Precipitation evolution in Al–Zr and Al–Zr–Ti alloys during isothermal aging at 375–425 °C

Keith E. Knipling a,b,*, David C. Dunand b, David N. Seidman b,c

a Naval Research Laboratory, Code 6356, 4555 Overlook Avenue, SW, Washington, DC 20375-5320, USA
b Department of Materials Science and Engineering, Northwestern University, 2220 Campus Dr., Evanston, IL 60208-3108, USA
c Northwestern University Center for Atom-Probe Tomography (NUCAPT), Northwestern University, 2220 Campus Dr., Evanston, IL 60208-3108, USA

Received 19 March 2007; received in revised form 7 September 2007; accepted 7 September 2007
Available online 29 October 2007

Abstract

Formation of Al₃Zr or Al₃(Zr₁₋ₓTiₓ) precipitates with a metastable L1₂ structure was investigated in conventionally solidified Al–0.1 Zr, Al–0.2 Zr, Al–0.1 Zr–0.1 Ti, and Al–0.2 Zr–0.2 Ti (at.%) alloys aged isothermally at 375, 400, or 425 °C. Pronounced hardening results from nanometer-scale, spheroidal Al₃Zr or Al₃(Zr₁₋ₓTiₓ) (L1₂) precipitates within solute-enriched dendrites. Interdendritic regions contain a significantly lower number density of coarser cauliflower-, rod- and plate-shaped precipitates with the L1₂ structure. Neither the magnitude of the peak-aged hardness, nor the subsequent loss in hardness due to overaging, is affected by ternary additions of Ti. After extended aging times (1600 h) at 425 °C, there is no difference in the mean precipitate radii of spheroidal Al₃Zr or Al₃(Zr₁₋ₓTiₓ) precipitates, confirming that Ti additions do not improve the coarsening resistance. Comparison with prior coarsening studies on Al₃Zr, and Al₃(Zr₁₋ₓVₓ), Al₃(Zr₁₋ₓTiₓ) and Al₃(Zr₁₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋xDC0₂₃2007 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Aluminum alloys; Zirconium; Titanium; Precipitation strengthening; Coarsening

1. Introduction

The Al–Zr system exhibits particular promise for developing thermally stable, precipitation-strengthened Al alloys [1,2]. In this system an ordered trialuminide, Al₃Zr, precipitates during aging from a supersaturated solid solution. While the equilibrium structure of Al₃Zr is tetragonal (D0₂₃), decomposition of supersaturated Al–Zr solid solutions occurs initially by the formation of metastable nano-meter-scale Al₃Zr precipitates with the cubic L1₂ structure (structurally and chemically analogous to the Ni₃Al (γ') phase in Ni-based superalloys [3,4]), which are thermally stable at high homologous temperatures [1].

Fine and co-workers [5–8] have suggested that even greater stability can be achieved by decreasing the lattice parameter mismatch between Al₃Zr and the α-Al solid solution, and showed that the lattice parameters of both the stable D0₂₃ and metastable L1₂ Al₃Zr precipitates are reduced by additions of Ti, Hf or V [7,9,10]. The Al–Zr–V system, in particular, has been extensively studied [7,11–13]. By substituting V for Zr, Al₃(Zr₁₋ₓVₓ) (L1₂) precipitates were shown to exhibit reduced coarsening compared with that of binary Al₃Zr precipitates [7,12,13]. The formation, however, of an additional Al₃V phase, particularly at grain boundaries, had an adverse effect on the mechanical properties [11,12].

Titanium also reduces the lattice parameter mismatch of Al₃Zr (L1₂) with α-Al [14] and, since Al₃Ti is the terminal intermetallic in the Al–Ti system [1], the problem of additional embrittling intermetallics is avoided. Furthermore, an investigation by Parameswaran et al. [15] showed that
an Al–0.20 Zr–0.17 Ti (at.%) alloy containing nominally 1 vol.% $\text{Al}_3\text{Zr}_{1-x}\text{Ti}_x$ precipitates exhibited significantly improved coarsening resistance at 425 °C compared to Al–Zr and Al–Zr–V alloys with similar precipitate volume fractions [7].

The present study reports on the effects of Ti additions to dilute Al–Zr alloys by examining their ambient-temperature mechanical properties, utilizing Vickers microhardness measurements, and correlating these results to their microstructures during isothermal aging at 375, 400 or 425 °C (0.69, 0.72 or 0.75 $T_m$, where $T_m$ is the absolute melting point of Al). The effect of Ti additions on the $\text{Al}_3\text{Zr}_{1-x}\text{Ti}_x$ (L1$_2$) coarsening rates at 425 °C is also assessed. In another study [16], we discuss the chemical compositions, measured by three-dimensional atom-probe tomography, of $\text{Al}_3\text{Zr}_{1-x}\text{Ti}_x$ (L1$_2$) precipitates in similar Al–0.1 Zr–0.1 Ti (at.%) alloys after aging at 375 or 425 °C. In a future publication [17], similar alloys will be studied at temperatures in excess of 450 °C, and microstructural coarsening and the L1$_2$ → D0$_{22}$ structural transformation of the $\text{Al}_3\text{Zr}$ or $\text{Al}_3\text{Zr}_{1-x}\text{Ti}_x$ precipitates will be discussed.

2. Experimental procedures

2.1. Alloy compositions and preparation

Two binary (Al–0.1 Zr and Al–0.2 Zr) and two ternary (Al–0.1 Zr–0.1 Ti and Al–0.2 Zr–0.2 Ti) alloys (all compositions are in at.% unless otherwise noted) were investigated; alloy designations, exact compositions and aging conditions are summarized in Table 1. Small (~7 g) buttons were prepared by melting 99.95 at.% Al (Atlantic Equipment Engineers, Bergenfield, NJ; containing 260 at. ppm Fe and 260 at. ppm Si as impurities) with an Al–25.0 Ti (bulk intermetallic) master alloy and a dilute Al–0.57 Zr master alloy, employing non-consumable electrode arc-melting in a gettered purified argon atmosphere. Arc-melting of the pure constituents (99.95% Al, Atlantic Equipment Engineers, Bergenfield, NJ; 99.99 + % Ti, Alfa Aesar, Ward Hill, MA) was used to obtain a stoichiometric single-phase Al$_3$Ti master alloy, the chemical homogeneity and structural uniformity of which was verified by X-ray diffraction. 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 at ATI Wah Chang (Albany, OR).

2.2. Aging treatments and analytical techniques

The initial distribution of solute in as-cast specimens was measured by energy-dispersive X-ray spectroscopy (EDS) using a JEOL JSM-7000F scanning electron microscope (SEM). As-cast specimens were isothermally aged at 375, 400 or 425 °C in air, within the range of temperatures shown to produce a strong precipitation strengthening response for Al–Zr alloys produced by rapid solidification [18–23] or chill-casting [24–26]. Precipitation of $\text{Al}_3\text{Zr}$ or $\text{Al}_3\text{Zr}_{1-x}\text{Ti}_x$ during aging was monitored by a number of techniques as now described.

Vickers microhardness measurements were performed at room temperature on metallographically polished sections using a load of 200 g and a dwell time of 5 s. Precipitation of $\text{Al}_3\text{Zr}$ or $\text{Al}_3\text{Zr}_{1-x}\text{Ti}_x$ was assessed directly by transmission electron microscopy (TEM). Foils for TEM were prepared by mechanical grinding sections of aged specimens to a thickness of ~100 μm. Discs of 3 mm diameter were punched from these sections and thinned to perforation by twin-jet electropolishing at 20 V DC (Struers Tenupol-5) using a 10 vol.% solution of perchloric acid in methanol at ~40 °C. Conventional TEM was performed with samples oriented along low-index <100>, <110>- or <111>-type directions, utilizing two-beam diffraction conditions. Centered dark-field images of the precipitates (L1$_2$ structure) were formed using superlattice reflections by tilting the incident illumination by an angle equal to the diffraction angle. Precipitate radii were determined by image analyses of digitized TEM micrographs, which were scanned at a resolution (typically 600–1200 dpi) two orders of magnitude greater than the characteristic size of the precipitates in the image. Individual precipitates within the images were manually traced using commercial software (Adobe Photoshop CS), and the dimensions of the traced areas were determined using the public domain NIH Image program by determining the diameter of an area-equivalent circle, which yields an effective precipitate radius.

Electropolished TEM foils were also examined using a LEO 1525 high-resolution field-emission gun SEM

---

Table 1: Compositions and aging conditions of the Al–Zr and Al–Zr–Ti alloys investigated

<table>
<thead>
<tr>
<th>Nominal compositions (at.%)</th>
<th>Verified compositions (at.%)</th>
<th>Aging temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>Ti</td>
<td>Zr</td>
</tr>
<tr>
<td>Al–0.1 Zr(a)</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>Al–0.1 Zr(b)</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>Al–0.2 Zr</td>
<td>0.2</td>
<td>–</td>
</tr>
<tr>
<td>Al–0.1 Zr–0.1 Ti(a)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Al–0.1 Zr–0.1 Ti(b)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Al–0.2 Zr–0.2 Ti</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
operated at 3 kV with a short working distance (3 mm) employing a secondary electron in-lens detector. As discussed below, the alloys are highly segregated on the micrometer scale, which is too large to be easily discerned with TEM. The advantage of SEM as complement to TEM is the much larger field of view because of the larger range in magnification and also because observations of specimens in the SEM are not subject to the limitation that the foil be electron-transparent. The resolution of the SEM employed, \( \sim 1 \) nm, is also capable of resolving nanometer-scale \( \text{Al}_3\text{Zr} \) or \( \text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x) \) precipitates.

3. Experimental results

3.1. As-cast microstructure

Fig. 1 shows the as-cast macrostructure of the alloys studied. The solidification macrostructure is typical of cast alloys, with coarse columnar grains, originating at the bottom surface of the ingot (which was in contact with the chilled copper crucible of the arc-melter), growing upward toward a zone of equiaxed grains near the center of the ingot. The relative sizes of the columnar and equiaxed zones are strongly dependent on the solute content of the alloy and, more precisely, the extent of properitectic \( \text{Al}_3\text{M} \) (\( \text{M} = \text{Zr} \) or \( \text{Zr}, \text{Ti} \)) precipitation, since these primary phases are potent grain refiners, as discussed below.

\( \text{Al–0.1Zr(b)} \) is the most dilute alloy of the series we studied (Table 1), and the extent of the columnar zone, which comprises the entire ingot cross-section in this alloy, is also greatest. The grains in the columnar zone are large, 0.2–1.0 mm wide and \( \sim 5 \) mm long. The effect upon grain size of doubling the solute concentration with an addition of 0.1 at.\% Ti is demonstrated for \( \text{Al–0.1 Zr–0.1 Ti(b)} \). For this alloy, the upper half of the ingot exhibits a zone of coarse equiaxed grains, 0.5–1.0 mm in width. Alloy \( \text{Al–0.2 Zr} \) exhibits a finer structure, where the grains in the columnar zone are typically 0.2 mm wide and the extent of this zone is also reduced. Consequently, the majority of the ingot is equiaxed, with smaller grain sizes (0.15–0.30 mm wide) than for \( \text{Al–0.1 Zr(b)} \). Finally, \( \text{Al–0.2 Zr–0.2 Ti} \), the most concentrated alloy studied (Table 1), exhibits the smallest grain size: the entire ingot cross-section is equiaxed with very small grains, \( \sim 0.1 \) mm wide.

Figs. 2 and 3 display SEM micrographs of metallographically polished \( \text{Al–0.2 Zr} \) and \( \text{Al–0.2 Zr–0.2 Ti} \) alloys, respectively. Both alloys exhibit petal-like precipitates of the properitectic phase (\( \text{Al}_3\text{Zr} \) or \( \text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x) \)), responsible for the grain refinement observed in Fig. 1. The primary precipitates in the ternary alloy (Fig. 3) are slightly Ti-rich with a Ti:Zr ratio of approximately 1.5, as confirmed by quantitative energy-dispersive spectrometry (EDS) [27]. The petal-like morphology is characteristic of the metastable \( \text{L}_{12} \) structure [28], whose cubic structure is commensurate with \( \alpha\text{-Al} \) (face-centered cubic) and acts as an effective heterogeneous nucleant of \( \alpha\text{-Al} \) during solidification. The presence of these primary properitectic precipitates indicates also that, for the conventional casting conditions we used, exceeding \( \sim 0.2 \) at.\% solute (Ti or Zr) results in primary precipitation of the properitectic trialuminide and hence decreases the amount of solute retained in solid solution. No primary precipitates are observed by SEM in the more dilute \( \text{Al–0.1 Zr} \) and \( \text{Al–0.1 Zr–0.1 Ti} \) alloys, consistent with the coarser grain structure observed (Fig. 1).

3.2. Solute segregation and the precipitated microstructure

In addition to the primary properitectic precipitates described, Figs. 2 and 3 also reveal solute-enriched dendrites in the as-solidified alloys. The dendritic regions exhibit lighter contrast (\( Z \)-contrast from backscattered electrons), reflecting the microsegregation of Zr and Ti solute atoms following solidification. Both solute species, when alloyed with Al, raise the melting point of the alloy

![Fig. 1. Macrostructure of the as-cast alloys Al–0.1Zr(b), Al–0.1 Zr–0.1 Ti(b), Al–0.2 Zr and Al–0.2 Zr–0.2 Ti (etched using Poultan’s reagent), showing various degrees of grain refinement.](image-url)
relative to that of pure Al. Consequently, the liquidus and solidus curves of the $\alpha$-Al solid solution have positive slopes and $k_0$, the equilibrium partition coefficient for solidification, is greater than unity for both systems. The first solid to form during solidification is therefore richer in Zr and Ti compared to the bulk alloy composition, resulting in solute-rich dendritic cells surrounded by solute-depleted interdendritic channels.

Measured composition profiles spanning three dendritic cells are displayed in Fig. 4 for alloys Al–0.1 Zr–0.1 Ti(b) and Al–0.2 Zr–0.2 Ti. The two composition profiles in Fig. 4 are similar in that the dendrite centers are enriched approximately twofold in Zr and threefold in Ti compared to their respective bulk compositions (Table 1). The interdendritic regions are concomitantly solute-depleted. The mean concentrations of Zr and Ti in Fig. 4a are 0.10 at.% Zr and 0.14 at.% Ti, respectively; in Fig. 4b these values are 0.28 at.% Zr and 0.40 at.% Ti, respectively. It is noteworthy that both composition profiles exhibit a bias in the measured Ti:Zr ratio of approximately 1.4. This apparent enrichment of Ti in the locally sampled region of the alloy (~10 $\mu$m) could represent macrosegregation of solutes. The fact that both composition profiles exhibit a similar bias, however, suggests that the apparent enrichment of Ti is an artifact of the EDS technique. The data in Fig. 4 were not calibrated with respect to known standards, and are therefore semi-quantitative. Nevertheless, the mean alloy composition measured by EDS is comparable to the bulk alloy composition (this is especially true for Zr), indicating that the EDS results are reasonably accurate.

During post-solidification aging, nanometer-scale Al$_3$Zr (L1$_2$) or Al$_3$Z($Zr_{1-x}Ti_x$) (L1$_2$) precipitates form, distributed non-uniformly throughout the alloy, reflecting the dendritic microsegregation of Zr and Ti solute atoms in the as-cast alloys. Fig. 5 shows the precipitated microstructure of the alloys, obtained after aging alloy Al–0.1 Zr–0.1 Ti(a) at 375 °C for 1600 h.

3.3. Age hardening

Fig. 6 displays plots of the Vickers microhardness of the Al–Zr and Al–Zr–Ti alloys as a function of aging time at
375, 400 or 425 °C. Each data point represents a minimum of 20 measurements, with the standard deviation of these measurements indicated by error bars. The position of the measurement within the ingot (i.e. ingot top, center, bottom) was also recorded since the cooling rate of the melt – and therefore the amount of solute retained in solid solution – varies with proximity to the chilled copper crucible. A positional-dependence on hardness was observed only in Al–0.2 Zr–0.2 Ti (Fig. 6 d), where the ingot’s bottom is consistently 70 MPa harder than the remainder of the alloy. This increased hardness is most likely a result of suppressed properitectic precipitation of Al\(_3\)(Zr\(_{1-x}\)Ti\(_x\)) near the ingot’s bottom, as shown in Fig. 3. To minimize measuring the effect of solute loss to this primary properitectic phase, only hardness data measured near the bottom surface of alloy Al–0.2 Zr–0.2 Ti are reported in Fig. 6d.

Comparing Fig. 6a,c and Fig. 6b,d, there is, in most cases, no significant hardness difference between the Al–Zr and Al–Zr–Ti alloys for a given Zr concentration (0.1 or 0.2 at.%) and aging temperature (375, 400 or 425 °C). For all alloys investigated, the peak hardness decreases with increasing aging temperature, attributable to the reduction in volume fraction of the dispersed phase due to the temperature dependence of solute solid solubility. There is a particularly pronounced drop in plateau hardness between aging at 400 and 425 °C in the alloys containing 0.1 at.% Zr (Fig. 6a and b), suggesting a significant decrease in the volume fraction of the Al\(_3\)Zr or
Al3(Zr1-xTi)x L12 precipitates. The reduction in hardness at 425 °C is, however, significantly less for Al–0.1 Zr–0.1 Ti(b), suggesting that Ti additions increase the volume fraction of L12 precipitates. We show, utilizing three-dimensional atom-probe tomography on similar alloys [16], that Ti partitions weakly to the Al3(Zr1-xTi)x (L12) precipitates, with a Zr:Ti ratio of at least 5 (x = 0.17) at 425 °C. Thus, the increased volume fraction of precipitates due to Ti additions is only slight. Moreover, partitioning of Ti to Al3(Zr1-xTi)x (L12) is also confirmed at 375 °C [16], yet there is no significant difference in peak hardness between Al–0.1 Zr and Al–0.1 Zr–0.1 Ti at 375 °C (Fig. 6). As will be discussed in more detail in a subsequent article [17], Ti additions increase the effective supersaturation of Zr, thereby increasing the volume fraction of the precipitate-rich dendrites.

Differences in age-hardening behavior are even less distinct between Al–0.2 Zr and Al–0.2 Zr–0.2 Ti (Fig. 6c and d). These alloys, however, contain primary proeutectic Al3Zr or Al3(Zr1-xTi)x precipitates (Figs. 2 and 3), which are especially numerous in Al–0.2 Zr–0.2 Ti. The solute retained in a-Al solid solution is therefore less than the bulk concentrations indicated in Table 1, and the overall volume fraction of precipitates formed during post-solidification aging is similarly unknown. The larger hardness value as compared to Al–0.1 Zr and Al–0.1 Zr–0.1 Ti indicates, however, that the solute concentration is higher.

In addition to the noticeable increase in peak strength at 425 °C, Ti additions appear also to accelerate the onset of precipitation hardening in the more dilute alloys containing 0.1 at.% Zr (Fig. 6a and b). According to classical nucleation theory [29–33], the incubation time for nucleation is inversely proportional to the square of the chemical driving force, which is proportional to the logarithm of the supersaturation ratio. The increased hardness at higher temperatures and the accelerated incubation time for nucleation in
Al–0.1 Zr–0.1 Ti(b) compared to Al–0.1 Zr(b) are also indicative of a larger supersaturation of solute from Ti additions [17].

The incubation time varies also with aging temperature. For Al–0.2 Zr and Al–0.2 Zr–0.2 Ti (Fig. 6c and d), the incubation time decreases with increasing aging temperature. The opposite effect is observed for Al–0.1 Zr–0.1 Ti(b) (Fig. 6b), where the onset of hardening at 375 °C is noticeably accelerated as compared with 400 or 425 °C. Finally, for alloy Al–0.1Zr(b) (Fig. 6a), there is little effect of aging temperature on the incubation time. The hardness values for short aging times ($t < 6.5$ h) in Fig. 6 were obtained for rather small (2–5 mm wide) specimens from various positions in the ingot cross-section, unlike measurements for longer aging times performed across the entire ingot. The inconsistent variations in incubation time may therefore reflect slight variations in solute concentration due to different solidification rates with respect to location in the ingot.

3.4. Precipitate morphologies

The SEM and TEM micrographs in Fig. 5 suggest that small, spheroidal, coherent Al$_3$Zr (L1$_2$) or Al$_3$(Zr$_{1-x}$Ti$_x$) (L1$_2$) precipitates are confined to the dendritic cells, which are surrounded by precipitate-free interdendritic channels. Due to the complicated solute concentration gradients associated with the dendrites, a gradient of precipitate size exists. Fig. 7 displays the precipitated microstructure in an interdendritic channel between two precipitate-rich dendrite arms, produced in Al–0.2 Zr–0.2 Ti after aging at 400 °C for 100 h (corresponding to peak hardness, Fig. 6d). The precipitate size is expected to decrease with increasing solute content (for a given aging temperature) since the chemical driving force for nucleation increases with supersaturation. This leads to a smaller critical radius for nucleation and hence smaller precipitates. Within the center of the dendrites, where the solute supersaturation is largest (Fig. 4), precipitates are small and homogeneously distributed at high number densities. The supersaturation decays with lateral position from the center of the dendritic cells and, correspondingly, the precipitates become progressively larger, which is a direct reflection of the supersaturation. The interdendritic regions contain insufficient solute to effect homogeneous nucleation, so these regions are largely precipitate-free. The precipitates that form in these regions do so heterogeneously (Fig. 7), as evidenced by their arrangement in linear arrays. These precipitates are most likely formed on dislocations since the strain energy barrier for precipitation by this mechanism is significantly reduced [34,35].

3.4.1. Cauliflower-shaped interdendritic precipitates

Fig. 8 displays SEM (panels a–c) and TEM (panels d–f) micrographs of larger interdendritic L1$_2$-structured Al$_3$Zr or Al$_3$(Zr$_{1-x}$Ti$_x$) precipitates. In the interdendritic regions, where the spheroidal L1$_2$ precipitates are largest and their volume fraction is smallest, cauliflower-like morphologies are observed. These arise from instabilities during the growth of the Al$_3$Zr or Al$_3$(Zr$_{1-x}$Ti$_x$) precipitates, as also observed for Al$_3$Sc (L1$_2$) [36–38] and Al$_3$Li (L1$_2$) [39] precipitates when they nucleate and grow under small supersaturations. In the present alloys, fewer precipitates nucleate in the interdendritic regions, and those that do have a larger initial size as discussed. Moreover, because of their small number density, the interdendritic precipi-

---

**Fig. 7.** Centered superlattice dark-field TEM micrograph of an interdendritic channel between two dendrite arms in alloy Al–0.2 Zr–0.2 Ti aged at 425 °C for 100 h. The foil edge is on the right-hand side of the micrograph, with increasing specimen thickness towards the left-hand side. Within the dendrites, the Al$_3$(Zr$_{1-x}$Ti$_x$) (L1$_2$) precipitates are small and homogeneously distributed. Because the foil is thicker in these regions (due to differential thinning), the small ($R < 10$ nm) precipitates are clearly resolved only near the foil edge.
tates can grow in a supersaturated matrix before their diffusion fields begin to overlap, further increasing the size difference between the precipitates in the dendritic and interdendritic regions at later aging times. The precipitate morphology thus evolves temporally by growth rather than by coarsening. Robson [40] has quantified this phenomenon in modeling precipitation of Al–Zr alloys with and without ternary additions of Sc.

The gradients in precipitate size occurring in the interdendritic channels provide an opportunity to assess the change in coherency of the Al3Zr (L12) or Al3(Zr1−x,Ti)x precipitates. Fig. 8f displays a bright-field TEM micrograph of interdendritic Al3Zr (L12) precipitates recorded under two-beam conditions. Under these imaging conditions, coherent phases exhibit characteristic Ashby-Brown [41] strain contrast, as shown for the precipitates in the upper portion of Fig. 8f, exhibiting distinct lines of no-contrast normal to the diffraction vector, \( \mathbf{g} \). For slightly larger interdendritic precipitates, coherency strain contrast is lost and striped lines of contrast normal to \( \mathbf{g} \) appear in the images of the precipitates. These striped lines are interpreted as a contrast effect due to interfacial dislocations, thus signaling the transition to semicoherency of the Al3Zr or Al3(Zr1−x,Ti)x precipitates. Iwamura and Miura [42] report similar transitions in strain contrast during coherency loss of Al3Sc (L12) precipitates. For the Al3Zr (L12) precipitates displayed in Fig. 8f, the transition from coherency to semicoherency occurs at about a radius of 35 nm. Fig. 8e indicates that this is also the approximate radius at which surface perturbations leading to cauliflower shapes are first

---

**Fig. 8.** SEM and TEM micrographs displaying gradients in interdendritic precipitate radii and the development of growth instabilities. (a–c) SEM micrographs of Al3Zr (L12) precipitates in Al–0.2 Zr aged at 425 °C for 400 h; (d,e) centered superlattice dark-field TEM micrographs of Al3(Zr1−x,Ti)x (L12) precipitates in Al–0.1 Zr–0.1 Ti(b) aged at 425 °C for 400 h; (f) bright-field TEM micrograph showing loss of coherency of Al3Zr (L12) precipitates in Al–0.1 Zr(b) aged at 425 °C for 400 h.
observed. The loss of coherency may therefore also contribute to the observed growth instabilities in the interdendritic L₁₂ precipitates.

3.4.2. Rod-like and plate-like interdendritic L₁₂ precipitates

A second precipitate morphology observed in the interdendritic channels is that of orthogonal rods and plates oriented along <100>-type matrix directions and having the metastable L₁₂ structure (Fig. 9). Both rod-shaped and plate-shaped morphologies are observed, as confirmed by TEM tilting experiments. A characteristic feature of the rod-shaped variant is their appearance as rod pairs that are closely spaced (∼10 nm apart) (Fig. 9b). These rod pairs are identical to those described by Nes [43] in a dilute hypoperitectic Al–0.05 Zr alloy aged at 460 °C. In the present alloys, these rod-shaped precipitates are predominantly in the interdendritic regions, where the solute concentration is smallest, indicating that small supersaturations favor their formation. Ryum [44] similarly observed orthogonal rod-shaped precipitates and plates during the decomposition of Al–0.027 Hf alloys after aging at 450 °C for 50 h.

Fig. 9c displays a bright-field TEM micrograph showing several interdendritic rod-shaped Al₃Zr precipitates observed along the [1 1 1] zone axis. Near to the rods are ∼500 nm long linear arrays of spheroidal L₁₂-structured precipitates, which are approximately parallel to the rods. Nes [43] observed similar Al₃Zr “rods partly chopped up into rows of spherical particles,” which he regarded as a continuous rod appearing divided due to variations in contrast caused by interfacial dislocations when viewed in dark-field. Bright-field (Fig. 9c) and dark-field (Fig. 9d) TEM micrographs indicate clearly, however, that these arrays are composed of discrete spheroidal precipitates. Nichols and Mullins [45] showed that a cylindrical rod is unstable with respect to individual spheres, and therefore the arrays of spheroidal L₁₂-structured precipitates may be descended from the rod-shaped morphology.
3.4.3. Small dendritic precipitates

The most prevalent precipitate morphology in terms of number density, and certainly the most important with respect to the observed mechanical properties, belongs to the small, coherent, homogeneously distributed spheroidal Al₃Zr (L₁₂) or Al₃(Zr₁₋ₓTiₓ) (L₁₂) precipitates found in the precipitate-rich dendritic cells (e.g. Fig. 5). The similarity in dendritic precipitate sizes between the Al–Zr and Al–Zr–Ti alloys after extended aging times is also reflected in the comparable hardnesses of the Al–Zr and Al–Zr–Ti alloys in Fig. 6. At 400 °C and below, the alloys exhibit identical precipitation hardening behavior after extended aging times. The Al–Zr–Ti alloys, however, tend to be harder at shorter aging times or at temperatures greater than 400 °C. This effect may be interpreted in terms of solute supersaturation influencing the incubation time for nucleation and the volume fraction of precipitate-rich dendritic regions, and is not an effect of precipitate radius or coarsening resistance [17].

The data in Table 2 illustrate a second point. The two mean precipitate radii reported for Al–0.2 Zr and Al–0.2 Zr–0.2 Ti were measured on two different TEM specimens for each alloy, i.e. in two dendrites widely separated from each other. The consistency in the observed mean radii suggests that the solute supersaturation (and hence the critical radius for nucleation as well as the local volume fraction) is nearly constant from one dendrite to the next, despite the enormous variations in precipitate sizes, growth kinetics and morphology (e.g. Figs. 7–9) observed outside the dendrites. This conclusion is also supported by the measured EDS line scans (Fig. 4), which indicates that the solute concentration is nearly identical for three adjacent dendritic regions.

### 3.5. Transformation to the equilibrium D0₂₃ structure

Despite extended aging times (1600 h) at 425 °C (0.75 Tₘ), precipitates with the equilibrium D0₂₃ structure are not observed by TEM, indicating that metastable Al₃Zr (L₁₂) precipitates are kinetically stable to high homologous temperatures. This is in agreement with reports of coarsening and transformation to the D0₂₃ structure commencing...
at ~500 °C (0.83 $T_m$) [17,46,47], which is much higher than the temperatures we investigated. However, some spheroidal metastable L1$_2$ precipitates exhibit structural faults, characterized by sharp lines of no-contrast parallel to {100}-type planes inside the precipitates (Fig. 11), which have been observed in other studies [7,13,48,49] in Al$_3$Zr-based precipitates. The faults are attributed to antiphase boundaries (APBs) generated in the transition to an imperfect tetragonal (D0$_{23}$) structure by the formation of an APB with a displacement vector of type $a/2<110>$ on {100}-type planes, and hence represent the early stages of the transformation to the D0$_{23}$ structure. We discuss this L1$_2$ to D0$_{23}$ transformation in more detail elsewhere [17].

4. Discussion

4.1. Loss of coherency in Al$_3$Zr and Al$_3$(Zr$_{1-x}$Ti$_x$) precipitates

Coherency across a precipitate-matrix heterophase interface is generally lost when the precipitate size exceeds a critical value, which typically corresponds to [33]:

$$n = \frac{1}{\delta},$$

where $n$ is the number of atomic planes in the matrix and $\delta$ is the lattice parameter mismatch between the two phases. For Al$_3$Zr (L1$_2$) precipitates observed in Al–0.1 Zr(b) aged at 425 °C for 1600 h, the transition from coherency to semi-coherency occurs at ~35 nm radius (Fig. 8f). This radius at which coherency is lost is larger than that for Al$_3$Sc precipitates, which retain coherency to ~20 nm radius [37,42,50,51]. This disparity may be understood by considering the lattice parameters of the L1$_2$ Al$_3$Zr and Al$_3$Sc phases, which are 0.408 nm [43,52,53] and 0.4103 nm [54], respectively, at room temperature. Given the lattice parameter of 0.40496 nm for Al [1], a coherent Al$_3$Zr (L1$_2$) precipitate has a smaller mismatch ($\delta = +0.75\%$) than that of an Al$_3$Sc (L1$_2$) precipitate ($\delta = +1.33\%$) and, by Eq. (1), should therefore retain coherency to larger radii. Marquis and Seidman [37] argued that for an Al$_3$Sc/z-Al heterophase interface, Eq. (1) predicts $n = 80$ planes, which, considering a 0.2 nm spacing between {200} planes, corresponds to a distance of 16 nm, in good agreement with the observed coherency loss for Al$_3$Sc precipitates of 20 nm radii. Using similar arguments, a metastable L1$_2$ Al$_3$Zr precipitate is expected to remain coherent to $n = 130$ planes, corresponding to a radius of 26 nm. This is in reasonable agreement with the precipitates exhibiting coherency loss for a radius of 35 nm in Fig. 8f. As discussed previously [50,51,55], the thermal expansion is greater for the Al matrix than the Al$_3$Sc (L1$_2$) precipitate phases, so coherency is expected to be maintained for larger precipitate radii at elevated temperatures.

4.2. Comparison to prior studies on Al–Zr–V/Ti alloys

As described in Section 1, improving the coarsening resistance of Al$_3$Zr with ternary or quaternary additions of V and/or Ti has generated considerable interest in the scientific literature. These studies are summarized in Fig. 12, which indicates the alloy compositions, nominal volume fractions of L1$_2$-structured Al$_3$(Zr$_{1-x}$M$_x$) (M = V and/or Ti) precipitates, and their measured precipitate
radii as a function of aging time at 425 °C. The present results on Al–Zr and Al–Zr–Ti alloys are also provided in Fig. 12. Because of the nonuniform distribution of precipitates occurring on the micrometer scale (Fig. 5c), there is no practical way to determine the precipitate volume fraction using traditional two-dimensional TEM microscopy. The values indicated in Fig. 12 for the present Al–Zr and Al–Zr–Ti alloys are therefore approximate estimates based on the lever rule, assuming that the precipitate volume fraction is dictated primarily by the Zr concentration. For an alloy containing nominally 0.1 at.% Zr, the volume fraction of Al3Zr is 0.4 vol.%, which assumes a negligible solubility of Zr at the aging temperature. Titanium has a slight effect on volume fraction, as evidenced by the hardness data in Fig. 6 in which peak-hardness is controlled primarily by the Zr content. We have also shown, using three-dimensional atom-probe tomography on similar Al–0.1 Zr–0.1 Ti alloys [16], that Ti atoms remain mainly in solid solution rather than partitioning to the Al3(Zr1–xTi)x precipitates. For this reason, Ti is assumed not to influence the volume fraction significantly. For the solute-riche alloys containing 0.2 at.% Zr, the situation is complicated further since these contain primary proeutectic Al3Zr or Al3(Zr1–xTi)x precipitates (Figs. 2 and 3), and hence the volume fraction of precipitates formed during subsequent aging is reduced from what the total solute concentration would predict.

4.2.1. Anomalous behavior in arc-melted alloys

An immediately apparent observation in Fig. 12 is that the initial studies on arc-melted Al–Zr, Al–Zr–V and Al–Zr–Ti alloys [7,15,56] containing nominally 1 vol.% of precipitates tend to exhibit larger precipitates with faster coarsening rates than the subsequent studies on melt-spun alloys [12,13,48,49,57–59] containing 5–10 vol.% of precipitates, as noted by several researchers [12,49,57,59]. The effect of a finite volume fraction of precipitates on coarsening rate, well-studied theoretically and experimentally [60–62], is an increasing coarsening rate with increasing volume fraction. The apparent violation of this rule further encouraged the belief that ternary additions of V and/or Ti had dramatically improved the coarsening resistance of Al3Zr, in spite of the higher volume fractions in the melt-spin studies. Lee and colleagues [49,57,59] attributed the discrepancies in coarsening behavior between the initial studies on arc-melted alloys [7,56] and those that followed to differences in the heat-treatment prior to aging, which decreased the supersaturation and thus the growth kinetics of the precipitates.

Another, more probable, explanation for the discrepancies in Fig. 12 is that the initial measurements of precipitate radii in Al–Zr and Al–Zr–V alloys [7,56] are affected by an inhomogeneous dendritic distribution of precipitates in the arc-melted alloys, a possibility that is acknowledged in Ref. [7]. As discussed in Fig. 8 (Section 3.4.1), the interdendritic precipitates can grow for longer times before their diffusion fields start overlapping, which means that the precipitate radii evolve in a growth regime rather than a coarsening one. Since the former is necessarily faster than the latter, this would explain the anomalously fast coarsening rates observed in Ref. [7]. Furthermore, the larger interdendritic Al3Zr (L12) or Al3(Zr1–xTi1–y) (L12) precipitates are typically nucleated heterogeneously on dislocations (Fig. 7), and rapid pipe diffusion between precipitates may also account for their faster growth as compared to the smaller dendritic precipitates coarsening by slower volume diffusion.

The extension of solid solubility by rapid solidification processes like melt spinning lead to smaller precipitate radii because of the larger achievable supersaturation of solutes, thus explaining the smaller precipitate radii produced in the melt-spun alloys as compared with those that are arc-melted (Fig. 12). A second effect of rapid solidification is the stabilization of plane-front solidification, thus minimizing or eliminating microsegregation [63–65]. Observations of the precipitates that form in the melt-spin alloy specimens are therefore not subject to biases related to inhomogeneities in radii and morphology associated with dendritically distributed precipitates in arc-melted alloys. The apparently improved coarsening resistance, despite the higher volume fraction of precipitates in the melt-spin alloys, is also not surprising, since Al3Zr precipitates (with or without ternary alloying additions) are intrinsically coarsening resistant at 425 °C. Furthermore, as discussed in Section 3.4.1, the high volume fraction of dendritic precipitates in the present alloys are apparently more coarsening resistant than the small volume fraction interdendritic ones because of their different nucleation and growth mechanisms.

4.2.2. Summary

The anomalously fast coarsening and anomalously large precipitates observed in the initial arc-melted studies [7,56] can be readily explained within the context of a dendritic distribution of precipitates. As illustrated in Fig. 7, the most apparent population is the spheroidal, ~20 nm radius, Al3Zr (L12) precipitates observed in the interdendritic regions of a specimen, where the foil is thinnest. The most numerous population is the ~5 nm radius precipitates within the dendrites, which are not as easily observable in most TEM foils because of their smaller radii and the significantly reduced absorption contrast (incoherent scattering) occurring in the thicker dendritic regions. The reported precipitate radii [7,56], <R> = 15–20 nm (Fig. 12), suggest that the precipitates studied are interdendritic. Moreover, as discussed in a forthcoming article [17], even after aging at a much higher temperature of 575 °C (0.91 Tm), spheroidal Al3Zr (L12) or Al3(Zr1–xTi1–y) (L12) precipitates with radii below 17 nm are present. Discounting the anomalous results from the prior studies on arc-melted alloys [7,56], the different results on Al3(Zr1–xV1–y) (L12), Al3(Zr1–xTi1–y) (L12) and Al3(Zr1–yVxTiy) (L12) precipitates in Fig. 12 have radii <R> = 3–7 nm after 400 h at 425 °C, which are comparable to the radii of the
5. Conclusions

Precipitation of Al3Zr (L12) and Al3(Zr1–x, Ti1–x) (L12) has been investigated in conventionally solidified Al–0.1 Zr, Al–0.2 Zr, Al–0.1 Zr–0.1 Ti and Al–0.2 Zr–0.2 Ti (at.%) alloys isothermally aged at 375, 400 or 425 °C. The following results have been obtained and discussed:

- For the conventional casting conditions investigated here, exceeding ~0.2 at.% solute (Ti or Zr) results in primary precipitation of the properctic trauliminide and hence decreases the amount of solute retained in solid solution. Primary precipitation of the properctic phase results in a progressive refinement of the as-cast grain structure (Fig. 1).

- Dendritic solidification results in nonuniform distributions of Zr and Ti, which segregate to the dendrite centers where they are enriched by a factor of 2 and 3, respectively, with respect to their bulk concentration values (Fig. 4). The interdendritic regions are concomitantly solute-depleted. During subsequent aging, Al3Zr and Al3(Zr1–x, Ti1–x) precipitates are similarly non-uniformly distributed in a dendritic manner (Fig. 5).

- Pronounced hardening accompanies precipitation of Al3Zr or Al3(Zr1–x, Ti1–x) at 375, 400 or 425 °C for all alloys investigated (Fig. 6). For short aging times (t < 10 h), Ti accelerates somewhat the nucleation kinetics, probably due to an increased solute supersaturation. The magnitude of the peak-aged hardness is, however, not affected by the presence of Ti (except for Al–0.1 Zr–0.1 Ti at 425 °C). The alloys overage sluggishly, even after 3200 h at 425 °C, with no benefit from Ti additions in delaying overaging.

- The precipitated microstructures in the alloys are complicated by the initial segregation of solute species and because of the significant local variations in solute concentration, different precipitate morphologies are observed. These include: (i) larger interdendritic precipitates, frequently exhibiting growth instabilities (Fig. 8); (ii) interdendritic rods and plates aligned along <10 0> type matrix directions (Fig. 9); and (iii) small (<10 nm) spheroidal L12 precipitates within the dendritic cells (Fig. 10). Even after aging at 425 °C (0.75 Tm) for 1600 h, the equilibrium D023 structure (Al3Zr or Al3(Zr1–x, Ti1–x)) is not observed.

- The original motivation for adding Ti to Al–Zr alloys was to form Al3(Zr1–x, Ti1–x) precipitates, which exhibit a reduced lattice parameter mismatch with respect to α-Al, thereby improving the coarsening resistance of the Ti-containing precipitates. Despite the confirmed partitioning of Ti to the Al3(Zr1–x, Ti1–x) precipitates in a related study by three-dimensional atom-probe tomography [16], there is no benefit in terms of coarsening resistance of the small dendritic Al3(Zr1–x, Ti1–x) (L12), as compared with Al3Zr (L12) precipitates during extended isothermal aging at 425 °C (Table 2), consistent also with the similar overaging behavior observed by Vickers microhardness (Fig. 6). The lack of coarsening resistance improvement also applies when analyzing the literature data on Al3(Zr1–x, Vx), Al3(Zr1–x, Ti1–x) and Al3(Zr1–x, Vx, Ti1–x) (L12) precipitates formed at 425 °C in rapidly solidified alloys.

Acknowledgments

This research was supported by the US Department of Energy, Basic Sciences Division, under contract DE-FG02-02ER45997. The EDS composition profile (Fig. 4) was obtained in the Center for Microanalysis of Materials, University of Illinois at Urbana-Champaign (UIUC), which is partially supported by the US Department of Energy under grant DE-FG02-91ER45439. We thank Dr J. Mabon (UIUC) for his assistance. We also thank Ms C.P. Lee and Mr J.D. Marvin (Northwestern University undergraduate students) for assistance with the microhardness measurements. We are pleased to acknowledge Professors M. Asta and D. Isheim (Northwestern University) for useful discussions.

References
