Precipitation Evolution in Al-0.1Sc, Al-0.1Zr, and Al-0.1Sc-0.1Zr (at.%) Alloys during Isochronal Aging

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Abstract

Precipitation strengthening is investigated in binary Al-0.1Sc, Al-0.1Zr, and ternary Al-0.1Sc-0.1Zr (at.%) alloys aged isochronally between 200 and 600 °C. A pronounced synergistic effect is observed when both Sc and Zr are present. Above 325 °C, where peak microhardness (670 MPa) occurs in the binary Al-Sc alloy due to Al3Sc (L12) nanometer-scale precipitates, Zr additions result in a secondary increase in strength due to additional precipitation of Zr-enriched outer shells onto these precipitates. The ternary alloy reaches a peak microhardness of 780 MPa at 400 °C, delaying overaging by >100 °C compared with the binary Al-Sc alloy and increasing strength compared with the binary Al-Zr alloy (peak microhardness of 420 MPa at 425–450 °C). Compositions, radii, volume fractions, and number densities of the Al3(Sc1−xZrx) precipitates are measured directly using atom-probe tomography. This information is used to quantify the observed strengthening increments, attributed to dislocation shearing of the Al3(Sc1−xZrx) precipitates.

Key words: Aluminum alloys, Precipitation, Scandium, Zirconium, Atom-probe tomography

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Preprint submitted to Elsevier December 22, 2009
1. Introduction

The Al-Zr system shows particular promise for developing creep-resistant, thermally stable Al-based alloys at elevated temperatures [1, 2]. During post-solidification aging, decomposition of supersaturated Al-Zr solid-solutions occurs initially by the formation of nanometer-scale Al$_3$Zr precipitates with a metastable cubic L1$_2$ structure, which transform to the equilibrium D0$_{23}$ phase after prolonged aging at elevated temperatures (>450 ºC) [3–11]. The stability of the L1$_2$ metastable phase at high homologous temperatures is attributed to slow diffusion kinetics of Zr in α-Al and a small lattice parameter mismatch of Al$_3$Zr (L1$_2$) with α-Al [1].

In previous studies by the authors, the microstructures and ambient-temperature mechanical properties of conventionally solidified Al-Zr alloys were studied during isothermal aging at 375, 400, 425 ºC [12] and 500 ºC [13] or during isochronal aging up to 600 ºC [13]. Precipitation of spheroidal, nanometer-scale Al$_3$Zr (L1$_2$) precipitates results in a pronounced hardening response at all aging temperatures investigated. There was no appreciable overaging effect despite extended aging times (3,200 h) at 425 ºC (0.75 $T_m$, where $T_m$ is the absolute melting temperature of Al) [12], and only at or above 500 ºC do the metastable L1$_2$ trialuminide precipitates transform to their equilibrium D0$_{23}$ structures [13].

The Al$_3$Zr precipitates are, however, heterogeneously distributed, reflecting the dendritic microsegregation of Zr solute atoms during solidification [12]. Because Zr forms a terminal peritectic with Al, the liquidus and solidus boundaries of the α-Al solid-solution have positive slopes and $k_0$, the equilibrium partition coefficient for solidification, is greater than unity. The first solid to form during solidification is therefore richer in Zr compared to the bulk alloy composition, resulting in solute-rich dendritic cells surrounded by solute-depleted interdendritic channels. Upon aging, only the enriched dendritic cells are supersaturated sufficiently to cause precipitation of Al$_3$Zr. The precipitate-free interdendritic channels have a deleterious effect on the mechanical properties, both at ambient temperature [13] and during creep experiments performed at 300, 350 or 400 ºC [14], with strengthening occurring on multiple length scales: (i) on the nanometer-scale by an Orowan strengthening mechanism; and (ii) on the micrometer-scale related to the volume fraction of the precipitate-rich dendrites [13].

Dendritically distributed Al$_3$Zr (L1$_2$) precipitates are also a significant problem in commercial wrought alloys, where Zr is added as a recrystallization inhibitor [1, 3, 15–19]. During solutionizing, which is typically performed at ~500 ºC, coherent Al$_3$Zr (L1$_2$) precipitates are formed which inhibit subsequent recrystallization by pinning migrating grain boundaries. The alloys are prone to recrystallization, however, in the interdendritic regions where the number density of Al$_3$Zr precipitates is small [20–23]. Several recent studies have aimed to minimize the extent of the precipitate-free interdendritic regions through multi-

There is a particularly strong interest in adding Sc to improve the precipitate distribution, thereby improving recrystallization resistance of Al-Zr alloys [22, 26–31, 33, 34]. Robson [28] and Forbord et al. [30] have demonstrated that by combining Sc, a solute forming a terminal eutectic with Al ($k_0 < 1$), with Zr, a peritectic solute ($k_0 > 1$), the precipitate-free regions associated with a Sc-free alloy may be eliminated. Their argument, supported by experimentally measured solute concentration profiles, claims that during solidification, Zr and Sc solute atoms segregate at the dendrite interiors and exteriors, respectively, effectively “filling-in” the interdendritic regions with Sc, which forms Al$_3$Sc ($L_1_2$) precipitates upon subsequent thermal aging. A similar effect has also been observed by Lieblich and Torralba [35, 36] with Al-Li-Ti alloys, where Ti (a peritectic-forming solute) segregates to the dendrite interiors and Li (a eutectic-forming solute) segregates to the periphery. A further advantage of combining Zr and Sc is the improved coarsening resistance of Al$_3$((Sc$_{1-x}$Zr$_x$)$_2$) ($L_1_2$) precipitates compared with Al$_3$Sc ($L_1_2$) [37–41]. Finally, first-principles calculations show that Sc should stabilize the $L_1_2$ structure of Al$_3$Zr [42], which may delay the transformation of those precipitates to their equilibrium D0$_{23}$ structures.

In this article, we describe the synergistic effects obtained when both Sc and Zr are added to Al. We measure the precipitate radius, volume fraction, and number density simultaneously using three-dimensional atom-probe tomography (APT) reconstructions, and correlate the strength predicted by using these parameters in classical precipitation hardening models with the measured microhardness.

2. Experimental procedures

2.1. Alloy compositions and preparation

Binary Al-0.1Sc and Al-0.1Zr alloys and the ternary Al-0.1Sc-0.1Zr alloy were investigated; alloy designations and exact compositions are summarized in Table 1 (all compositions are in at.% unless otherwise noted). Except for the Al-Sc binary alloy, the alloys were not homogenized prior to post-solidification aging. This is because Al-Zr alloys (with sufficient Zr concentrations to allow precipitation strengthening) cannot be homogenized without first creating Al$_3$Zr precipitates, which then coarsen rapidly at the solutionizing temperatures, resulting in minimal precipitation hardening during subsequent aging. This is consistent with the findings of Jia et al. [23], who observed that homogenizing an Al-0.04Zr-0.50Mn alloy at 630 °C decreased the number density of Al$_3$Zr precipitates during subsequent precipitation aging. The Al-Sc-Zr castings were intentionally left in their as-cast state to take advantage of the expected segregation of Sc at the Zr-poor dendrite peripheries. The Al-Sc alloy was studied in both the as-cast and homogenized states, with homogenization taking place at 640 °C for 28 h.
Small (∼7 g) buttons were prepared by melting 99.95 at.% Al (Atlantic Equipment Engineers, Bergenfield, NJ) with a dilute Al-0.12Sc master alloy (Ashurst Technology, Ltd., Baltimore, MD) and/or an Al-0.57Zr master alloy, employing non-consumable electrode arc-melting in a gettered purified-argon atmosphere. The pure Al contained 260 at. ppm Fe and 260 at. ppm Si as impurities, as determined by glow-discharge mass spectrometry (Shiva Technologies/Evans Analytical Group, Syracuse, NY). The Al-0.57 Zr master alloy was dilution cast from a commercial 10 wt.% Zr master alloy (KB Alloys, Reading, PA). The verified compositions in Table 1 were obtained by bulk chemical analysis performed by direct current plasma emission spectroscopy (ATI Wah Chang, Albany, OR). The microstructures of the as-cast specimens were observed using a JEOL JSM-7000F scanning electron microscope (SEM).

Two button ingots of Al-0.1Sc-0.1Zr, labeled (a) and (b), were prepared in order to ensure that sufficient material was available for subsequent analyses. Most analyses were performed on Al-0.1Sc-0.1Zr(a), which was only aged to 400 °C to preserve the bulk of the material in the peak-aged condition and to allow for subsequent isothermal aging. Likewise, the as-cast specimen of Al-0.1Sc was only aged to 400 °C, while the homogenized specimen was aged to 500 °C.

[Table 1 about here.]

2.2. Aging treatments and analytical techniques

The alloys were aged isochronally in 25 °C steps lasting 3 h each, beginning at 200 °C and terminating at 600 °C. After each aging step, the specimens were water-quenched and precipitation of Al$_3$Sc, Al$_3$Zr, or Al$_3$(Sc$_{1-x}$Zr$_x$) was monitored by Vickers microhardness and electrical conductivity measurements. The Vickers microhardness measurements were performed at ambient temperature on metallographically polished sections using a load of 200 g and a dwell time of 5 s. A minimum of 20 hardness measurements were recorded for each temperature. The electrical conductivity measurements were performed at ambient temperature using an eddy current apparatus (Sigmatest 2.069 from Forster Instruments, Pittsburgh, PA), placing the contact probe on a clean, planar surface. Five measurements were recorded, each corresponding to a different frequency (60, 120, 240, 480, or 960 kHz), on each specimen. For consistency, a single specimen of each alloy was used for the electrical conductivity measurements, which was measured between each isochronal aging step. An increase of electrical conductivity corresponds to a decrease in the supersaturation of Sc and Zr in the matrix due to an increased precipitate volume fraction [43–45]. Uncertainty in both measurements is reported as one standard deviation from the mean.

The compositions, mean radii ($\langle R \rangle$), volume fractions ($\phi$), and number densities ($N_v$) of the Al$_3$(Sc$_{1-x}$Zr$_x$) precipitates were measured employing three dimensional atomic reconstructions obtained using a local electrode atom-probe™ (LEAP) 3000X Si tomograph [46–50]. Needle-like APT specimens were prepared by a two-step electropolishing procedure. Specimen blanks, excised
from aged specimens and mechanically ground to approximately \(0.2 \times 0.2 \times 10\) mm\(^3\), were initially shaped into needle-like tips using a solution of 10 vol.\% perchloric acid in acetic acid at \(\sim 10\) V d.c. at ambient temperature. Final electropolishing involved formation of a neck near the tip apex, controlled by limiting the amount of chemical solution in contact with the area of the neck using a loop-polishing apparatus. A solution of 2 vol.\% perchloric acid in butoxyethanol was employed for this final tip sharpening procedure, with an applied potential of 3–8 V d.c. at room temperature. The resulting specimen has an end radius of curvature \(<50\) nm. Pulsed field-evaporation was conducted under ultrahigh vacuum (UHV) conditions \(<10^{-10}\) Torr gauge pressure) at a specimen temperature of 30 K utilizing a pulse fraction (ratio of the pulse voltage to the steady-state dc imaging voltage) of 15–20% and a pulse repetition rate of 200 kHz. A fixed flight path of 80 mm was used for all analyses. Post-analysis data visualization and evaluation were performed with IVAS v. 3.4.1 (Imago Scientific Instruments, Madison, WI). Precipitates were isolated and studied quantitatively using the proximity histogram [51, 52] and envelope methods [53, 54], as discussed in detail below.

3. Results

3.1. As-cast microstructure

The as-cast macrostructures of the binary Al-Sc [44, 55] and Al-Zr [12] alloys are typical of conventionally cast alloys, exhibiting coarse (millimeter-scale) columnar grains. The Al-Sc-Zr alloy, by contrast, has a much finer equiaxed macrostructure. Figure 2 displays a SEM micrograph of metallographically polished as-cast Al-0.1Sc-0.1Zr(a), where the grains have a diameter of \(\sim 50\) µm. This pronounced grain refinement is due to copious precipitation of primary \(\text{Al}_3(\text{Sc}_{1-x}\text{Zr}_x)\) precipitates, which are also visible in Fig. 2. These primary precipitates are 3–5 µm in diameter and have a petal-like shape. This morphology is characteristic of the L1\(_2\) structure of \(\text{Al}_3\text{Zr}\) (metastable) [56, 57] or \(\text{Al}_3\text{Sc}\) (equilibrium) [58–60] primary precipitates, whose cubic structure is commensurate with \(\alpha\)-Al (fcc) and acts as an effective heterogeneous nucleant of \(\alpha\)-Al during solidification. The primary precipitates are Zr-rich with a Zr:Sc ratio of \(\sim 3\) on an at.\% basis, as determined by quantitative energy-dispersive spectrometry (EDS) in the SEM.

3.2. Vickers microhardness and electrical conductivity

Figure 3 displays the precipitation behavior of Al-0.1Sc, Al-0.1Zr, and Al-0.1Sc-0.1Zr during isochronal aging, as monitored by Vickers microhardness and electrical conductivity measurements. Precipitation of Al\(_3\)Sc (L1\(_2\)) commences between 200 and 250 °C in the binary Al-Sc alloy, as evidenced by the increase in strength and the accompanying change in electrical conductivity, achieving a peak microhardness of 668±20 MPa at 325 °C. There is a continuous decrease in
microhardness above 325 °C. Peak electrical conductivity, which corresponds to a maximum φ of Al₃Sc (L1₂), is achieved at ~375 °C, which is 50 °C higher than the peak-microhardness temperature. The difference in electrical conductivity between the as-cast and maximum value is 2.7 ± 0.4 MS m⁻¹. Above 400 °C, the decreasing electrical conductivity and the concomitant increased scatter in the data suggests that Al₃Sc precipitates are dissolving. By 500 °C, virtually all precipitation strengthening is lost and the Al-0.1Sc alloy has returned to its initial as-cast microhardness. Homogenizing prior to aging has no effect on the observed microhardness or change in electrical conductivity. The Al-0.1Sc specimen that was homogenized exhibits a systematically smaller electrical conductivity (~0.6 MS m⁻¹), which is probably due to differences in specimen geometry.

In the Al-0.1Zr alloy, precipitation of Al₃Zr (L1₂) commences between 350 and 375 °C and leads to a peak microhardness value of 420±8 MPa at 425–450 °C, with a corresponding change in electrical conductivity of 3.6 ± 0.1 MS m⁻¹. Beyond 475 °C, there is a continuous decrease in microhardness with a concomitant decline in electrical conductivity, which is due to coarsening and dissolution of the spheroidal Al₃Zr (L1₂) precipitates and their transformation to their equilibrium D0₂₃ structure, as studied in detail in Ref. [13].

The as-cast electrical conductivity of Al-0.1Sc-0.1Zr (26.4 ± 0.3 MS m⁻¹) is significantly less than that of Al-0.1Sc (30.9 ± 0.4 MS m⁻¹) or Al-0.1Zr (29.7±0.1 MS m⁻¹) because the ternary alloy contains twice the nominal amount of solute as the binary alloys. The as-cast microhardness of Al-0.1Sc-0.1Zr is also ~50 MPa greater than that of the binary alloys, which may be attributable to greater solid-solution strengthening and/or Hall-Petch strengthening due to the finer grain size, Fig. 2. Precipitation strengthening of Al-0.1Sc-0.1Zr is equivalent to that of Al-0.1Sc up to 325 °C, with a comparable change in electrical conductivity, suggesting that a similar φ of precipitates is generated in both cases. The Al-0.1Sc alloy reaches peak hardness at 325 °C, while the Al-01Sc-01Zr alloy experiences additional precipitate nucleation and growth, as evidenced by the continued increases in microhardness and electrical conductivity above 325 °C. A peak microhardness of 782±37 MPa is achieved at 400 °C and peak electrical conductivity, corresponding to maximum φ, occurs at 475 °C. Additions of Zr delay overaging by 100–125 °C as compared with the Al-Sc alloy; note that at 600 °C (0.94Tₘ) there is still a perceptible strengthening effect for the Al-Sc-Zr alloy, although the decreased electrical conductivity suggests that significant precipitate dissolution has occurred.

3.3. Atom-probe tomography

The ternary Al-0.1Sc-0.1Zr(a) alloy was investigated by APT to determine the precipitate compositions, ⟨R⟩, φ, and Nᵥ values. Figure 3 indicates that the interesting aging compositions include 300 °C (before the departure from Al-Sc behavior), 350 °C (near peak microhardness), and 400 °C (peak microhardness and near peak electrical conductivity). Figure 4 presents APT reconstructions
for these isochronal aging conditions. The dimensions of the reconstructions, the total number of atoms contained within them, and the number of Al₃(Sc₁₋ₓZrₓ) precipitates wholly included or intercepted by the analysis boundaries are also indicated.

The reconstructions in Fig. 4 indicate that both Sc and Zr partition to the Al₃(Sc₁₋ₓZrₓ) precipitates. This information is conveyed more quantitatively in Fig. 5, which exhibits a proximity histogram, or proxigram for short [51, 52], displaying average solute concentration profiles in the α-Al matrix and Al₃(Sc₁₋ₓZrₓ) precipitates with respect to a constant 1.25 at.% Sc isoconcentration surface delineating the two phases in all reconstructions. For the three isochronal aging temperatures investigated, Zr is a minor constituent in the Al₃(Sc₁₋ₓZrₓ) precipitates, with the Zr content in the precipitates increasing with increasing aging temperatures from 0.39±0.03 at.% Zr at 300 °C, to 0.44±0.01 at.% Zr at 350 °C, and to 1.5±0.2 at.% Zr at 400 °C. The distribution of Zr atoms in the Al₃(Sc₁₋ₓZrₓ) precipitates is inhomogeneous, with the precipitates generally consisting of a Zr-poor Al₃Sc core surrounded by a Zr-enriched outer shell. This core-shell solute distribution becomes more apparent with increasing aging temperature. At 300 °C, the precipitates contain a maximum of only 1.9±0.4 Zr, segregated near the precipitate core. After 350 °C, there is an enrichment of 2.8±0.1 Zr at the α-Al/Al₃(Sc₁₋ₓZrₓ) heterophase interface. At 400 °C, the interfacial enrichment increases significantly to 7.4±0.2 Zr.

To assess the stability of these alloys for extended high-temperature usage, specimens were isothermally annealed at 400 °C for 400 h, after having been isochronally aged to 400 °C (Fig. 3). Figure 6 displays Vickers microhardness as a function of exposure time at 400 °C for Al-0.1Sc and Al-0.1Sc-0.1Zr(a). During isochronal aging, Al-0.1Sc is already overaged considerably from 668±20 MPa at 325 °C, peak microhardness, to 448±21 MPa at 400 °C. During further annealing at 400 °C, Fig. 6, the alloy continues to overage with the microhardness decreasing linearly on a semi-logarithmic scale to 295±9 MPa after 400 h. The Al-Sc-Zr alloy also overages at 400 °C, from a near-peak microhardness of 742±29 MPa to 549±28 MPa after 400 h at 400 °C. Significant coarsening in Al-0.1Zr does not occur below ~500 °C (not displayed in Fig. 6, but presented in Refs. [12, 13]); it is anticipated that the microhardness after 400 h at 400 °C would be ~370 MPa, the value obtained after the 400 °C isochronal aging treatment.
4. Discussion

4.1. As-cast microstructure

In dilute Al-based peritectic systems, for a specific cooling rate there is a corresponding critical solute concentration below which primary precipitation of Al$_3$M will not occur [1, 2, 61–63]. The presence of the primary precipitates in the Al-Sc-Zr alloys indicates that, for the conventional casting conditions we employed, 0.2 at.% total solute (Sc plus Zr) exceeds this critical concentration. No primary precipitates are observed in the more dilute Al-0.1Zr alloy [12], and primary Al$_3$Sc precipitates in Al-0.1Sc are not possible, given the eutectic composition of 0.23 at.% Sc [58]. This is consistent with the coarser grain structure observed in the two binary alloys.

The primary precipitation of Al$_3$(Sc$_{1-x}$Zr$_x$) observed for the Al-Sc-Zr alloy has several complicating consequences. The amount of solute retained in solid-solution is decreased, thus limiting the potential for precipitation hardening during post-solidification aging. The maximum strengthening effect achieved, Fig. 3, could be significantly larger had the formation of primary Al$_3$(Sc$_{1-x}$Zr$_x$) been suppressed. For developing creep-resistant alloys, there is the additional challenge of the potent grain refinement effect associated with the presence of primary precipitates, which act as heterogeneous nuclei during solidification of the melt. To avoid rapid diffusional creep associated with a refined grain structure, it is necessary to reduce the solute content of the Al-Sc-Zr alloys. We have shown that primary precipitation of Al$_3$(Sc$_{1-x}$Zr$_x$) can be suppressed during conventional solidification of more dilute Al-0.06Sc-0.06Zr alloys, producing coarse-grained castings that are suitable for creep studies [64]. The optimum composition for a creep-resistant alloy with Sc:Zr ratio of unity is thus between Al-0.06Sc-0.06Zr and Al-0.1Sc-0.1Zr.

4.2. Vickers microhardness and electrical conductivity

The maximum observed increase in microhardness, Fig. 3, as compared with the value of the as-cast specimens, is 434±24 MPa for Al-0.1Sc and 206±12 MPa for Al-0.1Zr. Thus, on a per atom basis, the maximum precipitation strengthening of Al-Sc is over twice that of Al-Zr. Indeed, it is known that Sc provides the highest increment of strengthening per atomic percent of any alloying element when added to Al [65, 66]. In cast Al-Zr alloys the initial distribution of Zr solute atoms is highly segregated [12], leading to precipitate-free interdendritic channels that have a deleterious effect on ambient-temperature strength [13], which further explains the disparity in strengthening between the Al-Sc and Al-Zr alloys.

The nucleation and growth of Al$_3$Sc (L1$_2$) occurs at much lower temperatures than for Al$_3$Zr (L1$_2$), which is, in part, reflective of the disparity in diffusivities between Sc and Zr in α-Al. These diffusivities are given by an Arrhenius relationship, $D = D_0 \exp(-Q/R_gT)$, where $Q = 173$ and 242 kJ mol$^{-1}$ and $D_0 = 5.31 \times 10^{-4}$ and $7.28 \times 10^{-2}$ m$^2$ s$^{-1}$ for Sc and Zr, respectively [1, 67, 68]. At 200 °C, where precipitation of Al$_3$Sc is first detected (Fig. 3), the diffusivity of Sc in α-Al is $4.16 \times 10^{-23}$ m$^2$ s$^{-1}$. A similar diffusivity of Zr in α-Al is
achieved at 322 °C, which is somewhat comparable to the first detection of Al₃Zr precipitation occurring at 375 °C. Since precipitate growth and coarsening are diffusion-limited, the precipitation of Al₃Sc is significantly more rapid than that of Al₃Zr.

The rapid overaging of Al-0.1Sc for $T > 325$ °C is consistent with prior studies on similar conventionally solidified Al-Sc alloys, which exhibit excellent coarsening and creep resistance up to 300 °C [37, 65, 69–73]. The overaging of the Al-0.1Zr alloy occurs at much higher temperatures ($T > 475$ °C), which again can be explained by the relative diffusivities of Sc and Zr in α-Al. The Al-Sc alloy overages beyond 325 °C, where the diffusivity of Sc in α-Al is $4.10 \times 10^{-19}$ m² s⁻¹. A comparable diffusivity for Zr occurs at 460 °C, which is in agreement with the onset of overaging beyond 450 °C.

The precipitation hardening behavior of both the as-cast and homogenized Al-0.1Sc specimens are identical, Fig. 3, which suggests that Sc atoms are homogeneously distributed prior to nucleation of Al₃Sc during post-solidification aging. Previous studies [28, 30, 33] quantifying solute segregation in Sc-containing commercial 7xxx alloys by electron microprobe analysis indicate that Sc atoms are much more uniformly distributed than the other solutes (e.g. Zn, Mg, or Zr), which reflects the fact that $k_0$ is near unity ($k_0 = 0.82$ [1]) for Sc. It is also possible that the relatively fast-diffusing Sc atoms are able to migrate into a more uniform distribution prior to nucleating Al₃Sc [30].

The change in electrical conductivity between the as-cast and peak-aged conditions is comparable for Al-0.1Sc (2.7 ± 0.4 MS m⁻¹) and Al-0.1Zr (3.6 ± 0.1 MS m⁻¹). Assuming that the specific resistivities of these elements are comparable, this suggests that a similar $\phi$ is formed during aging. That the maximum increase in microhardness of Al-0.1Zr is less than half that of Al-0.1Sc is probably due to the deleterious effect of the precipitate-free interdendritic channels in the Al-Zr alloy [13]. In Al-0.1Sc the peak electrical conductivity, where the maximum $\phi$ of Al₃Sc (L₁₂) is attained, is achieved at ~375 °C — 50 °C higher than the temperature at which peak microhardness is attained. Thus the initial decline in strength in the range 325–375 °C is likely due to a change in strengthening mechanisms from order strengthening to Orowan bypass as precipitates continue to grow. At higher temperatures ($T > 400$ °C), the decline in strength is due to precipitate coarsening (Ostwald ripening) decreasing the resistance to Orowan bypass further.

The electrical conductivity of the as-cast ternary Al-0.1Sc-0.1Zr alloy is approximately 4 MS m⁻¹ lower than those of the binary Al-0.1Sc or Al-0.1Zr alloys, due to the larger solute additions. The maximum change in electrical conductivity from the as-cast condition should be directly related to the amount of Sc and Zr in solid-solution. This value is, however, smaller in the ternary alloy than the sum of the differences for the binary alloys. This is consistent with the primary precipitates observed in the ternary alloy, Fig. 2, which indicate that not all alloying additions are dissolved in solution prior to aging. The microhardness of the as-cast ternary alloy is approximately 50 MPa greater than that measured for Al-0.1Sc or Al-0.1Zr. This value is also less than would be expected if all alloying contributions aided in solid-solution strengthening. In
addition to enhanced solid-solution strengthening, the finer grain size of the ternary alloy leads to Hall-Petch strengthening, $\Delta \sigma_{HP}$, given by [74, 75]:

$$\Delta \sigma_{HP} = K d^{-1/2}, \tag{1}$$

where $K$ is the material-specific locking parameter and the grain diameter, $d$ is $\sim 50 \, \mu m$. The value of $K$ varies as a function of alloying content [76, 77] and also depends on the range in $d$ investigated. Because the contributions of Sc and Zr on $K$ are not known and because of the dilute concentrations of these additions, we use an average value of $K = 30 \, MPa \, \mu m^{1/2}$ for pure Al over the range $30 \, \mu m \leq d \leq 500 \, \mu m$ [78] to find $\Delta \sigma_{HP} = 4 \, MPa$. The increase in microhardness alone cannot account for the $\sim 50 \, MPa$ increased as-cast microhardness of the Al-Sc-Zr alloys. Solid-solution strengthening must therefore also be playing a role.

For the Al-0.1Sc-0.1Zr alloys, the change in electrical conductivity between the as-cast specimens and those aged to 325 $^\circ$C is $2.6 \pm 0.3 \, MS \, m^{-1}$, which is close to what is observed in the binary Al-0.1Sc alloy over the same temperature range ($2.8 \pm 0.6 \, MS \, m^{-1}$), indicating that the Al$_3$(Sc$_{1-x}$Zr$_x$) precipitates formed up to 325 $^\circ$C contain mainly Sc, which is consistent with the proxigrams in Fig. 5. Between 325 $^\circ$C and 400 $^\circ$C (peak strength), there is an additional change in conductivity of about 3.5 $MS \, m^{-1}$, which is similar to the change between the as-cast and peak-aged conditions in Al-0.1Zr ($3.6 \pm 0.1 \, MS \, m^{-1}$). This suggests that between 325 $^\circ$C and 400 $^\circ$C, all of the available Zr in solid-solution has precipitated out. That the peak microhardness is not achieved until 400 $^\circ$C supports the APT evidence that Zr forms a shell around the Al$_3$Sc precipitates, hindering the coarsening of the Al$_3$Sc core.

### 4.3. Atom-probe tomography

The Zr concentration in the Al$_3$(Sc$_{1-x}$Zr$_x$) precipitates increases continuously with increasing isochronal aging temperature from 0.39$\pm$0.03 Zr at 300 $^\circ$C to 1.5$\pm$0.2 Zr at 400 $^\circ$C. The distribution of Zr in the Al$_3$(Sc$_{1-x}$Zr$_x$) precipitates is inhomogeneous, Fig. 5, with the precipitates consisting of an Al$_3$Sc core surrounded by a spherical Zr-enriched outer shell. Similar core-shell structure precipitates are well documented for Al-Sc-Zr alloys, as observed by APT [40, 80–82], analytical high resolution electron microscopy [81, 83, 84], small-angle X-ray scattering [81, 85], and atomic-scale simulations [81, 86]. Other systems also exhibit core-shell precipitates, as observed in APT studies on Al-Sc-Ti [87], Al-Sc-RE [88, 89], Al-Sc-Zr-Hf [90], and Al-Li-Sc-Zr [91, 92] alloys. The formation of a shell is due to a disparity in diffusivities among alloying elements, Sc and Zr in the present case. Because of the much larger diffusivity of Sc compared to Zr, only Sc atoms are kinetically able to participate in the early stages of nucleation and growth. These pre-existing precipitates then act as heterogeneous nucleation sites for the less-mobile Zr atoms, which forms shells on the Al$_3$Sc precipitates rather than nucleating new Al$_3$Zr precipitates.

The APT data in Fig. 4 were used to determine $\langle R \rangle$, $\phi$, and $N_\nu$ of the Al$_3$(Sc$_{1-x}$Zr$_x$) precipitates directly in three dimensions. The radius, $R$, of an
individual precipitate containing \( n \) atoms in the reconstruction is equated to the radius of the volume equivalent sphere:

\[
R = \left( \frac{3}{4\pi} \frac{n\Omega}{\eta} \right)^{1/3},
\]

where \( \Omega \) is the theoretical atomic volume and \( \eta \) is the estimated detection efficiency of 0.5 for the LEAP tomograph’s multichannel plate detector. The atomic volume is calculated using \( \Omega = a^3/4 \), where \( a \) is the precipitate lattice parameter and the factor 4 represents the number of atoms in an ordered fcc (L1\(_2\)) unit cell. The lattice parameter of Al\(_3\)(Sc\(_{1-x}\)Zr\(_x\)) (L1\(_2\)) is proportional to \( x \), varying from 0.4103 nm for \( x = 0 \) to 0.4092 nm for \( x = 0.5 \) [93].

For each aging temperature, the average of the measured precipitate compositions was used to determine \( \Omega \). The number of atoms, \( n \), contained in each precipitate was determined by taking the contents of an isoconcentration surface whose value is that of the inflection point of the Sc concentration profile (\( \sim 3 \) at.% Sc) in the proxigram [51, 52]. Due to the strong partitioning of Sc to the precipitates, the calculated radius is insensitive to the exact concentration chosen for this surface. The precipitate radius found by this method is also consistent with that found by using the envelope method [53, 54].

The precipitate volume fraction, \( \phi \), is determined directly from the ratio of the total number of atoms contained within the precipitates to the total number of atoms collected and the average atomic density of the two phases, as calculated from their respective lattice parameters (\( a = 0.40496 \) nm for Al [1]). The number density, \( N_v \), is calculated directly from the number of precipitates in the analyzed volume. For the purpose of measuring both \( \langle R \rangle \) and \( N_v \), precipitates fully contained in the reconstruction volume are counted as whole precipitates and those that are cut by the surface of the reconstructed volume are counted as half precipitates [54]. The difference in \( \langle R \rangle \) between precipitates counted as whole and half is less than one standard deviation of the precipitate radius, and is \( \sim 10\% \) for all measured data sets. This systematic error arises from the minimum detectable precipitate size preventing some precipitates that are cut by the analysis boundary from being measured. The measured \( \langle R \rangle \), \( \phi \), and \( N_v \) values of the Al\(_3\)(Sc\(_{1-x}\)Zr\(_x\)) precipitates aged isochronally to 300, 350, or 400 °C are presented in Table 2.

The values of \( \langle R \rangle \) and \( \phi \) increase substantially between 300 and 350 °C, as both Sc and Zr atoms continue to precipitate out onto the growing precipitates. Microsegregation (the alloys were not homogenized) and the small changes compared to measurement uncertainty both may explain why we do not observe the monotonic increase in \( \langle R \rangle \) and \( \phi \) between 350 and 400 °C that we would expect, based on the electrical conductivity results. The value of \( N_v \) remains in the same order of magnitude, changing by less than 25\%, over the three aging conditions studied by APT. This is expected during isochronal aging, since solute atoms nucleate onto preexisting precipitates formed at earlier aging treatments. This
small variation in $N_v$ also indicates that there is negligible precipitate coarsening for these aging times up to 400 °C.

We now compare our results to prior APT studies on Al-Sc-Zr alloys. Some studies have a comparable Sc content, but all have a smaller Zr concentration and employ greater aging temperatures and times. Forbord et al. [80] aged an Al-0.09Sc-0.02Zr at 475 °C for 15 h. Their higher aging temperature as compared with ours resulted in larger $\text{Al}_3(\text{Sc}_{1-x}\text{Zr}_x)$ precipitates ($\langle R \rangle = 9.6$ nm, as measured by transmission electron microscopy) containing more Zr (4.5 at.%), despite their smaller Zr:Sc ratio. The core-shell structure was, however, retained, as they observed an $\sim 8$ nm thick Zr-rich shell surrounding an $\sim 2.5$ nm radius Sc-rich core. Clouet et al. [81] studied a similar Al-0.09Sc-0.03Zr alloy aged for a longer time (128 h) at the same maximum temperature we have analyzed by LEAP tomography (400 °C), where they observed a 12 at.% Zr enrichment at the $\text{Al}_3(\text{Sc}_{1-x}\text{Zr}_x)/\text{Al}$ heterophase interface. This interfacial enrichment is larger than what we observed (7.4±0.2 at.% Zr) after 3 h at 400 °C, despite the smaller Zr:Sc ratio in their alloy [81]. Utilizing high-angle annular dark-field TEM for alloys aged for 32 h at 450 °C, Clouet et al. [81] also observed a 2–4 nm thick Zr-rich shell containing about 12 at.% Zr surrounding a $\langle R \rangle \sim 10$ nm Sc-rich core. Fuller et al. [40, 41] aged an Al-0.09Sc-0.05Zr isothermally at 300 °C, and observed via APT that the Zr in the precipitates increased from 0.4 at.% after 4.5 h (comparable to the amount we measured at this temperature) to 1.2 at.% after 2,412 h (less than the amount that we measured at 400 °C). The precipitates in their study were of a comparable size to ours ($\langle R \rangle \sim 2$ nm) for the extended aging treatments at 300 °C. When aged isothermally at 350 or 375 °C for at least 10 h, significant coarsening was, however, observed. The small $\langle R \rangle$ and increasing $\phi$ values that we have measured indicate that isochronal heat treatments may be effective at optimizing alloy strength in a short time. The results of Fuller et al. suggest, however, that longer thermal exposure at temperatures greater than 300 °C will reduce this strength.

4.3.1. Precipitation strengthening in Al-Sc-Zr alloys

Figure 3 demonstrates that the observed strength increase (as compared with the value of the as-cast, unaged specimens) for the Al-0.1Sc-0.1Zr(a) alloy is $\Delta \sigma = 131 \pm 11, 161 \pm 15, \text{ and } 162 \pm 10$ MPa at 300, 350, and 400 °C, respectively, using a conversion factor of $\frac{1}{3}$ between Vickers microhardness and strength [79]. The results in Fig. 5 indicate that this strength increase is attributable to segregation of Zr to pre-existing $\text{Al}_3\text{Sc}$ precipitates, effectively increasing $\phi$ of the precipitates without diminishing $N_v$, thereby increasing the yield stress of the alloy.

Theories of precipitation strengthening have been reviewed in Refs. [94–99]. Precipitate shearing, precipitate bypass by dislocation looping, or a combination of these two mechanisms can generally explain ambient-temperature strength in precipitate-strengthened alloys in the absence of other strengthening mechanisms (e.g., Hall-Petch strengthening, solid-solution strengthening, or strain hardening).
For small precipitate radii, $R$, the strength is controlled by dislocations shearing precipitates, as observed experimentally for Al-Sc [72, 73] and Al-Li [100, 101] alloys with shearable, coherent precipitates. For the shearing mechanism, the increase in yield strength results from three contributions: (i) modulus mismatch strengthening; (ii) coherency strengthening; and (iii) order strengthening.

First, the strengthening due to modulus mismatch, $\Delta \sigma_{ms}$, results from differences in the shear moduli of the precipitate and matrix phases and is given by [95]:

$$\Delta \sigma_{ms} = M \cdot 0.0055(\Delta G)^{3/2} \left( \frac{\phi}{\Gamma} \right)^{1/2} b \left( \frac{\langle R \rangle}{b} \right)^{3m/2-1}, \quad (3)$$

where $M = 3.06$ is the Taylor mean orientation factor [102], $\Delta G$ is the difference in the shear modulus between the matrix and precipitate, $\Gamma = \frac{1}{2}G_{Al}b^2$ is the line tension of the dislocation in Al, $b = 0.286$ nm is the magnitude of the Al Burgers vector [103], and $m = 0.85$ is a constant [95]. The shear modulus of the $\text{Al}_3(\text{Sc}_{1-x}\text{Zr}_x)$ precipitates is taken to be $G_{\text{Al}_3(\text{Sc}_{1-x}\text{Zr}_x)} = 68$ GPa, which is the value for $\text{Al}_3\text{Sc}$ (L1$_2$) [104–106] and also Fe-stabilized $\text{Al}_3\text{Zr}$ (L1$_2$) [107–109]. The shear modulus of the Al matrix is $G_{\text{Al}} = 25.4$ GPa [103].

Second, coherency strengthening, $\Delta \sigma_{cs}$, arises through the elastic strain-field interactions between coherent precipitates and dislocations and is given by [95]:

$$\Delta \sigma_{cs} = M \cdot \chi(\epsilon G_{Al})^{3/2} \left( \frac{\langle R \rangle \phi b}{\Gamma} \right)^{1/2}, \quad (4)$$

where $\chi = 2.6$ [95], $\epsilon$ is a mismatch parameter approximated by $\frac{2}{3}\delta$; $\delta = 1.3\%$ is the lattice parameter mismatch for the $\text{Al}_3(\text{Sc}_{1-x}\text{Zr}_x)$ precipitates estimated from the composition-dependent lattice parameters [39, 93]. Coherency strengthening occurs in parallel with modulus mismatch strengthening.

Third, order strengthening, $\Delta \sigma_{os}$, is due to the formation of antiphase boundaries (APBs), which occurs when matrix dislocations shear ordered precipitates. At peak strength, $\Delta \sigma_{os}$ is given by [95, 98]:

$$\Delta \sigma_{os} = M \cdot 0.81\gamma_{APB} \left( \frac{3\pi \phi}{8} \right)^{1/2}, \quad (5)$$

where $\gamma_{APB} \sim 0.5$ J m$^{-2}$ is an average value of the $\text{Al}_3\text{Sc}$ APB energy for the (111) plane taken from several reported values [104, 106–108, 110]. Because order strengthening acts serially to coherency and modulus mismatch strengthening, the alloy shear strength increment due to precipitate shearing is determined as the maximum value of $\Delta \sigma_{ms} + \Delta \sigma_{cs}$ and $\Delta \sigma_{os}$.

As $R$ increases, the theoretical shear strength of precipitates increases accordingly, until strength becomes controlled by another mechanism, Orowan dislocation looping, which is given by [111]:

13
\[
\Delta \sigma_{\text{or}} = M \cdot \frac{0.4 \cdot G_{\text{Al}} \cdot b}{\pi \sqrt{1 - \nu}} \cdot \frac{\ln \left( \frac{2R}{\phi} \right)}{\lambda_{c-e}},
\]
(6)
where \( \nu = 0.345 \) is Poisson’s ratio \([102]\) for Al. For a monodispersed population of precipitates, the mean planar radius is \( R = \frac{\pi}{2} \langle R \rangle \), and the edge-to-edge interpipet spacing is \( \lambda_{c-e} = \left( \sqrt{\frac{2\pi}{3}} - \frac{\pi}{2} \right) \langle R \rangle \) \([95, 97, 98]\); these equations are also valid for polydispersed arrays \([98]\).

Figure 7 displays the theoretical and measured increases in strength of isochronally aged Al-0.1Sc-0.1Zr(a) as a function of \( \langle R \rangle \). For all three aging temperatures, the small \( \langle R \rangle \) values predict an Orowan strengthening increment that is much larger than the calculated precipitate shear strength. The precipitates for the three aging treatments are therefore shearable, although the mechanism of shear resistance is debatable. While \( \Delta \sigma_{\text{os}} \) is in excellent agreement with measured values, \( \Delta \sigma_{cs} + \Delta \sigma_{ms} \) is still within error of the propagated uncertainty in the \( \langle R \rangle \) and \( \phi \) values. In other Al-Sc-X alloys, strengthening that is nearly independent of \( \langle R \rangle \) has been observed (as is predicted by \( \Delta \sigma_{\text{os}} \)), rather than the dependence that is predicted from \( \Delta \sigma_{cs} + \Delta \sigma_{ms} \) \([72, 73, 112]\). It may be that our estimation of \( \Delta \sigma_{cs} + \Delta \sigma_{ms} \) is too large (e.g., due to precipitates that are not fully coherent). Or alternatively the simplification that the precipitate shear strength is determined by the maximum of one of the two serial processes is not accurate. While there is some variation in the reported values of \( \gamma_{APB} \), the value employed is in agreement with TEM measurements of dislocation spacings \([72, 73]\), and our calculated values of \( \Delta \sigma_{\text{os}} \) have much less propagated uncertainty than \( \Delta \sigma_{cs} + \Delta \sigma_{ms} \) because there is no \( \langle R \rangle \) dependence. Thus, we propose that order strengthening is the controlling strengthening mechanism for these three heat treatments.

These results are in agreement with prior results on Al-0.18Sc \([72, 73]\) and several Al-Sc-Zr alloys \([39]\), for which Orowan dislocation looping is the main strengthening mechanism only for \( R > 2 \) nm, while smaller precipitates are shearable. In Refs. \([72, 73]\), we noted that strengthening increments much lower than those predicted by \( \Delta \sigma_{cs} + \Delta \sigma_{ms} \) may be due to simultaneous bypass of precipitates by shear and Orowan looping. Because of the large size of the present datasets and the small \( \langle R \rangle \) value leading to nearly maximum theoretical strength (for a given \( \phi \)), we are presently using these reconstructions in dislocation dynamics simulations \([113, 114]\) that may provide insight into this hypothesis.

4.4. Isothermal Aging at 400 °C

While the Al-Sc-Zr alloys reach peak microhardness at 400 °C during isochronal aging, Fig. 3, the Al\(_3\)(Sc\(_{1-x}\)Zr\(_x\)) precipitates undergo coarsening after extended exposure (starting at 100 h and pronounced at 400 h) at this temperature, Fig. 6. The decrease in microhardness observed at 400 °C is consistent
with prior studies on Al-Sc-Zr alloys isothermally aged at 300–500 °C. Elagin et al. [37] investigated an Al-0.24Sc-0.05Zr alloy during isothermal aging at 300–500 °C, and first observed a measurable decrease in microhardness after 278 h at 400 °C. Davydov et al. [38] investigated an Al-0.12Sc-0.04Zr alloy and observed negligible coarsening up to 278 h at 400 °C, but significant coarsening beyond 4 h at 450 °C. Thus, the threshold for long-term stability of Al$_3$(Sc$_{1-x}$Zr$_x$) seems to be ~400 °C. Nevertheless, Al-0.1Sc-0.1Zr is still stronger after 400 h at 400 °C than any other conventionally cast Al alloy known to the authors.

5. Conclusions

Precipitation of Al$_3$Sc, Al$_3$Zr, and Al$_3$(Sc$_{1-x}$Zr$_x$) (L1$_2$) precipitates has been investigated in conventionally solidified Al-0.1Sc, Al-0.1Zr, and Al-0.1Sc-0.1Zr (at.%) alloys, isochronally aged from 200 to 600 °C. The following results are obtained:

- The as-cast microstructure of the binary Al-0.1Sc and Al-0.1Zr alloys is typical of conventionally cast alloys, with large (millimeter-scale) columnar grains without primary Al$_3$Sc or Al$_3$Zr precipitates. The Al-0.1Sc-0.1Zr alloy has fine (~50 µm) equiaxed grains, which is a result of primary precipitation of Al$_3$(Sc$_{1-x}$Zr$_x$) acting as a grain refiner during solidification. Because these primary precipitates reduce the potential for precipitation hardening during post-solidification aging, the total (Sc+Zr) solute content should be below 0.2 at.% in conventionally cast alloys if ambient and creep strength are to be optimized.

- Precipitation of Al$_3$Sc (L1$_2$) commences between 200 and 250 °C in the Al-0.1Sc alloy, reaching a peak microhardness of 668±20 MPa at 325 °C. In the Al-0.1Zr alloy, precipitation of Al$_3$Zr (L1$_2$) commences between 350 and 375 °C, achieving a peak microhardness of 420 MPa at 425–450 °C. Sc diffuses much more rapidly than Zr at these temperatures, which explains the faster precipitation kinetics for the Al-Sc alloy. On a per atom basis, Sc is a significantly more potent strengthener than Zr, probably because of the nonuniform precipitate distributions in the Al-Zr alloys (Fig. 2), which are known to be deleterious to the mechanical properties [13].

- In the Al-0.1Sc-0.1Zr alloy, the precipitation hardening behavior follows that of Al-0.1Sc up to 325 °C. Beyond this temperature, Zr additions result in a secondary increase in strength, attaining a peak Vickers microhardness of 782±37 MPa at 400 °C. Overaging is delayed in Al-0.1Sc-0.1Zr by more than 100 °C compared with the Zr-free alloy.

- The average Zr concentration in the Al$_3$(Sc$_{1-x}$Zr$_x$) precipitates, as measured by atom-probe tomography, increases continuously with increasing isochronal aging temperature. At 300 °C the precipitates contain 0.39±0.03 at.% Zr; at 350 °C they contain 0.44±0.01 at.% Zr; and at 400 °C
they contain $1.5 \pm 0.2$ at.

\% Zr. Zirconium segregates to the Al/Al$_3$Sc heterophase interface forming a Zr-enriched outer shell surrounding the Al$_3$Sc precipitates, thereby increasing the precipitate volume fraction, $\phi$, from $\sim 0.3\%$ to $\sim 0.5\%$. The precipitates remain small ($\langle R \rangle \approx 3$ nm) and the number density remains large ($N_v \approx 10^{23}$ m$^{-3}$) and the increase in the yield stress of the alloy, by $\sim 30$ MPa, results from an increase in the alloy shear strength increment due to precipitate shearing.

- While the Al-0.1Sc-0.1Zr alloy achieves peak microhardness after isochronal aging to 400 °C, it overages after extended exposure at this temperature (Fig. 6), indicating that it is not suitable for extended use at 400 °C.

Acknowledgments

This research is supported by the US Department of Energy, Basic Sciences Division, under contracts DEFG0202ER45997 and DEFG0298ER45721. Atom-probe tomographic measurements were performed at the Northwestern University Center for Atom-Probe Tomography (NUCAPT), using a LEAP tomograph purchased with funding from the NSF-MRI (DMR-0420532, Dr. Charles Bouldin, monitor) and ONR-DURIP (N00014-0400798, Dr. Julie Christodoulou, monitor) programs. We are pleased to acknowledge Profs. M. E. Fine and D. Isheim (Northwestern University) for useful discussions.

References


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Table 1: Compositions of the Al-Sc, Al-Zr, and Al-Sc-Zr alloys investigated (at.%).

<table>
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<th>Alloy</th>
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<th>Verified composition†</th>
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<tr>
<td>Al-0.1Zr</td>
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†As measured by direct current plasma emission spectroscopy.
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<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( \langle R \rangle ) (Eq.(2)) (nm)</th>
<th>( \phi ) (%)</th>
<th>( N_v \times 10^{23} ) m(^{-3} )</th>
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<tr>
<td>300</td>
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