Mn and Mo additions to a dilute Al-Zr-Sc-Er-Si-based alloy to improve creep resistance through solid-solution- and precipitation-strengthening

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ABSTRACT

Compressive creep experiments were utilized to investigate the influence of small additions of 0.25 at.% Mn and 0.10 at.% Mo on the creep resistance of a cast Al-0.08Zr-0.02Sc-0.01Er-0.10Si at.% alloy. The Mn- and Mo-modified alloy displays significantly enhanced creep resistance at 300 and 400 °C, due to solid-solution strengthening and the formation of two types of precipitates: $\text{Al}_3(Zr,Sc,Er)(L1_2)$-nanoprecipitates and $\alpha$-Al/Mn, Mo/Si submicron platelets or cuboidal-shaped precipitates. The creep threshold stresses at 300 and 400 °C are 37 and 24 MPa, respectively, versus 19 and 15 MPa for the unmodified alloy. At 300 °C, the creep exponent n is found to change from 4.4 in the base alloy, to 3 in the modified alloy, consistent with a change from climb- to glide-controlled dislocation creep. The Mn- and Mo-modified alloy exhibits an as-cast grain-structure, which is finer (~0.35 mm versus 0.6 mm) and more equiaxed grains than the unmodified alloy, which is anticipated to enhance deformation by diffusional-creep. Nevertheless, diffusional-creep resistance at 400 °C remains high for the modified alloy, due to precipitation of submicron $\alpha$-Al/Mn/Mo/Si-precipitates at grain boundaries (GBs). At 400 °C, the diffusional creep threshold-stress is ~14 MPa, three times that of the unmodified alloy, which also display fewer and coarser $\text{Al}_3(Zr,Sc,Er)(D0_2_1)$ precipitates at GBs. Creep resistance in the modified alloy does not deteriorate after 16 days of stress testing at 400 °C, highlighting the excellent coarsening resistance of the L1_2- and $\alpha$-precipitates. This new castable, heat-treatable aluminum alloy therefore represents an important technological advance for utilization at higher temperatures under stress.

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1. Introduction

As reported for Ni- and Co-based superalloys, the formation of L1_2-ordered $\text{Al}_3\text{M}$ nanoprecipitates (where M is a transition metal, such as Sc, Zr, or Ti) improve dramatically the mechanical properties of aluminum [1–5]. These L1_2-strengthened Al-superalloys exhibit good coarsening resistance at 400 °C [6–9], which is ~72% of the absolute melting point of Al, and far above the maximum usage temperature of typical commercial aluminum alloys. Greater improvement of the mechanical properties employing L1_2-precipitation strengthening alone, has been difficult to achieve. Further increasing the concentration of L1_2-forming elements in conventionally cast alloys usually leads to grain refinement caused by the precipitation of primary $\text{Al}_3\text{M}$-intermetallic precipitates, which is detrimental for high-temperature creep. As part of a search for new candidate alloys, the present authors have recently investigated [10,11] the effect of adding small concentrations of a combination of Mn and Mn to an Al-Zr-Sc-Er-Si alloy [8,9]. While the base-alloy is strengthened solely by coherent (AlSi)$_3$($\text{Zr,Sc,Er}$)(L1_2)-nanoprecipitates, which form upon aging and exhibit slow coarsening up to 400 °C, the modified alloy displays improved microhardness values and increased coarsening resistance at higher temperatures (400 - 450 °C). This could be due to the observation that the modified alloy displays a high number density (~10^{23} \text{m}^{-3}) of $\text{Al}_3\text{M}$($L_2$)-nanoprecipitates, with Mn partitioning to their core, plus exhibiting improved coarsening resistance due to the formation of a Mo-enriched shell. Additionally, Mn and Mo also contribute to the solid-solution strengthening of the matrix, which increases further the microhardness. Lastly, the formation of $\alpha$-$\text{Al}$(Mn,Mo,Si)-precipitates provide additional strengthening when the alloy is aged beyond its peak microhardness (24 h at 400 °C). The $\alpha$-$\text{Al}$(Mn,Mo,Si)-precipitates form as platelets or cuboids, with different orientation relationships and coherency with the Al-matrix, and they also exhibit submicron (< 100 nm) thicknesses with lengths up to 1.5 \mu m, depending on the aging duration [11]. As an example, Fig. 1 displays the Mo- and Mn-containing (AlSi)$_3$($\text{Zr,Sc,Er}$)(L1_2)-nanoprecipitates and $\alpha$-$\text{Al}$(Mn,Mo,Si)-submicron-precipitates, which constitute the two-types of
precipitates that form in the Al-matrix of the (Mn plus Mo)-modified Al-Zr-Sc-Er-Si alloy after aging. Building on our previous investigations of the Mn-Mo-modified Al-Zr-Sc-Er-Si alloys [10,11], the objective of the current study is to investigate the effects of these elements, Mn and Mo, on the high-temperature mechanical properties, specifically the creep resistance, of this alloy at 300 °C and 400 °C.

2. Experimental procedures

The alloy with the nominal composition Al-0.08Zr-0.02Sc-0.005Er-0.10Si-0.25Mn-0.08Mo at.% was conventionally cast, using 99.99 at.% pure Al, and appropriate amounts of Al-8 wt.% Zr, Al-2 wt.% Sc, Al-3.9 wt.% Er, Al-12.6 wt.% Si, Al-10 wt.% Mn, and Al-4 wt.% Mo, in the form of master alloys. The alloy was melted in an alumina crucible at ~800 °C and the melt was stirred regularly in air for 1 h to ensure full dissolution of the master alloys, which were added after preheating to 450 °C (the Al-Si master alloy) and 640 °C (all the other master alloys). The alloy was then cast into a graphite-mold preheated to 200 °C and placed on an ice-cooled copper- plated immediately before casting, to enhance directional solidification. The chemical compositions of the alloy, Table 1 were evaluated by direct-current plasma mass-spectroscopy (DCP-MS) at ATI Wah Chang (Albany, OR). To facilitate comparisons, the composition of the base Al-Zr-Sc-Er-Si alloy [8,9] is included in Table 1. All alloy compositions in the remainder of this article refer to the DCP-MS composition. The base alloy (without Mn and Mo) is referred as alloy 1 and the Mn- and Mo-modified alloy as alloy 2. Alloy 2 was homogenized at 640 °C for 2 h, as this process promotes precipitation strengthening resulting from the dissolution of primary Er-rich precipitates [11]. All heat-treatments were performed in air and were terminated by water quenching.

Samples were creep tested under two conditions: (i) annealed to peak strength at 400 °C for 24 h, where the volume fraction of α-Al (Mn,Mo)Si in alloy 2 is negligible and only L12-nanoprecipitates contribute to the strengthening; and (ii) overaged at 400 °C for 11 days, where both L12-nanoprecipitates and α-Al(Mn,Mo)Si precipitates are present [11]. Fig. 2 illustrates the microstructure, for the two aging conditions, for alloy 1 (a,c) and 2 (b,d,e) annealed at 400 °C for 24 h (a, b) or 11 days (c,d,e). In the case of alloy 1, the L12-nanoprecipitates display radii of 1.9 ± 0.3 nm and 3.4 ± 0.9 nm after aging for 1 and 24 days at 400 °C, respectively. For alloy 2, the nanoprecipitates are 1.7 ± 0.3 nm and 2.8 ± 0.6 nm, after annealing at 400 °C for 24 h and 11 days, respectively. While no additional phases were observed after aging alloy 2 for 24 h, Fig. 2e illustrates the distribution of α-AlMnSi precipitates throughout the matrix after aging for 11 days. The α-platelets exhibit thicknesses of 20 to 130 nm (median 50 nm, 18 counts), while their long dimensions range from 80 to 1300 nm (median 400 nm, 135 counts). The cuboid variants typically have an edge length of ~80–100 nm. In-depth microstructural characterization of the precipitating phases, and their coarsening behavior, is reported in Ref. 11.

Constant-load compressive creep experiments were performed at 300 °C and 400 °C, with a thermal fluctuation of ± 1 °C. Cylindrical creep specimens, with a diameter of 10 mm diam. and a 20 mm height, were placed between boron-nitride-lubricated alumina platens and heated stress-free in a three-zone furnace. Upon the application of a load, sample deformation was measured with a linear variable displacement transducer (LVDT) with a resolution of 10 μm. The minimum strain rates at a given stress were determined by measuring the slope of the strain versus time curve in the steady-state creep regime. The applied load was increased when a clear steady-state (minimum) strain-rate was measured, following primary creep. The total accumulated creep strain for each specimen was maintained below 10%, to ensure that the shape of the specimens is maintained.
remained cylindrical (no barreling) and the applied stress was uniaxial. To correlate diffusional creep at 400 °C with the grain diameter, selected samples were cut radially and their cross-sections were polished to a 1 μm finish. The grain and dendritic structure were exposed using Tucker’s reagent (HCl:HF:HNO₃:H₂O 9:3:3:5).

3. Experimental results

3.1. Compressive creep at 300 °C

As the creep tests were performed at 300 °C, which is significantly below the aging temperature of 400 °C, no significant coarsening of the nanoprecipitates was anticipated during the duration of the experiment. Fig. 3a displays a double-logarithmic plot of the minimum compressive creep strain-rate versus applied stress for alloy 2 tested at 300 °C. Data from archival literature references for the control Mn- and Mo-free alloy 1 (homogenized at 640 °C for 8 h, then aged for 1 day at 375 °C, or for 11 days at 400 °C) [9], and for a ternary Al-0.06Sc-0.005Er alloy with a higher Er content (homogenized at 640 °C for 72 h, then aged at 300 °C for 1 or 16 days) [12] are included for comparison in Fig. 3b. Also included are prior creep-data [13,14] from two Al-Si-based alloys: Al-6.3Si-0.34Mg-0.21Cu-0.05Fe-0.05Ti (at.%) alloys modified with 0.09 at.% Mo and 0.08 at.% Mn to form α-precipitates. Due to their high concentrations of Si, Mg, and Cu, these alloys have a more complex heat-treatment and microstructure: (i) homogenization for 4 h at 500 °C and 1 h at 540 °C; (ii) followed by water-quenching; and (iii) aging for 5 h at 200 °C. In addition to the α-Al(Sc,Mo)Si-submicron-precipitates, β-Al₅Cu, Q-Al₅Cu₂Mg₈Si₆ and η-Al₅FeMg₆Si₆ are also present in these alloys and contribute to their strengthening at ambient temperature. The creep tests of the Al-Si-based alloys were performed after aging at 300 °C for 100 h [13,14].

Fig. 3 displays the results for two peak-aged and one overaged samples of alloy 2. The curves for the two peak-aged samples overlap, demonstrating the reproducibility of the measurements. Very high apparent stress-exponents (n_ap = 50–60) are observed, indicating the presence of a threshold stress, below which creep is unmeasurable. Unlike the base alloy 1, overaging alloy 2 for 10 days at 400 °C induces a 4 MPa shift of its curve toward lower stresses.

3.2. Compressive creep at 400 °C

The creep data at 400 °C in Fig. 4 are for alloys 1 and 2, both peak-aged at 400 °C for 24 h. Although for selected experiments, alloy 1 was also overaged for 11 days at 400 °C. To ensure that the microstructure did not evolve significantly during the creep test, the alloys were studied initially for total durations of less than two-days at relatively high strain-rates (>10⁻⁸ s⁻¹), which permits a good estimation of the dislocation creep threshold-stress. To investigate diffusion creep at low strain-rates, a second series of tests was performed on separate peak-aged specimens, with initial stresses smaller than the dislocation threshold-stress, which lasted for more than 48 h. These creep tests lasted 22 and 16 days for alloys 1 and 2, respectively. The two testing long duration conditions are labeled with different (empty) symbols in Fig. 4 for an improved visualization of the results.

Alloy 1 and 2 were tested at 400 °C and 11 days at 300 °C for (i) peak-aged Al-0.055Sc-0.005Er-0.02Zr-0.09Si; (ii) double-aged at 300 °C for 4 h and 425 °C for 8 h) and overaged (double-aged and then subsequently aged at 400 °C for ~200 h); and (iii) Al-0.055Sc-0.01Er-0.06Zr-0.03Si peak and overaged [16]. Alloy 1 displays a comparable creep-resistance to the overaged Al-0.055Sc-0.01Er-0.06Zr-0.03Si, while alloy 2 was stronger than the Al-0.055Sc-0.005Er-0.02Zr-0.09Si alloy, either peak- or overaged. The high apparent stress exponents (n_ap = 43 and 30 for alloys 1 and 2, respectively) are indicative of a threshold stress.

Diffusional creep was observed in peak-aged alloys 1 and 2 at strain rates below ~2 × 10⁻⁸ and 5 × 10⁻⁹ s⁻¹, respectively. In comparison, the Sc-rich alloys included in Fig. 4b exhibited diffusional creep at strain rates of 10⁻⁸ s⁻¹ or greater. To identify the underlying mechanisms most likely to be responsible for these differences, post-creep samples (subjected to the long duration tests) were etched to reveal the grain structure. The results shown in Fig. 5 indicate a clear reduction of grain size in alloy 2 compared to alloy 1 where the grain
diameters were estimated from the width of fitted ellipses. The average grain diameters in alloys 1 and 2 are 0.6 ± 0.4 mm and 0.35 ± 0.2 mm, respectively. There is additionally a difference in grain morphology. While alloy 1 displays highly elongated grains, up to 6 mm long, the smaller grains in alloy 2 exhibit equiaxed grains. These results indicate that the addition of Mo and Mn to alloy 1 induces grain refinement, which is generally associated with lower diffusional creep-resistance.

The GBs were also studied by SEM, Fig. 6a. After a homogenization anneal for 8 h at 640 °C, alloy 1 displays plate-like, micron-size, Al3(Zr, Sc, Er)(D023)-precipitates on the GBs [8], which did not dissolve during aging due to the small diffusivity of Zr in Al. These Al3(Zr, Sc, Er)(D023)-precipitates were relatively widely spaced along the GBs, with the edge-to-edge interprecipitate distances between them ranging from ~10 μm to >100 μm. In contrast, the high-Er Al-0.055Sc-0.005Er-0.02Zr-0.09Si alloy [16] exhibit Al3Er(L12)-primary precipitates at the GBs, which underwent Ostwald ripening (coarsening) upon aging, thereby reducing their number density per unit length. Finally, in alloy 2, α-Al(Mn,Mo)Si-rich precipitates form on the GBs upon casting, with additional precipitation occurring during homogenization [11]. The distances between the precipitates along a GB are typically between 20 and 50 μm [11].

Due to the short (2 h) homogenization time, there was no precipitation of Al3Zr(D023)-precipitates at GBs. Upon aging at 400 °C for 4 h new sub-micrometer (<500 nm) α-Al(Mn,Mo)Si-precipitates form on the GBs, separated typically by distances of 1–2 μm, Fig. 6b.

Fig. 4. Double-logarithmic plot of minimum creep strain-rate versus applied stress during compressive creep tests at 400 °C. (a) measured data for Mn-/Mo-free alloy 1 and Mn-/Mo-modified alloy 2 peak-aged for 24 h at 400 °C, as well as for alloy 1 overaged for 11 days at 400 °C. The full and empty symbols indicate tests performed for short (<48 h) and long times (>48 h), respectively. The data are fitted with curves for dislocation-creep and diffusional-creep for the peak-aged alloys 1 and 2, and the associated threshold stresses are calculated (13 and 23.5 MPa). Calculated creep curves for Nabarro-Herring-diffusional-creep [Eq. (2)] and Coble-diffusional-creep [Eq. (3)], with the corresponding threshold-stresses (5.8 and 14 MPa), are given for different grain diameters (measured in Fig. 5) to illustrate the diffusional-creep mechanism of the alloys. (b) experimental creep data for alloys 1 and 2 (as given in (a)) compared with the archival literature data for: (i) higher-Sc Al-0.055Sc-0.005Er-0.02Zr-0.09Si peak-aged (double-aged at 300 °C for 4 h and 425 °C for 8 h) and overaged (double-aged and subsequently aged at 400 °C for ~200 h at Tp = 745 °C) [15]; and (ii) higher-Sc Al-0.05Sc-0.01Er-0.06Zr-0.03Si peak aged and over aged [16]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. SEM micrograph showing grain-boundary precipitates: (a) Al3(Zr,Sc,Er)(D023), (with edge-to-edge distances ranging from 10 to >100 μm) in base alloy 1, after homogenization at 640 °C for 2 h; and (b) α-Al(Mn,Mo)Si-precipitates (1–2 μm edge-to-edge distance) for Mn-(Mo-modified alloy 2, after homogenization at 640 °C for 2 h and aging for 4 days at 400 °C.

Fig. 5. Optical micrographs of post-creep samples (400 °C) from: (a) the base Al-Zr-Sc-Er-Si alloy 1; and (c) Mn plus Mo-modified alloy 2. Samples were etched using Tucker’s reagent. The grains have been colored manually for easier visualization, (b) and (d). The mean grain diameters for alloys 1 and 2 are 0.6 and 0.35 mm, respectively.
4. Discussion

4.1. Dislocation creep

The high apparent slopes observed on the creep curves are an indication that a threshold-stress exists. To estimate values of the threshold-stress, we used a modified version of the Mukherjee-Bird-Dorn power-law equation [17] for the minimum strain rate $\dot{\varepsilon}$:

$$\dot{\varepsilon} = A(\sigma - \sigma_{th})^n \exp \left( \frac{Q}{k_BT} \right)$$

(1)

where $A$ is a constant, $\sigma$ is the applied stress, $\sigma_{th}$ is the threshold stress, $n$ is the Al-matrix's stress exponent, $Q$ is the activation energy for creep of the Al-matrix, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature (K). The values of the threshold stress, $\sigma_{th}$, and $n$ were obtained using a nonlinear multivariate regression analysis [18]. In preceding studies on high-temperature (300 to 400 °C) creep of L1$_2$-strengthened Al alloys, an exponent with the value $n = 4.4$, equal to the Al-matrix's stress exponent [19], was fixed and provided a good fit to the data, which was consistent with a dislocation-climb mechanism.

4.1.1. Dislocation creep at 300 °C

At 300 °C, corresponding to a homologous temperature of 0.61, the creep threshold-stresses determined utilizing Eq. (1), with a fixed value $n = 4.4$, are $\sigma_{th} = 36.4$ MPa and 32.4 MPa for the peak-aged and overaged alloy 2, respectively. The resulting fits are, however, unsatisfactory because there is a significant deviation from the data observed in the high strain-rate region. A nonlinear multivariate regression analysis (with no fixed parameters) provided a more accurate fit and yielded stress exponent values of $n = 2.7 \pm 0.3$ for both the peak and overaged alloy, Fig. 3a. The estimated threshold stress is also increased slightly to $\sigma_{th} = 37.2$ MPa and 33.5 MPa for peak-aged and overaged material, respectively.

The obtained creep exponent value, which within experimental error is equal to $n = 3$, is indicative of glide-controlled dislocation creep mechanism with solute-drag on dislocations as the limiting creep-mechanism. This mechanism is frequently found in solid-solution strengthened alloys [20] and is consistent with Mn and Mo solute-atoms in the Al-matrix interacting with gliding dislocations. The phenomenon was observed previously in an Al-Li-Sc alloy, which also displayed cumulative solid-solution- and $\text{Al}_3(\text{Sc,Li})(\text{L1}_2)$-precipitation strengthening [21]. No dislocation climb controlled behavior ($n = 4.4$) was observed. As previously reported for an arc-melted (Mn plus Mo) modified Al-Zr-Sc-Er-Si alloy [10], where the Mn concentration in the Al-matrix changed significantly during aging at 400 °C, decreasing from 0.22 at.% after 24 h to 0.045 at.% after 11 days, due to the precipitation of the $\alpha$-Al(Mn,Mo)Si-precipitate-phase. The concentration of the slow-diffusing Mo atoms in the Al-matrix remained essentially unchanged. Because the creep exponent $n = 3$ still provided a good fit with the creep data of the overaged sample, it can be concluded that even rather small concentrations of Mn (0.05 at.% and Mo (0.08 at.% interact strongly with the gliding-dislocations.

Compared to the (Mn plus Mo)-modified alloy 2, alloy 1 displays significantly smaller threshold-stresses of 17.5 ± 0.6 and 19.3 ± 0.6 MPa in the peak- and overaged-conditions, respectively [9]. Farkoosh et al. reported threshold stresses of 20 and 23 MPa (using $n = 4.4$) for the Al-6.3Si-0.34Mg-0.21Cu-0.05Fe-0.05Ti alloy modified with 0.09 at.% Mo or 0.09 at.% Mo plus 0.08 at.% Mn, respectively [13,14]. These results confirm that a rather small (0.08 at.% concentration of Mn induces a sizeable (3 MPa) increase in the threshold stress for peak-aged conditions. The quality of the data points is insufficient to refine further estimations of the stress exponent, $n$. A value of 3, however, could accurately fit the data points, Fig. 3a, with only a small shift in threshold stresses (+1 MPa). It is noted that there is some diffusional creep below 25 MPa, due to the small grain-diameter (~50 μm [22]) in these complex alloys. Fig. 3b includes creep data published previously for a ternary Al-0.06Sc-0.02Er alloy [12]. The fitting procedure for this alloy used all the data points except the ones at the three lowest stresses (below 40 MPa), highlighted by blue arrows in Fig. 3b, which we expect to correspond to diffusional creep given the small sensitivity to applied stresses. The resulting threshold stresses are 27 ± 3 and 28 ± 2 MPa, with $n = 4.4$, for the peak and over-aged Al-0.06Sc-0.02Er alloy, respectively. Although the grain diameter of the Al-0.06Sc-0.02Er alloy was not reported in Ref. [12], Er is known to be a potent grain-refiner when in excess of its maximum solubility in Al [16]. Since it is most likely to have been exceeded at the high Er concentration of 0.02 at.% used, a refined grain structure may be responsible for the observed diffusional creep below 40 MPa in these alloys.

The results in Fig. 3 highlight clearly the strong improvement in creep-resistance obtained by modifying alloy 1 with small concentrations of Mo and Mn. We do not expect the somewhat higher concentrations of L1$_2$-forming elements in alloy 2 compared to alloy 1 (Zr: +50 at. ppm, 0.080 versus 0.075 at.%; Sc: +100 at. ppm, 0.024 versus 0.014 at.% Table 1 ), to be responsible for the large increase in the threshold-stress. In the peak-aged samples, the threshold-stress is doubled, from 17.5 MPa to 37.2 MPa, which suffice to cause deformation of the base-alloy 1 at extraordinarily high strain-rates, given the high apparent stress exponents. While, at peak aging, the L1$_2$-nanoprecipitate radius is slightly smaller in alloy 2 compared to alloy 1 (~1.7 vs. ~1.9 nm); this small difference cannot solely explain this impact on the threshold stress, especially since larger precipitates usually increase the dislocation creep resistance. The same arguments can be applied for the overaged conditions concerning the L1$_2$-nanoprecipitate strengthening. Unlike alloy 1 whose threshold-stress increased by 2 MPa after overaging, due to the larger precipitates (11 days at 400 °C) [9], overaging alloy 2 (11 days at 400 °C) decreased the threshold stress by 3.7 MPa, despite the larger L1$_2$-precipitate population. This phenomenon is probably related to the decrease of solid-solution strengthening from Mn, and Si precipitation to form the $\alpha$-Al(Mn,Mo)Si-precipitates [11]. Increasing the concentration of Mn is anticipated to decrease the lattice parameter of the Al-Mn solid-solution [23], and increase the lattice-parameter mismatch between the $\text{Al}_3(Zr,Sc,Er)(\text{L1}_2)$-nanoprecipitates and the Al-matrix. Thus, a decrease of Mn in solid-solution as it is removed from the Al-matrix to form $\alpha$-Al(Mn,Mo)Si-precipitates, is expected to reduce the $\text{Al}_3(Zr,Sc,Er)(\text{L1}_2)/\alpha$-Al lattice-parameter mismatch, leading to a decrease in the threshold stress [24]. For comparison, the addition of 0.08 at.% Mn to modified Al-Si alloys was reported previously to induce an increase of 3 MPa in the threshold-stress [13,14]. Nonetheless, the decrease in creep-resistance due to overaging of alloy 2 is small compared to the improvement in the creep-strength with respect to the base alloy 1. The new alloy, Mn plus Mo-modified alloy, described herein display threshold stresses at 300 °C, which are higher than the strongest L1$_2$-strengthened Al-0.06Sc-0.02Er alloy developed in our group. The latter alloy contains a single-population of $\text{Al}_3(\text{Sc,Er})$-nanoprecipitates with high lattice-parameter mismatch with the Al-matrix, which increases its creep resistance [12], Fig. 3b. Alloy 2 is strengthened, however, through: (i) solid-solution strengthening from Mn and Mo; and (ii) precipitation strengthening from $\text{Al}_3(Zr,Sc,Er)$-nanoprecipitates, with a small lattice-parameter mismatch and the relatively coarse $\alpha$-Al(Mn,Mo)Si-precipitates [11].

Additionally, alloy 2 displays no sign of diffusion creep at the smallest measured strain-rate, $1.5 \times 10^{-4}$ s$^{-1}$, which may reflect its coarser grain diameter. Unlike the creep-resistant Al-0.06Sc-0.02Er, alloy 2 displays a higher apparent stress exponent, so that it makes a transition from unmeasurably small creep-rates to fast creep-rates over a few MPa. Another difference is that the $\text{Al}_3(\text{Sc,Er})$ nanoprecipitates in Al-0.06Sc-0.02Er alloy coarsen rapidly at 300 °C, while alloy 2 displays excellent high-temperature stability at 400 °C, Fig. 4. An additional advantage of alloy 2 is that, given the high cost of Sc (and, to a lesser extent Er), the much smaller requirement for Sc and Er...
decrease dramatically the cost of alloy 2 when compared to Al-0.06Sc-0.02Er [25]. Although it is possible that the higher creep-resistance of alloy 2 may be due to the effect of Mo on increasing the lattice-parameter of the Al3M(1L2) (found at levels 1–2 at% [10]), and thus its mismatch with the Al-matrix; there is no confirmation of this point in the archival literature. At peak aging, the number density per unit volume and the volume fraction of α-precipitates are negligible, and thus the improvement in creep resistance can only be attributed to solid-solution strengthening and Al3M(1L2) nanoprecipitate strengthening. Interestingly, three microstructural changes occur in an overaged sample, which result in a small decrease in creep-resistance: (i) coarsening of the Al3M(1L2)-nanoprecipitates; plus (ii) precipitation of α-Al(Mn,Mo)Si-precipitates; and (iii) a concomitant decrease of Mn, Mo and Si in solid-solution [11].

4.1.2. Dislocation creep at 400 °C

Applying a nonlinear multivariate regression analysis to Eq. (1), we calculated the threshold-stresses for creep at 400 °C; 13.1 ± 0.03 and 14.9 ± 0.2 MPa for alloy 1 aged at 400 °C for 1 and 11 days, respectively, and 23.5 ± 0.4 MPa for alloy 2 aged at 400 °C for 1 day. In contrast to the situation at 300 °C, where the rate limiting mechanism for alloy 2 is dislocation glide, at the higher temperature of 400 °C, both alloys are characterized by a creep-exponent n = 4.4, which is indicative of a dislocation-climb mechanism. Assuming a value n = 2.7–3 does not provide a satisfactory fit to the experimental datasets. Although static (stress-free) overaging of alloy 1 increased the threshold stress by 1.8 MPa, there are no significant differences in the creep resistance observed for the alloys; that is, after peak aging and testing for a short time (~2 days) or a long time (~22 days). The fitted data published in Ref. 11 demonstrate that L12-nanoprecipitates in alloy 1 should have grown from ~1.9 nm, to ~2.2 and ~3.8 nm, after additional 2 and 22 days, respectively, during the creep test at 400 °C. It is possible that the decrease of creep resistance, due to larger spacing between precipitates, is compensated for by the increase in lattice parameter mismatch for aging durations longer than 11 days. The same phenomenon is observed for alloy 2, for which the L12-nanoprecipitates would grow from ~1.7 nm, to ~1.8 and ~2.6 nm, respectively, after the additional 2 and 16 days at 400 °C [11]. As observed during creep at 300 °C, the addition of Mo and Mn nearly in alloy 2 doubled the dislocation-controlled threshold-stress of alloy 1 crept at 400 °C. For comparison, the high-Sc Al-0.055Sc-0.005Er-0.022Zr-0.09Si alloy displays dislocation climb threshold-stresses of 17.9 ± 2.4 and 22 ± 2.6 MPa for the peak-aged and overaged conditions, respectively [15], while the Sc- and Er-rich Al-0.05Sc-0.01Er-0.06Zr-0.03Si alloy displays dislocation threshold-stresses of 9.3 ± 0.7 MPa and 13.9 ± 1.6 MPa at the peak-aged and over-aged conditions, respectively [16].

Whereas, at 400 °C, the dislocation-climb creep of alloy 1 is comparable to that of the over-aged Al-0.05Sc-0.01Er-0.06Zr-0.03Si alloy; alloy 2 is, however, less creep-resistant than the more expensive Al-0.055Sc-0.005Er-0.022Zr-0.09Si, Fig. 4b. Since alloy 1 has a similar concentration of Si (0.1 at%), which is known to enhance the creep resistance in the Al-0.055Sc-0.005Er-0.022Zr-0.09Si alloy, the inferior mechanical properties can be attributed to differences in the lattice-parameter mismatch induced by the nanoprecipitate’s composition, Zr-rich Al3(Zr,Sr,Er)-nanoprecipitates having a smaller lattice-parameter mismatch with the Al-matrix than the Sc-rich Al3(Sc,Zr,Er)(1L2)-nanoprecipitates [3]. Fig. 4b demonstrates that the (Mn plus Mo)-modified alloy 2 displays a remarkable increase in creep resistance, making it stronger than the Al-0.055Sc-0.005Er-0.022Zr-0.09Si alloy, which has threshold stresses between 18 and 22 MPa, depending on the exact aging conditions. In contrast, the higher threshold-stress of 23.5 MPa for alloy 2 is accompanied by a smaller stress-sensitivity of the strain-rate. As for the situation described at 300 °C, the improved creep resistance of alloy 2 at 400 °C is attributable to solid-solution strengthening due to Mo and Mn, and the incorporation of Mo into the Al3M(1L2) nanoprecipitates, as previously demonstrated by our atom-probe tomography results [10]. A difference at 400 °C is, however, that there is a complete overlap of the peak-aged- and “over-aged” curves (creep for 2 days vs. 16 days). This may be due to changes in the microstructure over the time-frame of the creep-tests (days) at 400 °C; that is (i) coarsening of L12-nanoprecipitates, and (ii) precipitation of Mn, Mo, and/or Si into the platelet- or cuboidal-shaped α-Al(Mn,Mo)Si-nanoprecipitates, which may be affected by the applied stress. Such a phenomenon is known to be the case in the Al-Cu system, where the direction of the applied stress favors or inhibits the growth of the θ’-Al3Cu platelet on specific (hkl)-habit-planes [26].

4.2. Diffusional creep

Assuming a matrix stress exponent n = 1, characteristic of diffusional creep, a nonlinear multivariate regression analysis applied to Eq. (1) yields a diffusional creep threshold stress σ\(_{th}\) of 5.8 ± 0.2 MPa for alloy 1. The resulting curve is displayed in Fig. 4a. It is not possible to determine the threshold-stress for alloy 2 as only two data points for the smallest-stresses are within the diffusional-creep regime. Fortuitously or not, these two data points fall on the best-fit line for the diffusional-creep of alloy 1, Fig. 4a. Therefore, to a first approximation, the diffusional creep threshold-stress for alloy 2 may be the same as for alloy 1, ~6 MPa. To assess the underlying mechanism behind the observed diffusional-creep, the parameter A in Eq. (1) was developed to take into account the grain diameter, d. Considering a diffusional threshold-stress, σ\(_{th}\), the Nabarro-Herring (vacancy diffusion in the Al-matrix) and Coble (grain-boundary diffusion) diffusional-creep mechanisms are, respectively, described by the following equations [17,27]:

\[ \dot{\epsilon}_{NH} = \frac{42\Omega D_V}{kT} \left( \sigma - \sigma_{th}^{\text{diff}} \right)^n \exp\left( -\frac{Q_V}{RT} \right) \]  
\[ \dot{\epsilon}_{Coble} = \frac{42\Omega D_B}{kT} \left( \sigma - \sigma_{th}^{\text{diff}} \right)^n \exp\left( -\frac{Q_B}{RT} \right) \]

where \( \Omega \) is the atomic volume, \( \delta \) the GB thickness, \( n \) the stress exponent of unity, and \( D_V \) and \( D_B \) are the volume (or lattice) and GB diffusion coefficients, respectively. \( D_{th} \) and \( Q_{th} \) are the preexponential diffusion coefficients and activation energies, respectively, for the above two different creep mechanisms. The values of \( \Omega \), \( D_{th} \), \( Q_{th} \), and \( Q_{th} \) are taken from Ref. [17] for pure Al. The grain diameters, \( d \) (Fig. 5) were measured on post-crept specimens to be 0.6 mm and 0.33 mm for alloys 1 and 2, respectively. Theoretical creep-curves for Nabarro-Herring- and Coble-diffusional-creep for different grain diameters were calculated utilizing the diffusional threshold-stress estimated for alloy 1 (5.8 MPa), to identify the active diffusional creep-mechanism of the studied alloys, Fig. 4a. For alloy 1, the Nabarro-Herring mechanism is in good agreement with the experimental results employing a mean measured grain diameter of 0.6 mm. In the case of alloy 2, neither of the two mechanisms can replicate the measured strain-rate for the measured grain diameter of 0.35 mm, with the strain-rate being underestimated by Nabarro-Herring-creep and underestimated by Coble-creep. This may be due to the calculation being based on the alloy 1 threshold stress of 5.8 MPa, which may not be applicable for alloy 2. These observations indicate that the addition of Mo and Mn may have an effect on the diffusional creep-rate.

A threshold-stress for diffusional-creep may be attributed to the inability of GBs to act as a perfect source and sinks for vacancies [27]. This is a consequence of the presence of second-phase precipitates on GBs, which may prevent vacancies from achieving their local equilibrium thermodynamic values at GBs, inducing localized stress concentrations. Alternatively, a threshold-stress for diffusional-creep can result from inhibited GB sliding, due to the tendency of second-phase precipitates to decrease the mobilities of GBs. In the case of the Al-0.05Sc-0.01Er-0.06Zr-0.03Si alloy [16], the diffusional-creep
with coarse, micron-size $\text{Al}_3(\text{Zr,Sc,Er})(\text{D}023)$-precipitates at GBs, thus decreasing the number of obstacles to GB sliding. All the primary $\text{Al}_3\text{Er}(\text{L}12)$ precipitates are, however, dissolved by the homogenization step, removing obstacles to GB sliding, and eliminating the threshold stress. As a result, the Nabarro-Herring equation for a grain diameter of 0.5 mm provides a good fit to the experimental data.

In summary, the results of the present study indicate that, after homogenization, *alloy 1* exhibits a large grain diameter ($0.6$ mm) with coarse, micron-size $\text{Al}_3(\text{Zr,Sc,Er})(\text{D}023)$-precipitates at GBs ($\text{Fig. 6a}$) [8]. Although the inter-precipitate edge-to-edge distances can be quite large ($\text{from 10 }\mu\text{m to >100 }\mu\text{m}$), the precipitates are not anticipated to coarsen significantly upon aging or creep testing, due to the extremely small lattice diffusivity of Zr in Al at 400 °C. It is likely that these GB-precipitates are responsible for the diffusional-creep threshold-stress, as they prevent grain-boundary sliding. In the case of *alloy 2*, the higher linear number density of GB precipitates, identified as the $\alpha$-$\text{AlMnSi}$ phase ($\text{Fig. 6b}$), appear to counteract the smaller grain size ($0.35$ mm), which should produce higher diffusional creep-rates, as the strain-rate equation for Nabarro-Herring and Coble creep are inversely proportional to the grain-diameter squared or cubed, respectively, Eqs. (2) and (3). Employing the measured grain diameter of 0.35 mm, Eq. (2) can predict the strain-rates for the two diffusional-creep data points for *alloy 2* as illustrated in *Fig. 6b*, if a diffusional-creep threshold stress of $\approx14$ MPa (between 13–15 MPa) is used for the Nabarro-Herring creep mechanism. In this case it appears that the GB $\alpha$-$\text{Al(Mn,Mo)Si}$-precipitates provide GB strengthening, allowing the alloy to maintain a good diffusional creep-resistance at the high temperature of 400 °C, which is 0.72 of the homologous temperature. This is similar to the strategy used in polycrystalline Ni-based superalloys, where carbides at GBs are employed to inhibit diffusional-creep.

**Conclusions**

This study involves an investigation of the creep-related effects of adding 0.11 at.% Mo and 0.25 at.% Mn to a dilute Al-0.08Zr-0.02Sc-0.01Er-0.10Si at.% base alloy. Addition of a combination of Mo and Mn to the base-alloy greatly enhances dislocation and diffusional-creep resistance at both 300 °C and 400 °C. Specifically, the following conclusions are reached:

1. Addition of Mn and Mo leads to grain refinement of the modified alloy, where the mean grain diameter decreases from 0.6 mm in the base-alloy to 0.35 mm, and the grain morphology changes from elongated to equiaxed, *Fig. 5*.
2. When creep-tested at 300 °C under compression, *Fig. 3*, the modified alloy exhibits a threshold-stress for dislocation glide of 37.2 ± 0.1 MPa at peak-aging (with $-1.7$ nm radius $\text{Al}_3\text{M}(\text{L}12)$-nanoprecipitates) and 33.5 ± 0.1 MPa, for overaged conditions (with $-2.8$ nm radius $\text{Al}_3\text{M}(\text{L}12)$-nanoprecipitates and additional $\alpha$-$\text{Al(Mn,Mo)Si}$-precipitates). In contrast, the base-alloy indicates smaller dislocation climb threshold-stresses of 17.5 ± 0.6 and 19.3 ± 0.6 MPa in the peak- and over-aged-conditions, respectively (with $-1.9$ and $-3.4$ nm radius $\text{Al}_3\text{M}(\text{L}12)$-nanoprecipitates).
3. Under compressive creep at 400 °C (*Fig. 4a*), the dislocation climb threshold-stress for the modified, peak-aged alloy is $23.5 ± 0.4$ MPa, which is almost twice the 13.1 ± 0.03 MPa value of the base *alloy 1*. We hypothesize that this large improvement in dislocation creep-resistance is due to the Mo and Mn solid-solution strengthening, as well as an increased lattice-parameter mismatch with the Al-matrix, possibly due to the partitioning of Mo into the $\text{Al}_3\text{M}(\text{L}12)$ nanoprecipitates.
4. Diffusional-creep at 400 °C was observed for both base- and modified- alloys 1 and 2, *Fig. 4a*, with threshold stresses of $-6$ and $-14$ MPa, respectively. These diffusional-creep threshold-stresses are associated with two types of precipitates residing at GBs: $\text{Al}_3(\text{Zr,Sc,Er})(\text{D}023)$-precipitates for the unmodified *alloy 1*, and $\alpha$-$\text{Al(Mn,Mo)Si}$-precipitates for the modified *alloy 2*, *Fig. 6*. For *alloy 2*, the smaller edge-to-edge spacing between the GB precipitates is consistent with reduced GB sliding as compared to the base-alloy, despite a smaller grain diameter.
5. Creep resistance in the modified alloy does not deteriorate after 16 days of testing under stress at 400 °C, highlighting the excellent coarsening resistance of all the precipitates ($\text{Al}_3\text{M}(\text{L}12)$ and $\alpha$-$\text{Al(Mn,Mo)Si}$).

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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