Cyclic tensile response of Mo-27at.%Re and Mo-0.3at.%Si solid solution alloys

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Abstract:

Stress-controlled uniaxial cyclic tensile tests were conducted on binary Mo-27 at.% Re and Mo-0.3at.% Si solid solutions as a function of temperature and compared against the previously reported cyclic response of pure Mo. The Mo-27at.%Re alloy with a recrystallized grain size of $\sim 30\text{ }\mu\text{m}$ was evaluated in the temperature range 25°C to 800°C at $R=0.1$ and stress range that was 80% of the ultimate tensile strength (UTS); a peak in fatigue life was observed between 300°C and 500°C . The decrease in fatigue life at the higher temperatures of 700°C and 800°C is attributed to dynamic strain aging. Transmission electron microscopy of the cyclically-deformed alloy revealed parallel bands of dislocation at room temperature that transitioned to a uniform cell structure at 500°C and back to orthogonal planar arrays at 800°C . The as-extruded Mo-0.3at.%Si alloy was evaluated from 25°C to 1200°C and showed superior fatigue life and ratcheting strain resistance as compared to pure Mo and the Mo-27at.% Re alloy (within the temperature range where data were available for comparison). The superior resistance is attributed to the high density of dislocations within the material in this mostly unrecrystallized state rather than Si in solid solution. Above 800°C , the ratcheting strain increases and fatigue life decreases rapidly with increasing temperature and is associated with dynamic recovery.

Keywords: Molybdenum solid solution alloys, stress controlled cyclic deformation; ratcheting strain, dynamic strain aging;

Introduction

Mo-Si-B multiphase alloys are potential candidates for high-temperature applications beyond the capabilities of Ni-based super alloys and are therefore of research interest to the aerospace and aircraft engine communities [1-6]. The high temperature creep resistance in tension and compression, monotonic and fatigue crack growth behavior as a function of temperature and fatigue-creep interactions have been previously examined in two-phase and three-phase Mo-Si-B alloys produced by powder metallurgy techniques [7-10] and from these studies and others, it was inferred that the Mo-rich, Mo-(Si,B) solid solution is capable of providing some low-temperature damage tolerance but could limit high temperature creep resistance [7-9]. Boron solubility in Mo is thought to be negligible at ambient temperature [11] and therefore emphasis was placed on the effect of Si on the properties of pure Mo. It has also been shown that in some of the multiphase alloys examined in [7-10], the Si content in the Mo-solid solution phase substantially exceeded what is believed to be the equilibrium solubility level ($< 1 \text{ at.}\%$ below 1200°C). Furthermore Si diffusion in Mo is thought to be sluggish at elevated temperature, making it difficult to relieve this supersaturation by subsequent annealing as previously shown in [12]. Thus, little is known about the mechanical behavior of dilute Mo-Si solid solution alloys although they constitute an important component of the microstructure of the multiphase alloys. In particular, a systematic study of the monotonic and cyclic properties of binary Mo-Si alloys with Si level below the perceived low temperature solubility limit (i.e. $< 1 \text{ at.}\%$ Si) and a comparison of these properties against the properties of pure Mo would enable an understanding of the effect of small amounts of Si on mechanical properties of the solid solution. This is relevant as an early report from

the 1950s has claimed that Si is a potent solid solution strengthener of Mo even in dilute levels [13].

To address this uncertainty/gap in the literature, we undertook a systematic study of the monotonic and cyclic response of commercially pure Mo, a Mo-0.3 at. % Si alloy and a commercially available concentrated Mo-27 at. % Re alloy. The cyclic deformation response of pure Mo in the temperature range 25°C to 500°C as well as the monotonic tensile response of the Mo-0.3 at. % Si and the Mo-27 at. % Re alloys as a function of temperature were previously reported [14, 15]. It was shown that, i) unrecrystallized Mo was more resistant to ratcheting strain at room temperature as compared to recrystallized Mo, ii) that ratcheting strain increased with test temperature, mean stress and stress amplitude, iii) a cell structure developed during cycling, the ease of which increased with test temperature, and iv) the cells transformed to well-defined subgrains at higher test temperatures. The uniaxial tensile study of the Mo-Re and Mo-Si solid solutions revealed that the Mo-Re solid solution was significantly stronger than pure Mo and retained strength at least till 800°C; furthermore, this alloy revealed serrated flow in the 500°C-800°C regime wherein, a continuous decrease in tensile ductility was noted with increasing temperature. In the worked condition, the Mo-0.3 at.% Si alloy was significantly stronger than pure Mo at room temperature; however when the Mo-Si alloy was annealed and recrystallized, the alloy was *actually softer than* recrystallized Mo. In the unrecrystallized condition, the Mo-Si alloy exhibited 10% tensile elongation at room temperature which increased to ~60% in the recrystallized state, demonstrating that 0.3 at.% Si addition to Mo neither hardens it nor causes a loss in tensile elongation at room temperature. Serrated flow was also noted in the Mo-Si alloy around 700°C.

The effect of serrated flow and dynamic strain aging (DSA) on cyclic deformation response of Mo-based alloys has not been studied in any detail. However, the cyclic response in other bcc metals and alloys that exhibit serrated flow, notably ferritic steels, has been examined. Thus, in a 1045 plain carbon steel, where dynamic strain aging is pronounced around 300°C, Weisse et al [16] demonstrated that fatigue life was a maximum in stress-controlled tests whereas it was a minimum in plastic strain controlled tests. Post deformation microstructural analysis illustrated that dislocations were arranged in dense tangles and in parallel dislocation walls, whereas at other temperatures outside of the DSA regime, dislocation cell structures were primarily observed. Other cyclic deformation studies on ferritic steels [17-19] within the DSA regime have confirmed hardening and a reduction in low-cycle fatigue life as well.

In this paper, we report on the cyclic response of Mo-27 at.% Re and Mo-0.3 at.% Si solid solution alloys. To the best of our knowledge, there have been no reports in the literature on the cyclic response of Mo-Re alloys either as a function of temperature or even at room temperature, although this is an important mode of deformation. Likewise, information on the cyclic deformation of Mo-Si solid solution alloy is non-existent; yet the solid solution phase is an integral part of the multiphase alloys intended for aero-engine applications where this loading mode is important and further is the only phase in that alloy system capable of any plastic deformation below 1000°C and is therefore susceptible to fatigue. On a fundamental note, characterizing, contrasting and understanding the cyclic behavior of a concentrated and a dilute solid solution of Mo, both of which are susceptible to serrated flow in a temperature interval of interest (550°C-800°C), is scientifically relevant and interesting, and together with the technological

reasons described above, are the motivation for this paper. Thus, stress-controlled cyclic response of a concentrated Mo-Re solid solution and of a dilute Mo-Si solid solutions are compared to the response of commercially pure Mo. Cyclic tensile tests were conducted as a function of temperature from 25°C to 800°C for the Mo-Re alloy and from 25°C to 1200°C for the Mo-Si alloy. The deformed microstructure was characterized using TEM to understand the deformation substructure evolution and to recognize temperature and solute effect on the structure and cyclic response.

Experimental procedure

The Mo-27at. % Re solid solution alloy was purchased in sheet form from Rhenium Alloys Inc in Elyria, OH (USA); the as-received sheet had a recrystallized microstructure with an average grain size of around 30µm. The sheet was produced by powder metallurgy methods and C, N, and O (wt. %) content was measured to be 0.0059, 0.0001 and 0.0018 respectively (average of four measurements). The Mo-0.3at. %Si solid solution in rod form was fabricated at Pittsburgh Materials Technology Inc. in Pittsburgh, PA (USA) by vacuum arc re-melting an ingot followed by hot extruding at 1550°C using a 4:1 reduction ratio. Additional processing details were provided in a previous paper [15]. Chemical analysis of the extruded rod was performed in duplicate at two different locations in the rod by Luvak, Inc (Boylston, MA) to determine the level of Si and these averaged out to be 0.085 wt.% Si (0.29 at. % Si) and is in good agreement with the target composition of 0.3 at. % Si. C, N and O levels (in wt. %) were found to be about 0.008, 0.0003, and 0.013 respectively.

The microstructure of the two solid solutions was initially characterized using an optical microscope and the results were previously reported [15]. Next, dog bone-shaped flat specimens with a gauge length of 18 mm, and thickness of 1.5 mm were electro-discharge machined from the Mo-Re sheet and the longitudinal axis of the Mo-Si rod. The specimens were ground and polished to eliminate surface defects including scratches and machining marks.

Cyclic tensile tests from ambient temperature to 200°C were conducted in air, whereas tests at higher temperatures were conducted in vacuum using an Instron servo-hydraulic testing machine (Model 1332) that was fitted with a diffusion pump vacuum furnace (typically maintaining a high vacuum of $\sim 10^{-3}$ Pa) heated with a tungsten mesh and capable of reaching 1800°C. Typically, a stress range of 80% of the UTS was used together with an R ratio of 0.1. Different stress ranges that were 80%, 85% and 90% of the UTS were also examined for the Mo-Re at 300°C. Load-controlled cyclic tensile tests were performed using a sinusoidal loading profile at a frequency of 10 Hz for both solid solutions. At 800°C, 2 Hz and 6 Hz cyclic tests were additionally performed to investigate frequency effect on deformation response. In order to manage data collection and storage during the cyclic tests, load and position values were recorded in a logarithmic manner for most of the specimen life (i.e. 1st, 2nd, 3rd... 10th, 20th, 30th, ...100th, 200th, 300th, ...1000th...until failure) except when approaching failure when data for every cycle was recorded. Ratcheting strain was calculated from displacement data saved for each cycle.

Subsequently, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were utilized to analyze the fracture surface and the substructure evolution respectively. For these purposes, a Leo 1530 VP high resolution

VP FE-SEM scanning electron microscope and a Philips CM20 transmission electron microscope operating at an accelerating voltage of 200 kV were used. Transmission electron microscopy (TEM) specimens were prepared by first grinding a foil from the deformed gage section to less than 100 micrometers in thickness and then using a standard 3-mm diameter punch to obtain the discs; these were thinned and perforated using a twin-jet polisher (Tenupol-5) and an electrolyte of 12.5 vol.% sulfuric acid and 87.5 vol.% methanol solution. Optimal thinning conditions were obtained at -25°C and 20 V for Mo and Mo solid solution alloys.

3. Results

3.1. Initial microstructure

The microstructure of the as-received Mo-27at.% Re sheet as well as the microstructure of the Mo-Si extruded rod was characterized and reported in figure 1 of Ref. [15] and therefore these figures are not repeated here. Briefly, the Mo-Re sheet exhibited a fully annealed microstructure with a uniform average grain size of ~30 μm . Examination of the microstructure in the TEM showed a fairly dislocation-free structure. The microstructure of the Mo-Si extruded rod was for the most part homogeneous with an average grain size that appeared to be around 100 μm as resolved at the optical level. At the TEM level however, a heterogeneous substructure was noted; in some locations, elongated subgrains were observed that were highly dislocated whereas in other locations, a fine recrystallized microstructure was evident (1-3 μm grain size); in these recrystallized areas, there were abnormal grain growth as observed as well.

3.2. Cyclic tensile response of Mo-27at. %Re

Stress-controlled cyclic tension-tension tests with a sinusoidal waveform load-time signal and 10 Hz frequency were performed on the Mo-27at.% Re solid solution. Also the minimum stress to maximum stress ratio (the R ratio) was kept at 0.1. Stress range was chosen to be 80% of the ultimate tensile strength (UTS) obtained from the monotonic tensile tests that were conducted at various temperatures. Cyclic tests were performed on the Mo-27 at.% Re alloy from room temperature to 800°C.

Cyclic tests from 25°C to 200°C were run in air and the tests were taken to specimen rupture. Ratcheting strain evolution with cycles is compared in Fig.1a for the 25°C, 100°C and 200°C tests. The three curves follow a similar pattern. Ratcheting strain increases rapidly with cycles initially (Stage 1), then the rate decreases (Stage 2) but increases once more (Stage 3), reaching a final ratcheting strain of around 10 percent. Ratcheting strain build-up rates appear to increase with temperature in this regime. Fatigue life did not show a significant dependence on temperature, with the room temperature fatigue life being about 16,300 cycles, 7,600 cycles at 100°C and 10,800 cycles at 200°C, all falling in the low cycle fatigue regime. From 300°C upwards, cyclic tests were conducted in vacuum, as Mo-Re alloy is prone to oxidation above 300°C. At 300°C and 500°C, the ratcheting strain curves exhibit only two distinct stages (Fig. 1.b). Ratcheting strain builds up quickly to 8 percent at 300°C and 10 percent at 500°C in the first stage and then saturates at that value for the rest of the test. These tests were interrupted after 10^7 cycles.

Additional cyclic tests were performed at 300°C with stress range increased to 85% and 90% of the UTS and the response is compared in Fig.1c. Remarkably, the cyclic response does not appear to be significantly affected in terms of fatigue life although saturation

ratcheting strain values increase with increased stress range to 9 percent for a stress range of 85 percent of the UTS, but doubling to 20 percent for a stress range that is 90 percent of the UTS. All three specimens survived 10,000,000 cycles even for the 90% stress range, where the applied maximum stress is equivalent to the ultimate tensile strength. At higher test temperatures, fatigue life was reduced to $\sim 2.7 \times 10^6$ cycles at 700°C and $\sim 5 \times 10^5$ cycles at 800°C (Fig. 1d). Ratcheting strain at 700°C increases quickly to around 10 percent and then does not change much for most of the fatigue life (stage 2). There is a rapid increase in ratcheting strain by an additional 8 percent (Stage 3) prior to failure with a final total ratcheting strain of 18 percent. At 800°C, ratcheting strain increases rapidly to 8 percent, exhibits a short Stage 2 behavior and then rapidly increases again by an additional 15 percent prior to failure with a final total ratcheting strain of around 23percent.

The sharp increment of ratcheting strains prior to failure is attributed substantially to the rapid decrease in specimen cross-section leading to substantial overload failure. The onset of the secondary stage of ratcheting strain at 800°C is at a somewhat smaller strain compared to that at 700°C. However, fatigue life at 800°C was reduced to one fifth of that at 700°C. In our earlier study on the monotonic response of this alloy [15], it was shown that serrated flow prevailed at both 700°C and 800°C and that plastic strain to failure was reduced in this temperature regime. These features in the monotonic tensile tests were attributed to dynamic strain aging[20] a phenomenon associated with the interaction of diffusing solute atoms with mobile dislocations during plastic deformation and one that depends on deformation rate and temperature. In order to understand the effect of deformation rate on cyclic response within this regime, additional tests were

conducted at 800°C using lower frequencies (6 Hz and 2 Hz). At present, there is no published literature that we are aware of on the dynamic strain aging effects on cyclic deformation in Mo-based solid solutions. Therefore, selection of temperature and strain rates was driven by literature on steels as well as our previous work [15] on monotonic testing of these alloys; Thus in [21], it was shown that for a low carbon steel, at a frequency of 5Hz, dynamic strain aging effect could be observed and was most pronounced around 600K.

The fatigue life is reduced from over 500,000 cycles at 10 Hz to ~286,000 cycles at 6 Hz and ~42,800 cycles at 2Hz respectively (Fig. 2a). A closer look at the early stage of the ratcheting strain curve (Fig. 2b) shows a transition from Stage 1 to stage 2 at a smaller ratcheting strain when cycled at 2 Hz as compared to 6Hz and 10 Hz; this reduced strain plateau is maintained in Stage 2 although the extent of Stage 2 is dramatically decreased with a decrease in test frequency (Fig. 2c). The reduced ratcheting strain in the second stage and the shorter fatigue life at lower frequency at this temperature is likely related to dynamic strain aging.

In these load-controlled cyclic tests performed at 800°C as a function of frequency, serrations in the form of stress drops normally associated with dynamic strain aging in monotonic loading could not be delineated with confidence in individual stress-strain hysteresis loops in the first few hundred cycles (beyond that, the loop collapses into a line). Reasons include i) insufficient data points being collected in unit time (~100 points per cycle) as these are long tests running into millions of cycles; consequently, any observed oscillations cannot be definitively associated with serrated flow, ii) only the initial part of the plastic portion of the stress-strain curve is sampled in the first several

hundred cycles and in each cycle, small plastic strains are sampled; ratcheting strain builds up, but predominantly in Stage 2 and Stage 3 at which point the hysteresis loop has already collapsed into a straight line, and iii) significant serration amplitudes are only observed in the later stages of the monotonic stress-strain curve [15].

However, more reliable indirect effects are observed that suggest that dynamic strain aging may play a role at 800°C especially when coupled with the observation of serrated flow at this temperature in the monotonic tensile test. Thus, the hysteresis loops obtained for the 100th cycle and the 200th cycle for tests performed at 800°C at 10Hz, 6 Hz and 2Hz are compared in Fig. 3a-f. After 100 cycles, in the case of the specimens cycled at 10Hz and 6 Hz (Fig. 3a,c), the hysteresis loop is open and has a loop width which is roughly similar (0.15-0.165 strain) whereas the specimen cycled at 2 Hz has hardened and has no measurable loop width (Fig. 3e). The ratcheting strain accumulated after 100 cycles also is higher for the 6Hz and 2Hz specimen relative to the 10 Hz specimen. After 200 cycles, the 10 Hz specimen (Fig. 3b) still displays a measurable loop width (0.02% strain) whereas the loop has now degenerated to a straight line for the 6Hz specimen (Figure 3d); as expected, the 200th cycle loop for the 2 Hz specimen is a line with no measurable width. Together, these confirm that the hardening response increases more rapidly with decreasing frequency. Furthermore, it is noted that the ratcheting strain does not change significantly for the 2 Hz specimen compared the 100 cycle response (compare Fig. 3e and 3f) whereas this is not the case for the 10 Hz and 6 Hz specimens. Lastly, there is a considerable reduction in Fatigue life at 2 Hz compared to the 10 Hz specimen, again pointing to the possibility of the adverse effect of dynamic strain aging as mentioned above.

Reduced cyclic frequency enables longer pinning time of dislocations by the solute atoms and the formation of larger solute clouds at dislocations and increased strain hardening. In general, dynamic strain aging is also accompanied by reduced tensile elongation as was shown previously for this alloy [15]. As pointed out in the Introduction section, in ferritic steels, dynamic strain aging has been shown to have an adverse effect on fatigue life.

The cyclic stress-strain curves exhibit hysteresis and therefore the mid-loop width can be measured (as % strain) and its evolution with cycles at 25°C, 500°C and 700°C is compared in Fig.4. For the room temperature test, the hysteresis loop is stable from the first cycle onwards; for the higher temperature tests conducted in vacuum, the first several cycles (sometimes several tens, but at other times as many as 100-150 cycles) were typically not stable with respect to the applied stress-range; data for mid-loop width plotted in Fig. 4 therefore start at around 150 cycles. The intent here is to demonstrate a rapid decrease in loop width as a consequence of cyclic hardening signaling the end of the first stage. Initial cyclic stress-strain hysteresis loop mid-width increases with increasing temperature. With progression in number of cycles, the hysteresis loop mid-width decreases and implies cyclic hardening. It decreased from 0.05% to 0.01% within 200 cycles at 25°C. At 500°C, the mid loop-width decreased from 0.12% to 0.01% in about 100 cycles, whereas at 700°C, in about 100 cycles, the mid-width decreased from 0.22% to 0.01% illustrating the higher cyclic hardening rate as compared to 500°C.

The evolution of the shape of individual hysteresis loops are illustrated in Fig. 5a,b for specimens cycled at 25°C and 500°C. At room temperature (25°C), with an increase in the

number of cycles, the hysteresis loop collapse into a line after 200 cycles (pair of images designated Fig. 5a and corresponding to the first cycle and the 200th cycle). A similar response is observed at 500°C where the 181st cycle shows a significant loop width but one that collapses into a straight line after 300 cycles (pair of images labeled as Fig. 5b). Thus, within the first several hundred cycles, the material cyclically hardens rapidly and during this stage (Stage 1), ratcheting strain evolves rapidly but the evolution rate decreases soon after and the material enters Stage 2.

Fracture surfaces of the RT and 800°C specimens were examined in the SEM. The RT specimen exhibited a mixture of transgranular cleavage and intergranular failure as seen in Fig. 6a. A higher magnification image of a location that is circled by the red dashed line Fig. 6a shows limited striations resulting from fatigue crack propagation (Fig. 6b). In this context, it is noted that intergranular fracture at ambient temperature has been previously noted in recrystallized Mo and is thought to be an intrinsic characteristic [22] (although it can be further exacerbated by segregation of interstitials, particularly oxygen, to grain boundaries), and in sintered Mo-Re alloys as well at 77K [23]. The fracture surface at 800°C is rough and it appears that transgranular failure dominates at this temperature (Fig. 6c). Small shallow ‘pockets’ that appear to be dimples were seen on the fracture surface as well (Fig. 6c). Within the small pockets, wavy striation lines were observed at higher magnifications, once again indicative of fatigue crack propagation (Fig. 6d).

3.3 Cyclic tensile response of Mo-0.3at.%Si

Due to limited material availability, a few stress-controlled cyclic tension-tension tests were also performed on the Mo-0.3 at. % Si dilute solid solution alloy using a sinusoidal

waveform load -time signal and these tests were conducted in the temperature interval from 25°C to 1200°C. Frequency was set at 10 Hz for all tests and the minimum stress to maximum stress ratio was kept at 0.1. Stress ranges were chosen to be 80% of the UTS as determined from the monotonic tensile tests at each test temperature from [15]. All the tests were conducted on the as-extruded (mostly unrecrystallized) material.

Ratcheting strain evolution with cycles is shown in Fig. 7a for tests conducted at 25°C and at 500°C. In both instances, the tests were terminated after 10 million cycles. Ratcheting strain at these two temperatures exhibited two distinct stages. It increased rapidly to 0.003 and 0.012 in the first stage at RT and 500°C respectively. In the second stage, ratcheting strain remains constant till the tests were terminated. It is also worth noting that the ratcheting strain at RT is negligible at the end of the test and significantly lower than that for pure Mo and Mo-27 at. % Re at 500°C; it is however worth recalling that the Mo-Si alloy was tested in the as-extruded condition whereas the other two materials were tested in the annealed condition. When cyclic tests were performed in the temperature range from 700°C to 1200°C, all specimens failed before reaching 10 million cycles (Fig. 7b.) At 700°C, ratcheting strain increases to 0.02 and saturates for most of the life ($\sim 6 \times 10^6$ cycles); it jumped to about 0.05 prior to failure after 6.7 million cycles. These can be contrasted against the results for Mo-27 at. % Re tested under similar conditions at 700°C (Fig. 1) where the ratcheting strain in the second stage saturates at 0.1. At 800°C, the ratcheting strain at the end of the first stage (onset of stage 2) decreased to 0.01 and fatigue life was also reduced to 2.5 million cycles. This trend in decreased fatigue life continued monotonically with increased test temperature (800°C and higher) implying a

decreasing stage 2 and rapid onset of overload failure (stage 3). Ratcheting strain to failure increased rapidly with temperature as well (Fig. 7b).

Final ratcheting strain and fatigue life as a function of temperature for annealed Mo-27at% Re and as-extruded Mo-0.3at%Si are compared to that for pure Mo in Fig. 8a,b. Among the three materials, Mo-0.3at.%Si exhibited the lowest ratcheting strain for all temperatures examined with Mo-27at%Re being next. Ratcheting strains increase with temperature, the extent for each material being different. The Mo-0.3at%Si also exhibited the best fatigue life from 25°C up to 1200°C of the three materials, with Mo-27at%Re second to it at the higher end of the temperature regime. Clearly, the addition of substantial amounts of Re to Mo improved the fatigue life while the dilute Mo-0.3 at. % Si is superior to the Mo-Re alloy; this response is more likely a consequence of the initial high dislocation density in the as-extruded material rather than a consequence of Si solid solution. Unfortunately, material availability precluded a similar study on the annealed Mo-0.3 at. %Si counterpart and this work is necessary and will be performed in the future. To fully recrystallize the as-extruded material, previous work confirmed the need to anneal in excess of 1400°C for at least four hours [15]. Thus, dynamic recrystallization is not anticipated at 1200°C during the cyclic deformation test of the as-extruded material.

3.4 Post cyclic deformation microstructure

The microstructure of some of the cyclically deformed Mo-27 at.% Re and the Mo-0.3 at.% Si specimens were examined in the TEM to develop an appreciation for substructure development at room- and elevated temperatures. Specifically, the 25°C, 500°C and

800°C deformed Mo-27Re specimens and the 700°C and 1200°C deformed Mo-0.3Si specimens were examined.

In the Mo-27Re specimen cyclically deformed at 25°C that exhibited ~10% ratcheting strain and survived 16,300 cycles, a high dislocation density was observed but distributed heterogeneously; dense dislocation bands were observed to run across the whole grain with a band spacing of roughly 1-2 μm (Fig. 9a). The impingement of these dislocation bands on grain boundaries can induce stress concentration at the grain boundary, and initiate intercrystalline cracks that can lead to crack propagation along grain boundaries [24]. A lower density of dislocation segments was found distributed in between the bands that showed the beginnings of organizing into cell structures. At 500°C, the specimen also experienced ~10% ratcheting strain but remained in stage 2 for 10 million cycles when the test was ended. In this situation, dislocations form dense cell structures with these cells being distributed homogeneously within the grains (Fig. 9b). The average cell size is of the order of 1 μm . At 800°C, the Mo-27 Re alloy exhibited serrated flow in monotonic tensile loading [15], while in cyclic loading at 10Hz, it failed after ~700,000 cycles with a ratcheting strain of ~25 percent. It is noted however that as the specimen transitioned from stage 2 to stage 3 (Fig. 2a), it had experienced about 15% ratcheting strain at around 600,000 cycles; thus, the large increment in strain in the last 100,000 cycles is attributed to stage 3 overload. In this case, the homogeneous cell structure that was observed in the 500°C deformed specimen was no longer present. Instead, dislocations arrange into two orthogonal arrays, generating dislocation walls that form a grid indicative of the activation of two orthogonal slip systems (Figure 9c). The formation of such a dislocation arrangement is suggestive of the inability of screw

dislocation cross-slip and edge dislocation climb, possibly arising from solute segregation (Re and/or interstitial impurities like C and O) to dislocation cores.

Examination of the cyclically deformed Mo-0.3at% Si microstructure following the one-week long 700°C test (Fig. 10 a,b) confirms the presence of a subgrain structure indicative of dynamic recovery and is reminiscent of the microstructure of CP Mo cycled at 400°C [14]. Within these subgrains, dislocation tangles as well as long, rather straight segments are present (see inset in Figure 10b). Furthermore, the subgrains appear somewhat coarser in the vicinity of the fracture surface than at locations away from it.

These features are even more readily recognized in Figure 11 a,b which represent the post deformed microstructure following the 1200°C cyclic test. Here, the long, straight dislocations within the subgrains appear pinned at various locations along the line and bowing out between the pinning points (see inset in Figure 11b). Such pinning in a single phase solid solution is usually due to jogs resulting from climb of edge dislocations, jogs generated due to dislocation intersections, or due to solute segregation to dislocation cores or all of these reasons. Segregation of Si to dislocation cores in a Mo-Si solid solution deformed at 1200°C has been previously reported [9].

4. Discussion

Ratcheting strain over the life of a cyclically loaded specimen can be divided into three stages. In general, in an initially recrystallized microstructure, the primary stage of ratcheting strain evolution is associated with the motion of edge and screw dislocations and the end of the stage typically signifies the evolution of a cell structure and hardening associated with dislocation interactions and intersections. In the second stage, the ratcheting strain rate is more or less steady and can even be zero. The associated

dislocation substructure changes have been claimed to be minimal in the case of steel [25]. The ease of thermally activated cross-slip of screw dislocations within the cells that develop in the first stage could enable further ratcheting strain to accumulate in Stage 2 and this process would also be aided at elevated temperatures if dynamic recovery is enabled. The third stage is when the ratcheting strain rate increases sharply again and this has been attributed to specimen damage including micro-cracking and micro-crack linkup prior to macroscopic failure [25, 26].

In order to develop an appreciation for the cyclic response of the Mo-27Re alloy and specifically of the high concentration of Re in solid solution, it is useful to briefly recall the previously reported [14] ratcheting strain evolution behavior of recrystallized Mo with a similar grain size as the Mo-Re alloy examined in this study ($\sim 30\ \mu\text{m}$) in the 25°C to 500°C interval at $R = 0.1$ and an applied stress range that is 80% of the UTS. This cycling condition is similar to one that was adopted in the present study. In the case of recrystallized Mo at room temperature (UTS of $\sim 450\ \text{MPa}$), the specimen exhibited a fatigue life of 400,000 cycles and a ratcheting strain to failure that was 0.1. A large part of this strain was accumulated in Stage 1. At failure, the microstructure consisted of a dense uniform distribution of dislocation tangles. In contrast, the Mo-27 Re alloy exhibited a much shorter life ($\sim 10,000$ - $20,000$ cycles) in the room temperature, 100°C and 200°C tests (note that the UTS of Mo-27 Re is $\sim 830\ \text{MPa}$ at room temperature [15]), a similar level of ratcheting strain as Mo, about half of it being accumulated in Stage 1. Unlike in Mo, the Mo-Re alloy displayed parallel bands of dislocations (Fig. 9a) within which the beginning stages of the development of a cell structure is seen. The formation of such bands in the Mo-Re alloys but its absence in Mo at room temperature may be a

consequence of the immobility of screw dislocations typical of bcc metals at low homologous temperatures being further exacerbated by the presence of a high concentration of Re in solid solution that can modify the core structure (unfortunately, nothing is known about the role of high concentrations of Re on the screw dislocation core structure in Mo). The formation of cells requires wavy slip that requires thermally activated screw dislocation cross-slip and edge dislocation climb, both of which are hampered at low temperatures by solute pinning of dislocations. In addition, the role of interstitials segregating to dislocation cores also needs to be given consideration; this is particularly so in bcc crystals where interstitials can elastically interact with both edge and screw dislocations due to the asymmetric nature of the octahedral and tetrahedral interstices and can adversely affect cross slip and climb.

The abrupt large increase in fatigue life of the Mo-27 Re alloy in the 300°C to 500°C temperature interval to over a ten million cycles without a recognizable change in final ratcheting strain for comparable loading conditions, coupled with the observation of a well-developed uniform cell structure at 500°C (Fig. 9b) fully supports the above assertions. Furthermore, after 5 million cycles at 400°C ($R=0.1$; stress range of 70% UTS), pure Mo exhibits a recovered microstructure [14], implying that dynamic recovery is significantly hampered in the Mo-Re alloy, again supporting the idea that the large solute concentration present in the alloy discourages dislocation cross-slip and climb that are necessary for the recovery process to proceed. Lastly, dynamic recovery enables a progressively increasing ratcheting strain rate in stage 2 with temperature in pure Mo in this temperature range whereas its absence in the Mo-27Re alloy causes the stage 2 slope

to be negligible and the final ratcheting strain remains about the same as that obtained at the end of Stage 1.

Previous examination of the monotonic tensile response of this Mo-27Re alloy [15] had confirmed the presence of serrated flow at 800°C; a comparison of the yield strength, UTS and elongation at 500°C with those at 800°C confirms that the yield strength and UTS are not very different but the elongation is considerably less at 800°C (~35% versus 22%). This implies a higher work-hardening rate at 800°C in the uniform plastic deformation regime with serration amplitude progressively increasing with increasing plastic strain within this regime. Thus as individual elastic-plastic cycles experience this regime during cyclic deformation, cross-slip and climb can be inhibited by solute interactions with the core of moving dislocations encouraging slip planarity, heterogeneous deformation and dislocation band development as evidence in Fig.9c. These effects can be aggravated as cyclic test frequency is reduced with the onset of stage 2 occurring at smaller strains at the lowest frequency of 2 Hz at 800°C and the overall consequence of frequency being reflected in a significant loss in fatigue life.

The dilute, binary Mo-0.3 at.% Si alloy demonstrates substantial resistance to ratcheting strain evolution to ten million cycles and at least up to 500°C. A significant part of this fatigue life is spent in stage 2. This response is superior to pure Mo and the Mo-27Re alloy as well and is thought to be primarily a consequence of an unrecrystallized microstructure rather than due to Si in solid solution. Earlier work on the monotonic tensile response of this alloy [15] confirmed that the yield strength of the alloy in the as-extruded state is of the order of 550 MPa with an elongation of about ten percent. When the material is annealed at 1600°C/4h, the yield strength decreases to ~240 MPa and

tensile elongation increases to sixty percent. Thus in the annealed state, the Mo-0.3 at.% Si alloy is actually softer than pure Mo. It is therefore anticipated that in the annealed state, the ratcheting strain of Mo-0.3 at.% Si will be significantly higher than that recorded in the as-extruded unrecrystallized state in this study.

In the 600°C to 800°C interval, the as-extruded Mo-0.3 at.% Si alloy appreciably retained the yield strength at 500°C but displayed a loss in tensile elongation [15] that is thought to be related to dynamic strain aging. A well-developed cell structure was observed in the 700°C post-deformed specimen and within these cells, tangles of dislocations were present. In parallel, during cyclic loading in this temperature range (Fig. 7b, Fig 8a,b), ratcheting strain remains low and fatigue life begins to decrease. An examination of the microstructure of the specimen cycled at 700°C that experienced in excess of 6×10^6 cycles, confirms a similar microstructure to that observed in monotonic loading. This is perhaps due to the fact that most of the strain accumulated in the cyclic test occurs in Stage 3 between 6 and 7 million cycles where overload failure dominates and the ratcheting strain to failure is roughly the same as the plastic tensile elongation in monotonic loading.

At temperatures higher than 900°C, fatigue life decreases, Stage 2 progressively decreases and ratcheting strain increases sharply with temperature (Fig. 7b). This temperature regime also is coincident with a sharp decrease in yield strength in monotonic loading and a concomitant increase in tensile elongation [15]. The deformed microstructure in monotonic loading is one of well-developed subgrains with a relatively low dislocation density within the subgrains. In contrast, although the cyclically loaded specimen also illustrates a well-developed subgrain structure, within the subgrains, long

parallel dislocation segments are observed perhaps as a consequence of the large strain that builds up rapidly at 10Hz in Stage 3 of the test at this temperature.

5. Conclusions

The stress-controlled cyclic behavior of Mo-27at% Re and Mo-0.3at% Si was studied in the temperature range of RT-800°C and RT-1200°C respectively and the deformed microstructures were characterized; significant findings follow:

- 1) The cyclic response of Mo-27at% Re can be classified into three distinct temperature regimes (RT to 200°C, 300°C to 500°C, 700°C-800°C) in terms of ratcheting strain versus cycle. At low temperatures (Regime I), the formation of parallel dislocation walls within grains is thought to be a consequence of the immobility of screw dislocations limits fatigue life. The longer fatigue life in the 300°C to 500°C temperature regime is attributed to homogeneous deformation as evidenced by the presence of dislocation cells. At 700°C, and more so at 800°C, fatigue life is likely adversely affected by dynamic strain aging; decreasing the cycling frequency further reduces fatigue life as would be anticipated if repeated solute pinning of dislocations occurred in this regime.
- 2) The initial hysteresis loop width increases with temperature but decreases rapidly at a particular temperature with increasing cycles in the first several hundred cycles implying cyclic hardening. At 700°C, the reduction in loop width with increasing cycles is faster compared to 500°C; Likewise, at 800°C, the loop width decreases more rapidly with increasing cycles at a frequency of 2 Hz as compared to the response at 10 Hz. These manifestations are perhaps related to dynamic strain aging.

- 3) As-extruded Mo-0.3 at% Si shows excellent fatigue resistance at RT and 500°C. Fatigue life begins to decrease at elevated temperatures (700°C and 800°C) and rapidly deteriorates in the 900°C to 1200°C regime. This response is attributed to the highly dislocated, unrecrystallized as-extruded microstructure.

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Figure Captions:

Fig. 1: Effect of temperature and cyclic stress range on ratcheting strain evolution for Mo-27 at.% Re: (a) 25°C-200°C; stress range is 80% of UTS, (b) 300°C and 500°C; stress range is 80% of UTS, (c) Cyclic stress range effect at 300°C and (d) 700°C and 800°C; stress range is 80% of UTS.

Fig. 2: (a) The effect of cycling frequency on ratcheting strain evolution until failure for Mo-27at%Re at 800°C; (b) the response in the first 10^4 cycles, and (c) the response for the first 3×10^4 cycles.

Fig. 3: Stress-strain hysteresis loops for the $N=100^{\text{th}}$ cycle (a,c,e) and $N=200^{\text{th}}$ cycle (b,d,f) at 800°C for Mo-27 at.% Re specimens cycled at frequencies of 10 Hz (a,b), 6 Hz (c,d) and 2 Hz (e,f).

Fig. 4: The effect of test temperature on the evolution of the cyclic stress-strain hysteresis loop mid-width with cycles.

Fig. 5: Examples of individual cyclic stress-strain hysteresis loops and their evolution in Stage 1: (a) 25°C for $N=1$, and $N=200$ and (b) 500°C for $N=181$ and $N=300$.

Fig. 6: Fracture surface of Mo-27at % Re resulting from cyclic tests. (a,b) 25°C test and (c,d) 800°C test.

Fig. 7: Effect of temperature on ratcheting strain evolution for the as-extruded Mo-0.3at%Si alloy when cycled at 10Hz, $R = 0.1$ and a stress range that is 80% of UTS. (a) at 25°C and 500°C, and (b) 700°C to 1200°C.

Fig. 8: Total ratcheting strain (a) and fatigue life (b) as a function of test temperature for pure Mo, Mo-27at% Re and Mo-0.3at% Si.

Fig. 9: Deformed substructure in Mo-27at% Re tested at different temperatures showing dislocations that (a) are arranged in parallel bands and the beginnings of a cell structure between these bands after 10% ratcheting strain at 25°C, (b) form dense cell structures after 10% ratcheting strain at 500°C, and (c) form two orthogonal planar arrays generating a grid structure after 15% ratcheting strain at 800°C.

Fig. 10: Cyclically deformed Mo-0.3 at.% Si alloy (700°C; $> 6 \times 10^6$ cycles) revealing a fairly well-developed subgrain structure at a location in the gage section (a) away from the fracture surface and (b) near the fracture surface. The microstructure is indicative of dynamic recovery. The inset in (b) confirms the presence of several long dislocation segments within the subgrains.

Fig. 11: Cyclically deformed Mo-0.3 at. % Si alloy (1200°C; 1.08×10^5 cycles; ~16% ratcheting strain-to-failure) revealing a well-developed subgrain structure (a) at a location in the gage section away from the fracture surface and (b) at a location near the fracture surface. The inset in (b) confirms the presence of long dislocation segments within the subgrains and in many instances, the long segments appear locally pinned and bowing out.

Figure(s)

Fig. 1a-d

Fig 2.

Figure 3a-f (new)

Fig. 4.

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11