. Additionally, the fracture toughness improved at higher temperatures; specifically the “medium” alloy displayed a 50% rise in peak toughness

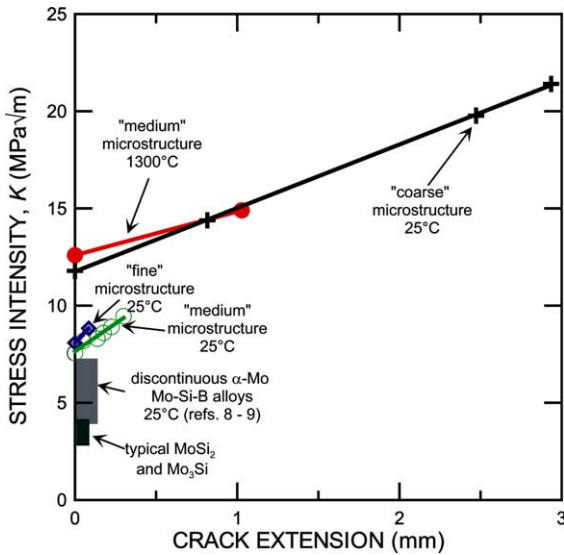


Fig. 2. R-curves showing the fracture resistance of the continuous α -Mo matrix Mo-Si-B alloys. Additionally shown are previously reported values for unreinforced molybdenum silicides [13,14] and Mo-Si-B alloys with a discontinuous α -Mo phase [8,9].

from 10 to 15 MPa \sqrt{m} on increasing the temperature from 25 to 1300 °C.

3.2. Fatigue-crack growth

Room temperature and 1300 °C fatigue-crack growth results are shown in Fig. 3. It is apparent that crack-growth rates at 25 °C have a high dependence on ΔK , which is characteristic of brittle materials. Indeed, when considered in terms of a standard Paris power-law, $da/dN \propto \Delta K^m$, the Paris-law exponents, m , are, respec-

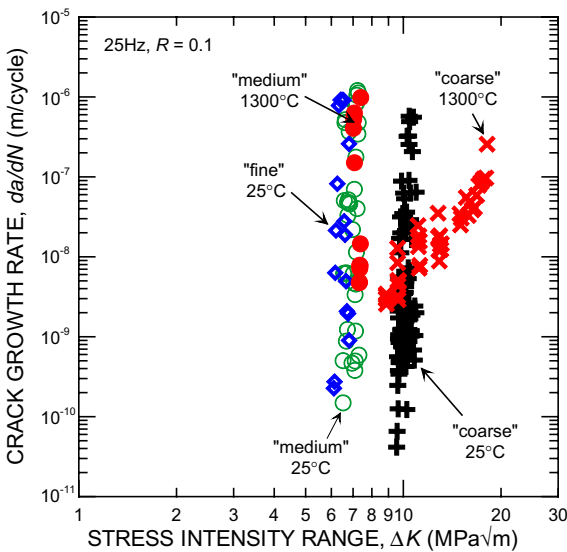


Fig. 3. Variation in fatigue-crack growth rates, da/dN , as a function of the stress-intensity range, ΔK , for continuous α -Mo matrix Mo-Si-B alloys at 25° and 1300 °C.

tively, 125, 87, and 78 for the “fine”, “medium”, and “coarse” microstructures. At 1300 °C, although the “medium” alloy had a similarly high ΔK dependence, the “coarse” alloy displayed more than an order of magnitude decrease in the Paris-law exponent to 4, which is typical of ductile materials.

ΔK_{TH} thresholds of 6, 6.5, and 9.5 MPa \sqrt{m} were measured at 25 °C for the “fine”, “medium”, and “coarse” microstructures, respectively (Fig. 3). At 1300 °C, due to experimental difficulties and limited samples, data were not collected near the operationally-defined threshold; however, based on extrapolation, the threshold for the “medium” microstructure was found to be similar to that at 25 °C, whereas the “coarse” microstructure showed a decrease in ΔK_{TH} at 1300 °C.

4. Discussion

4.1. Toughening mechanisms

In order to identify the toughening mechanisms responsible for the rising R-curve behavior, tests were periodically interrupted to observe crack trajectories using optical and scanning electron microscopy. Such examinations revealed a combination of intrinsic and extrinsic toughening mechanisms, most importantly crack trapping and crack bridging (Fig. 4). Intrinsic toughening mechanisms act ahead of the crack tip and serve to raise the inherent toughness, or crack-initiation point on the R-curve; extrinsic toughening mechanisms generally act behind the crack tip and “shield” the crack from the applied driving force, thereby contributing to rising (crack-growth) toughness with crack extension [15]. With these alloys, intrinsic toughening appears to derive primarily from crack trapping, whereby the propagating crack becomes locally impeded at the α -Mo phase (Fig. 4a). Because the trapped crack front preferentially samples the more “ductile” α -Mo, the driving force needed to initiate crack advance is higher relative to the Mo₃Si and T2 phases. By utilizing a *continuous* α -Mo matrix, crack trapping becomes more potent because the crack cannot bypass the α -Mo phase. Consequently, the initiation toughness of these alloys ranges from 7.5 to 12 MPa \sqrt{m} , values up to four times higher than unreinforced molybdenum silicides [13,14].

With respect to the crack-growth toughness, evidence of crack bridging in the wake is also apparent in Fig. 4. Such bridges serve to resist the opening of the crack and are predominantly composed of the α -Mo phase, although some intermetallic bridges were also observed. Based on crack-profile observations, bridge formation appears to be a result of cracks renucleating in the more brittle Mo₃Si and T2 phases ahead of the relatively ductile α -Mo regions, i.e., as the crack extends, crack trapping leads to crack bridging (Fig. 4a). Such a

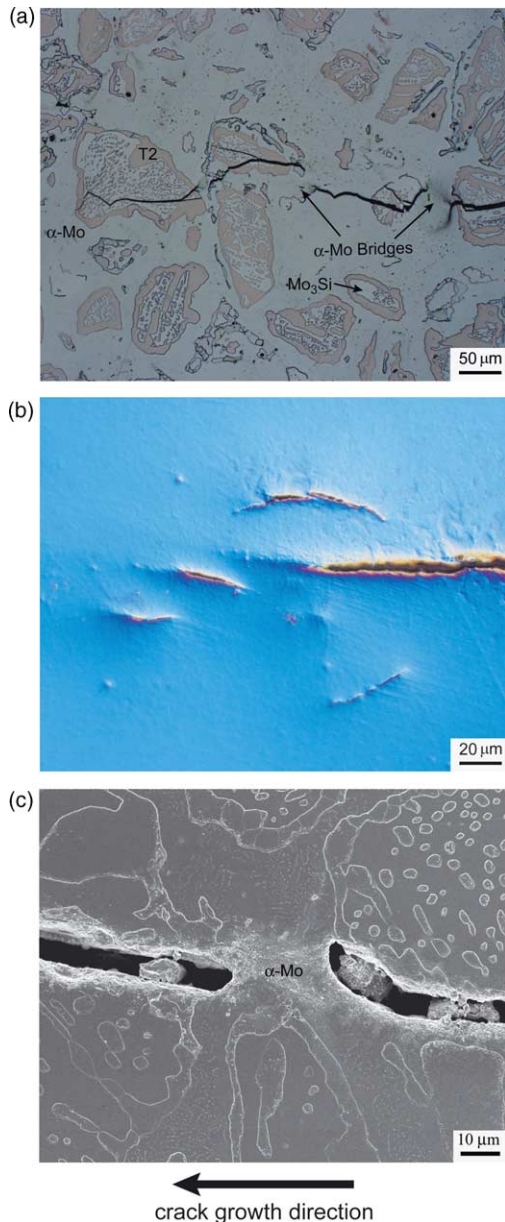


Fig. 4. (a) Crack trapping and bridging at the α -Mo phase in the “coarse” Mo–Si–B alloy. The crack locally arrests at the α -Mo phase, leaving α -Mo bridges in the crack wake; (b) the crack tip in the “medium” alloy after R-curve testing at 1300 °C, demonstrating crack blunting at the α -Mo phase, together with the formation of uncracked-ligament bridges near the crack tip and (c) one such “ductile” bridge of an intact α -Mo region, located \sim 200 μ m behind the crack tip, in the “medium” alloy, again fractured at 1300 °C ((a) and (c) etched in Murakami’s reagent).

process yields regions of α -Mo that bridge the crack wake and sustain load that would otherwise contribute to crack growth. Accordingly, bridging acts to lower the near-tip stress intensity, K_{tip} , relative to the applied stress intensity, K_{app} , by an amount referred to as the bridging stress intensity, K_{br} , i.e., $K_{tip} = K_{app} - K_{br}$. Because bridging is active in the crack wake, it only serves

as a toughening mechanism after some crack extension (i.e., $K_{br} = K_{br}(\Delta a)$), resulting in rising fracture resistance with crack growth. As with crack trapping, the *continuous* α -Mo phase is crucial for the effectiveness of this mechanism because it implies that the crack must interact with the α -Mo phase, i.e., again the crack cannot avoid the α -Mo regions. Toughening from crack bridging gives these materials significantly enhanced damage-tolerance, which is important for many structural applications.

While high-temperature structural materials must have a balance between ambient and elevated-temperature strength and fracture resistance, most of the functional life of the component is expected to be at service (elevated) temperatures. In this regard, the increase in fracture resistance exhibited by the “medium” alloy at 1300 °C is a highly desirable property, consistent with other Mo–Si–B alloys [8,9]. Observations of crack profiles (Fig. 4) revealed no change in toughening mechanisms between 25° and 1300 °C, implying that the increase in toughness can be associated with the improved ductility of the α -Mo at higher temperatures. Unalloyed Mo typically undergoes a “brittle-to-ductile” transition at 1000–1100 °C [16], although this temperature can be significantly lower at slow strain rates or for high purity material. Accordingly, the resulting increases in α -Mo ductility allow for improved effectiveness of both the crack trapping and bridging mechanisms at 1300 °C. Indeed, the increased potency of crack trapping is evidenced by the rise in initiation toughness from 7.5 to 12 MPa \sqrt{m} , while the enhanced rising R-curve behavior implies an increased effectiveness of the bridging. Moreover, direct observations of cracking that occurred at 1300 °C show significant crack blunting (Fig. 4b) at the trapping α -Mo phase which can be related to the higher measured crack-initiation toughness values; such blunting is not observed at room temperature. Additionally, bridges that formed at 1300 °C displayed improved ductility over those formed at low temperatures (Fig. 4c). Higher ductility allows for bridges to deform and remain intact farther behind the crack tip instead of failing prematurely; this leads to larger bridging zones and higher peak toughness values.

4.2. Fatigue-crack growth

The high Paris-law exponents measured for the Mo–Si–B alloys indicate that they show little susceptibility to fatigue damage at room temperature. Additionally, due to this high dependence of growth rates on the stress-intensity range, it is apparent that if cracks do begin to propagate under cyclic loading conditions, they will quickly lead to failure unless they are growing into a diminishing stress field. Accordingly, the fatigue threshold, below which cracks are presumed to be dormant, should be considered as an important parameter

characterizing fatigue behavior at low temperatures in these alloys. In this regard, the ΔK_{TH} fatigue thresholds in the Mo–Si–B alloys are a high proportion of the fracture toughness; specifically, the maximum stress intensity at the threshold, $K_{max,TH}$, is $\sim 90\%$ of the initiation toughness for all microstructures, representing behavior typical of brittle materials.

The paths of the fatigue cracks looked similar to those observed for the fracture specimens, with bridges readily observed to span the crack wake (Fig. 5a). Upon further fatigue-crack propagation, these bridges were observed to fail in the wake (Fig. 5b), while new bridges formed near the crack tip. For the fatigue data shown in Fig. 3, a steady-state condition was thought to have been achieved, whereby bridges were created and exhausted at an equal rate, and a bridging zone of roughly constant size was carried along behind the crack tip. This process is similar to the extrinsic fatigue mechanism observed in bridging ceramics [17,18], where fatigue-crack growth is promoted by the failure of bridges in the crack wake, which in turn causes a decrease in K_{br} and a corresponding increase in K_{tip} , leading to crack advance. It is believed that this process is the primary cyclic loading-induced mechanism involved in fatigue-crack propagation in these Mo–Si–B alloys at room temperature.

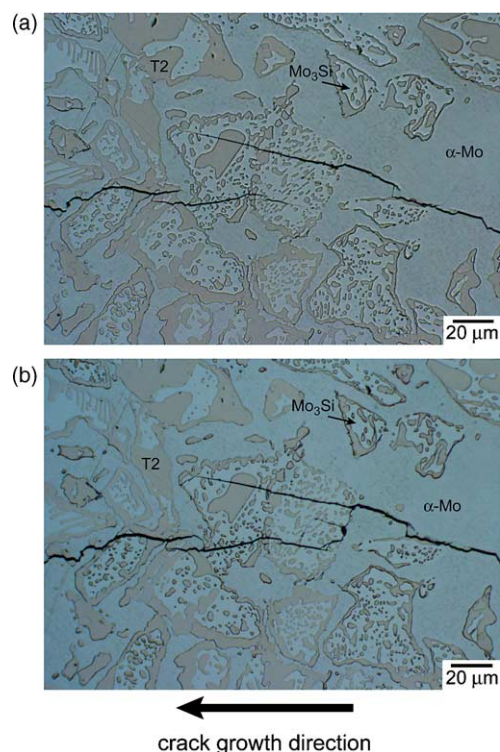


Fig. 5. (a) Micrograph showing crack bridging $\sim 400 \mu\text{m}$ behind the crack tip in the “medium” Mo–Si–B microstructure during fatigue-crack growth at ambient temperature; (b) the same region after the crack tip has extended an additional $800 \mu\text{m}$, where the degradation of the bridging can be seen (etched with Murakami’s reagent).

In contrast to ceramics though, the present alloys contain a comparatively “ductile” phase (α -Mo), which should allow for intrinsic mechanisms to additionally contribute to crack advance, i.e., by alternating blunting and resharping of the crack tip, as in metals. As noted above, at 25°C where the Paris-law exponents are so high, the extrinsic (bridging degradation) mechanism for crack advance dominates; however, for the “coarse” microstructure at 1300°C , the order of magnitude decrease in Paris-law exponent clearly implies more “metal-like” fatigue behavior.

5. Conclusions

Based on an experimental investigation into the ambient- to high-temperature fracture toughness and fatigue-crack propagation behavior of three Mo–Si–B alloys, containing Mo_3Si and Mo_5Si_2 intermetallic phases dispersed within a continuous α -Mo matrix, the following conclusions may be made:

1. All three alloys had far superior fracture toughness properties (including rising R-curve behavior) compared to unreinforced molybdenum silicides; moreover, they were significantly tougher than previously reported Mo–Si–B alloys with discrete α -Mo particles. Specifically, at 25°C , the crack-initiation and peak toughness values were $7.5\text{--}12$ and $9\text{--}21 \text{ MPa}\sqrt{\text{m}}$, respectively, with the highest toughnesses achieved with coarse intermetallic particles and higher α -Mo volume fractions.
2. The high toughness of these alloys was attributed to a combination of crack trapping at the α -Mo phase, which raised the initiation toughness, and crack bridging in the crack wake, which contributed to the rising R-curve behavior. Both mechanisms were promoted by the presence of the continuous α -Mo matrix phase.
3. Based on limited experiments, the fracture resistance appeared to further increase at 1300°C as a result of improved α -Mo ductility; specifically, the “medium” microstructure demonstrated a $\sim 50\%$ increase in both the crack-initiation and peak toughness values at 1300°C compared to room temperature.
4. Although these alloys were not particularly susceptible to fatigue damage at room temperature, fatigue-crack growth was observed to occur via a mechanism of cyclic loading-induced degradation of crack bridging in the crack wake. This extrinsic mechanism resulted in a marked sensitivity of fatigue-crack growth rates to the stress intensity, with Paris-law exponents ranging from 80 to 125. ΔK_{TH} fatigue thresholds ranged from 6 to $9.5 \text{ MPa}\sqrt{\text{m}}$, with the maximum stress intensity $\sim 90\%$ of the crack-initiation toughness for all alloys.

5. At 1300 °C, the “coarse” microstructure demonstrated a change in fatigue behavior marked by an order of magnitude decrease in the Paris-law exponent. This shift to more “metal-like” behavior was attributed to the high α -Mo content and its increased ductility at elevated temperatures, which suggested that an intrinsic fatigue mechanism of alternating blunting and resharpening at the crack tip begins to dominate at 1300 °C.

Acknowledgements

Supported by the Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Contract No. DE-AC03-76SF00098 (for JJK, ROR), and Office of Fossil Energy, Advanced Research Materials Program under Contract No. DE-AC05-00OR22725 (for JHS).

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