Atom Probe Tomographic Studies of Precipitation in Al-0.1Zr-0.1Ti (at.%) Alloys

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Abstract: Atom probe tomography was utilized to measure directly the chemical compositions of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates with a metastable L_{12} structure formed in Al-0.1Zr-0.1Ti (at.%) alloys upon aging at 375°C or 425°C. The alloys exhibit an inhomogeneous distribution of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates, as a result of a nonuniform dendritic distribution of solute atoms after casting. At these aging temperatures, the Zr:Ti atomic ratio in the precipitates is about 10 and 5, respectively, indicating that Ti remains mainly in solid solution rather than partitioning to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates. This is interpreted as being due to the very small diffusivity of Ti in α -Al, consistent with prior studies on Al-Sc-Ti and Al-Sc-Zr alloys, where the slower diffusing Zr and Ti atoms make up a small fraction of the $\text{Al}_3(\text{Sc}_{1-x}\text{Ti}_x/\text{Zr}_x)$ precipitates. Unlike those alloys, however, the present Al-Zr-Ti alloys exhibit no interfacial segregation of Ti at the matrix/precipitate heterophase interface, a result that may be affected by a significant disparity in the evaporation fields of the α -Al matrix and $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates and/or a lack of local thermodynamic equilibrium at the interface.

Key words: atom probe tomography, Al_3Zr precipitates, local magnification, Al-Zr-Ti

INTRODUCTION

The Al-Zr system exhibits particular promise for developing creep-resistant, thermally stable Al-based alloys (Knipling et al., 2006). It is well established that decomposition of supersaturated Al-Zr solid solutions occurs initially by the formation of nanometer-scale Al_3Zr precipitates with a metastable cubic L_{12} structure, which transform to the equilibrium D_{023} phase after prolonged aging at elevated temperatures ($>450^\circ\text{C}$). The high stability of the L_{12} metastable phase is attributed to slow diffusion kinetics and a small lattice parameter mismatch with α -Al (Knipling et al., 2006).

Fine and coworkers showed that this lattice parameter mismatch is reduced by additions of Ti, V, or Hf (Tsunekawa & Fine, 1982; Zedalis & Fine, 1983, 1986), resulting in improved coarsening resistance of L_{12} $\text{Al}_3(\text{Zr}_{1-x}\text{V}_x)$ (Zedalis & Fine, 1986; Chen et al., 1987, 1990; Lewis et al., 1987) and $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (Parameswaran et al., 1989) precipitates, which they ascribed to a reduced matrix/precipitate interfacial free energy. These findings motivated subsequent studies on Al-Zr-V (Park & Kim, 1988; Han et al., 1995), Al-Zr-Ti (Chuang & Tu, 1994; Malek et al., 1994, 1999, 2000a, 2000b, 2000c, 2002; Sato et al., 1996; Tsau & Chen, 2002), and

Al-Zr-Ti-V (Lee et al., 1993; Chung et al., 1995; Han et al., 1995) alloys, in which the precipitated ternary and quaternary trialuminides were reported to offer improved coarsening resistance and thermal stability compared to binary Al_3Zr precipitates (Zedalis & Fine, 1986). This improved stability was attributed to a reduced lattice parameter mismatch, but in none of these studies (with the exception of Sato et al., 1996) was the composition of the precipitates (and hence the lattice parameter mismatch) measured directly.

Three-dimensional atom probe tomography (3-D APT) (Blavette et al., 1993; Miller et al., 1996; Hono, 1999; Miller, 2000a) is based on the field evaporation of surface atoms, as ions in different charge states that are identified chemically by time-of-flight mass spectrometry and whose positions are deduced from the coordinates of ion impacts on a 2-D position-sensitive detector. Small, nanometer-scale concentration fluctuations are examined on the sub-nanometer-scale in direct space, without data deconvolution and without comparison to standards. In this respect, 3-D APT is uniquely suited to examine directly the effects of microalloying in nanoscale precipitation processes (Cerezo et al., 1990; Ringer & Hono, 2000; Marquis & Seidman, 2001, 2004; Seidman et al., 2002; Marquis et al., 2003a, 2003b, 2006; Fuller et al., 2005; van Dalen et al., 2005; Karnesky et al., 2006). In the present study we measure, using 3-D APT, the compositions of nanometer-scale $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates formed upon aging at two temperatures (375°C and 425°C) and various

Table 1. Compositions and Aging Conditions of the Al-0.1Zr-0.1Ti Alloys Investigated by Conventional or LEAP 3-D APT.

	Nominal composition (at.%)		Verified composition (at.%)		Aging conditions	
	Zr	Ti	Zr	Ti	Temperature (°C)	Times (h)
Al-0.1Zr-0.1Ti(a)	0.1	0.1	—	—	375	20, 100, 400, 1600
Al-0.1Zr-0.1Ti(b)	0.1	0.1	0.089	0.099	425	400

aging times (up to 1600 h) of aluminum micro-alloyed with Zr and Ti.

MATERIALS AND METHODS

Two ternary Al-0.1Zr-0.1Ti (all compositions are given in at.% in this article) alloys were investigated, designated Al-0.1Zr-0.1Ti(a) and Al-0.1Zr-0.1Ti(b). The alloys were prepared by melting 99.95 at.% Al (from Atlantic Equipment Engineers, Bergenfield, NJ, and containing 260 at. ppm Fe and 260 at. ppm Si as impurities) with pure Al-25.0 Ti master alloy and a dilute Al-0.57 Zr (at.%) master alloy, employing nonconsumable 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_3Ti master alloy whose chemical homogeneity and structural uniformity was verified with 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 chemical composition of alloy Al-0.1Zr-0.1Ti(b) was confirmed by bulk chemical analysis performed by direct-current plasma-emission spectroscopy (ATI Wah Chang, Albany, OR). As-cast specimens were isothermally aged at 375°C or 425°C, which is within the range of temperatures shown to produce a strong precipitation strengthening response for Al-Zr alloys (Ichikawa & Ohashi, 1968; Ohashi & Ichikawa, 1970; Park & Kim, 1988; Sato et al., 1996; Malek et al., 2000b). The alloy designations, compositions, and aging conditions investigated by 3-D APT are summarized in Table 1.

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) equipped with a Thermo NORAN EDS detector.

Needlelike 3-D APT specimens were prepared by a two-step electropolishing procedure. Specimen blanks, excised from aged specimens and mechanically ground to approximately $0.2 \times 0.2 \times 10 \text{ mm}^3$, were initially shaped into long needlelike tips with a slight taper angle using a

solution of 10 vol% perchloric acid in acetic acid at ca. 10 Vdc at room temperature. Final electropolishing involved formation of a neck near the tip apex, controlled by carefully limiting the amount of chemical solution in contact with the area of the neck using a loop-polishing apparatus. For this final tip preparation procedure, a solution of 2 vol% perchloric acid in butoxyethanol at room temperature with an applied potential of 3–8 Vdc was employed. The resulting specimen is a sharply pointed tip with an end radius of less than 50 nm.

A local electrode atom probe (LEAP) tomograph (Kelly et al., 1996, 2004; Kelly & Larson, 2000), belonging to a new class of atom probe tomographs (APT), was used for the majority of the 3-D APT analyses. 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 frequency of 200 kHz. A fixed flight path of 80 mm was used for all analyses. Some 3-D APT analyses were also performed using a conventional 3-D APT (Cerezo et al., 1988, 1998; Miller, 2000b), with a pulse fraction of 20%, 1.5 kHz pulse repetition frequency, and a specimen temperature of 30 K in a vacuum of $<10^{-9}$ Torr gauge pressure.

Postanalysis data visualization and evaluation were performed with IVAS (Imago Scientific Instruments, Madison, WI) and custom software developed at Northwestern University called ADAM or currently APEX (Hellman et al., 2002). Quantitative precipitate compositions and solute composition profiles were obtained using the proximity histogram method (Hellman et al., 2000; Hellman & Seidman, 2002), measuring solute concentration profiles in the α -Al matrix and $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate phases with respect to a 5 at.% Zr isoconcentration surface delineating the two phases.

RESULTS

Solute Segregation and Precipitated Microstructure

Figure 1 displays the precipitated microstructure of the alloys, obtained after aging alloy Al-0.1Zr-0.1Ti(a) for 1600 h

Figure 1. Centered superlattice dark-field TEM micrographs of alloy Al-0.1Zr-0.1Ti(a) aged at 375°C for 1600 h. **a:** Low magnification image showing dendritic distribution of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates. **b:** Magnified view of small (3–5 nm radius), coherent, homogeneously distributed L_{12} $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates within the highly supersaturated dendrites. A representative $50 \times 50 \times 200 \text{ nm}^3$ 3-D APT analysis volume is indicated for comparative purposes.

at 375°C. The nanometer-scale $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}) precipitates are nonuniformly distributed throughout the specimens, 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 relative to that of pure Al. Consequently, the liquidus and solidus curves of the α -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. Upon aging, only the enriched dendritic cells contain enough solute in solid solution to cause precipitation of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$. The composition profile across three dendrites spanning 35 μm (Fig. 2) demonstrates that the dendrite centers are enriched nearly twofold in Zr and threefold in Ti, compared to their respective bulk compositions (Table 1). The interdendritic regions are similarly virtually solute free.

The initial inhomogeneous supersaturation of solute atoms after solidification influences not only the spatial distribution of precipitates, but also the precipitate size and morphology, as well as the nucleation mechanism. Consider the precipitates labeled A and B in Figure 1b. Within the center of the dendrites (A), where the Zr and Ti supersaturations are greatest, the precipitates are small (3–5 nm radius), coherent, and are homogeneously distributed. Other precipitates outside the dendrites (B) are larger (ca. 25 nm radius) and are distributed inhomogeneously, indicating that they are most likely heterogeneously nucleated. We describe in detail, in a subsequent publication, the nucleation and growth of these precipitates during aging at 300°C–600°C.

Figure 2. Concentration profiles of Zr and Ti, measured by EDS, across three solute-rich dendrite arms in as-cast Al-0.1Zr-0.1Ti(b). Both Zr and Ti segregate to the dendrite centers ($k_0 > 1$).

A typical $50 \times 50 \times 200 \text{ nm}^3$ ($5 \times 10^5 \text{ nm}^3$) analysis volume for 3-D APT is displayed in Figure 1b. As compared to the relatively coarse (micrometer-scale) dendritic distribution of solute and precipitates, the 3-D volume analyzed by 3-D APT is very small, and therefore the locally measured solute composition of the alloy, as well as the likelihood of intersecting precipitates, varies among 3-D APT analyses. Indeed, we demonstrate later (Table 2) that the solute concentration measured during an analysis is correlated to the probability of intersecting a precipitate. This also means that the local alloy composition from which the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates form is *a priori* unknown.

Table 2. Number of Precipitates Intersected by Conventional or LEAP 3-D APT, Total Number of Atoms Collected, Number of Ti Atoms Collected, and Resulting Ti Concentration of the α -Al Solid Solution (Expressed in Terms of the Bulk Value, $C_0 = 0.099$ at.% Ti).

Alloy	Number of precipitates	Total number of atoms ($\times 10^6$)	Ti atoms	C/C_0
Al-0.1Zr-0.1Ti(a), 375°C, 100 h	0	0.287	—	0.00 ± 0.07
Al-0.1Zr-0.1Ti(a), 375°C, 100 h	0	0.814	252	0.31 ± 0.04
Al-0.1Zr-0.1Ti(a), 375°C, 1600 h	0	1.272	416	0.33 ± 0.03
Al-0.1Zr-0.1Ti(a), 375°C, 1600 h	1	0.455	176	0.39 ± 0.05
Al-0.1Zr-0.1Ti(a), 375°C, 1600 h	0	1.300	576	0.44 ± 0.03
Al-0.1Zr-0.1Ti(b), 425°C, 400 h	0	2.254	1369	0.61 ± 0.04
Al-0.1Zr-0.1Ti(a), 375°C, 20 h	0	0.275	169	0.61 ± 0.08
Al-0.1Zr-0.1Ti(a), 375°C, 1,600 h	6	3.700	2539	0.69 ± 0.03
Al-0.1Zr-0.1Ti(a), 375°C, 100 h	1	0.632	606	0.96 ± 0.07
Al-0.1Zr-0.1Ti(a), 375°C, 1,600 h	1	0.547	551	1.01 ± 0.08
Al-0.1Zr-0.1Ti(a), 375°C, 400 h	1	0.161	164	1.02 ± 0.12
Al-0.1Zr-0.1Ti(b), 425°C, 400 h	1	0.575	627	1.09 ± 0.07
Al-0.1Zr-0.1Ti(a), 375°C, 20 h	4	0.496	657	1.32 ± 0.08
Al-0.1Zr-0.1Ti(a), 375°C, 1600 h	4	3.068	4115	1.34 ± 0.06
Al-0.1Zr-0.1Ti(a), 375°C, 1600 h	10	0.909	1272	1.40 ± 0.08
Al-0.1Zr-0.1Ti(b), 425°C, 400 h	1	0.986	2120	2.15 ± 0.10

Three-Dimensional Atom-Probe Tomographic Reconstructions

Figure 3 presents a 3-D reconstruction of an $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate intersected during a LEAP tomographic analysis. The reconstructed volume is $39 \times 39 \times 29 \text{ nm}^3$, containing 7.69×10^5 identified atoms represented by dots. Figure 3a displays the Al atoms, with only 20% shown for the sake of clarity. The paucity of atoms in the precipitate interior and the shell of atomic enrichment at the matrix/precipitate interface are reconstruction artifacts, characteristic of a strong local magnification effect arising from the disparate evaporation fields of the α -Al matrix and $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$

precipitates. We discuss this artifact and its possible influence on the measured precipitate compositions below. Figure 3b shows only the Zr atoms, indicating that most of the solute atoms partition to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ phase. Although the precipitates are Zr rich (i.e., primarily Al_3Zr as we discuss below), Figure 3c shows unambiguously that Ti atoms also partition to the precipitate, forming an $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ ternary intermetallic.

Quantitative Chemical Composition of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ Precipitates

The reconstructions in Figure 3 indicate that both Zr and Ti partition to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates. This information is conveyed more quantitatively in Figure 4, which exhibits a proximity histogram, or proxigram for short (Hellman et al., 2000; Hellman & Seidman, 2002), displaying the composition of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate depicted in Figure 3. Similar to a linear composition profile, the proxigram is a plot of concentration as a function of distance, indicating the partitioning behavior of solute atoms between the α -Al matrix and the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates. Rather than using a single linear direction, however, the proxigram considers each point of 3-D space with respect to a reference surface (a 5 at.% Zr isoconcentration surface), which is physically more representative of the actual concentration profiles. Hence, a proxigram displays in two dimensions information that is characteristic of three dimensions.

Figure 4 indicates that, compared to the nominal value of 25 at.% solute expected for a trialuminide (Al_3M -type) ordered phase, the precipitate in Figure 3 is substoichiometric, containing approximately 20 at.% total solute. Similar substoichiometric compositions have been observed in metastable L1_2 primary (formed in the melt) trialuminides in Al-Ti alloys, with precipitate compositions (determined by EDS) containing approximately 20 at.% Ti, corresponding to Al_4Ti (Cisse et al., 1974; Kerr et al., 1974; Majumdar & Muddle, 1993; Chu, 1994).

This departure from stoichiometry may be attributable to unpositioned solute ions (Zr and Ti) field evaporated from the precipitate phase. Sha and Cerezo (2005) showed that it is necessary to include both correctly positioned as well as unpositioned ions in order to obtain stoichiometric compositions of Al_3Zr precipitates formed in a commercial 7050 Al alloy. The precipitates require a much higher electric field for field evaporation than the α -Al solid solution (discussed below), which generates more multiple ionization events during field evaporation, resulting in higher proportions of these ions not being positioned. Assuming the fraction of unpositioned ions is independent of solute ion species, the ratio of solute atoms measured in the present $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates herein should reflect the correct precipitate composition. Despite the overall substoichiometric precipitate composition, Figure 4 demonstrates that Ti is a minor constituent in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipi-

Figure 3. LEAP tomographic reconstruction of an $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate in alloy Al-0.1Zr-0.1Ti(b) aged for 400 h at 425°C. The dimensions of the rectangular parallelepiped are $39 \times 39 \times 29 \text{ nm}^3$, containing 7.69×10^5 identified atoms. **a:** Reconstruction showing only Al atoms, with only 20% of the atoms displayed for the sake of clarity. **b:** Reconstruction showing Zr atoms, indicating that the solute atoms partition to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate. **c:** Reconstruction showing only Ti atoms.

Figure 4. Proxigram displaying the distribution of Zr and Ti atoms relative to the position of a 5 at.% Zr isoconcentration surface for the precipitate reconstructed in Figure 3 (Al-0.1Zr-0.1Ti(b) aged at 425°C for 400 h). The precipitate is Zr rich, with a small fraction of the Zr lattice sites replaced by Ti atoms. The ratio of Zr:Ti is about 5, corresponding to $\text{Al}_3(\text{Zr}_{0.83}\text{Ti}_{0.17})$.

tate, with an average Zr:Ti ratio of 5 (corresponding to $x = 0.17$). This is significantly greater than the overall Zr:Ti ratio of unity in the alloy (Table 1).

Figure 5 shows proxigrams for precipitates formed in Al-0.1Zr-0.1Ti(a) aged for 20, 400, or 1600 h at 375°C. Compared to Figure 4, these concentration profiles are closer to the trialuminide stoichiometry (25 at.% total solute) and, as shown in Figure 4 Ti is clearly a minor constituent in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates at 375°C. After 20 h at 375°C, the concentration of Ti in the precipitate is 3–4 at.%,

Figure 5. Proxigrams displaying the distributions of Zr and Ti atoms in $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates formed in alloy Al-0.1Zr-0.1Ti(a) aged at 375°C for the times indicated. The 20-h aging time results are based on four precipitates and a total of 4.96×10^5 atoms (conventional 3-D APT), the results for 400 h are based on 10 precipitates and a total of 9.09×10^5 atoms (conventional 3-D APT), and the results for 1600 h are based on four precipitates and a total of 3.07×10^6 atoms (LEAP 3-D APT). The ratio of Zr:Ti is about 10, independent of aging time, corresponding to $\text{Al}_3(\text{Zr}_{0.91}\text{Ti}_{0.09})$.

comparable to that displayed in Figure 4 for Al-0.1 Zr-0.1 Ti(b) aged 400 h at 425°C. Figures 4 and 5 indicate that the composition of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates varies little with aging temperature (425°C, Fig. 4), or aging time (20–1600 h at 375°C, Fig. 5). At 375°C, the compositions of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates displayed in Figure 5 each have a Zr:Ti ratio of ca. 10, corresponding to $x = 0.09$.

Figure 6. LEAP time-of-flight mass spectrum of Al-0.1Zr-0.1Ti(b) aged for 400 h at 425°C (reconstruction shown in Fig. 3). **a:** Mass spectrum for the entire analysis, representing 7.67×10^5 identified atoms, of which 5.21×10^3 atoms (0.679 ± 0.009 at.%) are identified as Zr and 2.16×10^3 atoms (0.282 ± 0.006 at.%) are Ti. **b:** Mass spectrum indicating the composition of the matrix (α -Al solid solution). This mass spectrum represents 2.09×10^5 identified atoms, of which 224 atoms (0.107 ± 0.007 at.%) are Ti; there is no evidence of Zr (<0.010 at.%), indicating that all detectable Zr atoms have partitioned to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate. **c:** Mass spectrum indicating the core composition of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate. This spectrum represents 8.88×10^3 atoms, of which 1508 atoms (17.00 ± 0.40 at.%) are Zr and 335 atoms (3.77 ± 0.20 at.%) are Ti. This corresponds to the plateau composition in Figure 4.

Time-of-Flight Mass Spectra

Figure 6a shows the time-of-flight mass spectrum for the entire analysis volume reconstructed in Figure 3. The prominent Al peaks correspond to singly (Al^{1+} , 27 amu) and doubly charged (Al^{2+} , 13.5 amu) ions produced during pulsed field evaporation; Al has only one isotope. The peaks for the Zr and Ti solute atoms, although less pronounced (a result that is anticipated considering the compositions in Table 1), are nevertheless clearly identifiable. Zirconium is field evaporated in both the doubly (Zr^{2+} , 45–48 amu) and triply charged (Zr^{3+} , 30–32 amu) states, whereas Ti atoms are observed only in the doubly charged (Ti^{2+} , 23–25 amu)

state. For all species, the stable isotopes are clearly distinguished from one another, demonstrating the excellent mass resolution of the 3-D APT technique.

We now compare the mass spectrum in Figure 6a to the one displayed in Figure 6b, which represents an analyzed volume from the α -Al solid solution below the precipitate displayed in Figure 3. The Zr peaks, which are distinct in Figure 6a, are no longer present in Figure 6b, indicating that all detectable Zr atoms partition to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ phase. The Ti peaks, in contrast, are still quite prominent in Figure 6b. By counting the number of atoms corresponding to these peaks, we determine the concentration of Ti in α -Al solid solution to be 0.109 ± 0.006 at.%, which is somewhat greater than the overall composition of alloy Al-0.1Zr-0.1Ti(b) (Table 1). This result is not surprising considering the strong microsegregation of solute atoms demonstrated in Figure 2. The compositions in Table 1 are bulk chemical compositions, whereas those measured by 3-D APT are locally sampled values. Furthermore, as we show in the next section, there is a correlation between measured solute concentration in the α -Al solid solution and proximity to precipitates, as anticipated. The mass spectrum in Figure 6c represents the ions field evaporated from the core of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate displayed in Figure 3; as anticipated, the Zr and Ti peaks from this solute-rich phase are distinct.

There is also a shift in charge states of the field-evaporated ions between the two phases. The spectrum of field-evaporated ions from the α -Al solid solution matrix (Fig. 6b) shows that 95% of the Al ions are field evaporated in the singly charged state (Al^{1+}), whereas in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates (Fig. 6c), Al is almost entirely doubly charged (Al^{2+}). These higher charge states are indicative of the larger evaporation fields required to field evaporate ions from $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$, leading to a pronounced local magnification effect as discussed below.

Correlation between Measured Ti Concentration Proximity to Precipitates

Considering the initial dendritic distribution of solute species after solidification (Fig. 2) and the resulting nonuniform distribution of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates after aging (Fig. 1), it is anticipated that 3-D APT analyses would frequently be precipitate-free. Indeed, at least half of all performed analyses fail to intersect precipitates but rather sample interdendritic precipitate-free volumes of α -Al solid solution. These analyses, though precipitate-free, are nevertheless valuable because they provide a direct, atom-by-atom chemical verification of the local solute concentration in the particular volume sampled. As shown in Figure 1, the spatial distribution of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates is correlated directly to the initial dendritic distribution of solute atoms formed during solidification. Figure 6 indicates that, during aging, nearly all of the Zr atoms partition to the precipitates, whereas a substantial fraction of the Ti is

Figure 7. LEAP tomographic reconstruction of Al-0.1 Zr-0.1 Ti(a) aged for 1600 h at 375°C. The dimensions of the rectangular parallelepiped are $28 \times 27 \times 30 \text{ nm}^3$, containing 4.42×10^5 identified atoms. One large ($>25 \text{ nm}$ radius) $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate is detected. **a:** Reconstruction showing only Al atoms, with only 20% of the atoms displayed for clarity. **b:** Reconstruction showing Zr atoms. **c:** Reconstruction showing only Ti atoms.

observed in the α -Al solid solution around the precipitates (in a typical volume analyzed by 3-D APT, ca. 10^4 – 10^6 nm^3). Because Zr and Ti partition in the same manner (Fig. 2), there should be a correlation between measured Ti concentration in the α -Al solid solution and proximity to the precipitate-rich dendrites in the microstructure. Table 2 compares the results of several LEAP tomographic and conventional APT analyses for various aging conditions of the Al-0.1Zr-0.1Ti alloys, arranged in order of increasing measured Ti concentration in the α -Al solid solution. For all but three analyses that intersected precipitates (Table 2), the Ti concentration measured locally in the α -Al solid solution is enriched relative to the overall value of 0.099 at.% Ti (i.e., $C/C_0 > 1$). Similarly, all analyses that do not detect precipitates have smaller Ti concentrations than the nominal value ($C/C_0 < 1$), with the α -Al solid solutions of some analyses containing undetectable amounts of Ti ($C/C_0 \rightarrow 0$). There appears to be a critical value, between $C/C_0 = 0.61$ and 0.69 , as indicated by the horizontal rule in Table 2, which separates the precipitate-free analyzed volumes from the precipitate-containing ones.

There is one outlier at $C/C_0 = 0.39$ (Table 2), which represents an analysis that intersected a precipitate but whose surrounding α -Al solid solution is depleted in Ti compared to its overall concentration in the alloy. A portion of the corresponding 3-D reconstruction is shown in Figure 7, in which a large ($R > 25 \text{ nm}$) $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate is intersected at the end of the analysis. The reconstructed precipitate is comparable in radius to precipitate B in the TEM micrograph in Figure 1b; the large radius of this precipitate suggests that the analyzed volume is interdendritic, consistent with the depleted measured Ti concentration in the α -Al solid solution (Table 2).

This hypothesis is supported by the composition (proxigram in Fig. 8) of the precipitate reconstructed in Figure 7. Not only is the matrix depleted in Ti ($C/C_0 = 0.39$; Table 2),

Figure 8. Proxigram showing the distribution of Zr and Ti atoms in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate displayed in Figure 7, Al-0.1Zr-0.1Ti(a) aged at 375°C for 1600 h. The precipitate contains very little Ti (ca. 1 at.%).

but the measured Ti concentration in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate is also small (ca. 1 at.% Ti) compared to the values in the proxigrams displayed in Figures 4 and 8. That there is little Ti in both the α -Al solid solution and precipitate phases suggests that this analysis intersected an interdendritic precipitate (e.g., B in Fig. 1b).

DISCUSSION

Effects of Solute Microsegregation after Solidification

Because of the significant microsegregation of solute species in these alloys (Fig. 1), each localized region sampled by a

Figure 9. Isothermal sections at 375°C or 425°C of a calculated ternary phase diagram for the Al-Zr-Ti system in the Al-rich corner, showing the α -Al solid solution in equilibrium with the metastable $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}) and stable Al_3Ti (D_{022}). The locally measured alloy compositions (by EDS; Fig. 2) are indicated by the circles. Phase diagram calculated by Dr. J.L. Murray (Alcoa).

given 3-D APT analysis can be thought of as probing a unique and *a priori* unknown alloy composition. Figure 9 shows calculated isothermal sections of the Al-Zr-Ti phase diagram at 375°C (solid lines) or 425°C (dashed lines), which indicates three-phase equilibria among α -Al, $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}), and Al_3Ti (D_{022}) in the Al-rich corner; this partial phase diagram was calculated by Dr. J. L. Murray (Alcoa). Superimposed are the data from the EDS line scan in Figure 2, showing measured ternary alloy compositions across solute-rich dendritic and solute-depleted interdendritic regions in the alloy. Although the local alloy composition varies significantly, Figure 9 illustrates that at 375°C or 425°C, most of the alloy is in the α -Al + $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}) two-phase field, with a few points (from the interdendritic regions) lying in the single-phase α -Al solid solution. No points are situated in the α -Al + $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}) + Al_3Ti (D_{022}) three-phase field. This is consistent with the observed precipitated microstructure (Fig. 1), which shows only $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}) precipitates concentrated in the dendrite centers and precipitate-free α -Al solid solution in the interdendritic channels.

The bulk ratio of solute atoms in the alloy is nearly unity (Table 1), yet the data in Figures 2 and 9 show a bias in the measured Zr:Ti ratio of approximately 2:3. This apparent enrichment of Ti in the locally sampled region of the alloy (35 μm line scan; Fig. 2) could represent macrosegregation of solutes. It is also possible that this apparent enrichment of Ti is an artifact of the EDS technique. The data presented in Figure 2 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 (Fig. 9), indicating that the EDS results are fairly accurate.

The variation in alloy composition, shown in Figures 2 and 9, makes the discussion of the measured compositions of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates difficult because the local alloy composition from which these precipitates form is *a priori* unknown. The situation is complicated further by a significant disparity in evaporation fields between the α -Al and $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ phases, resulting in distortions in atomic density in the reconstructed volumes as well as potential biases in the measured precipitate compositions. Nevertheless, consistent with the proxigrams presented in Figures 4, 5, and 8 (as well as others measured), two conclusions are drawn: (1) The precipitated phase is predominantly Zr-rich with a small amount of Ti partitioning to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates and (2) there is no evidence of interfacial segregation of solute at the α -Al/ $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ heterophase interface.

Local Magnification of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ Precipitates

Before considering the measured precipitate compositions, the disparate evaporation fields of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ and α -Al phases and the potential effects on measured solute concentrations in these phases and at their interface are discussed. Figures 3 and 7 exhibit noticeable aberrations in the reconstructed volumes, including (1) reduced atomic density of the reconstructed precipitates, (2) a shell of enriched atomic density at the matrix/precipitate heterophase interface, and (3) compression of the precipitate dimension in the analysis direction. These artifacts are attributable to a local magnification effect, which can occur during field evaporation of two-phase systems when the phases have disparate evaporation fields, leading to variations in local curvature of the specimen surface and, ultimately, to aberrations in the trajectories of field-evaporated ions (Miller et al., 1996; Miller, 2000a; Vurpillot et al., 2000). These aberrations are not accounted for in the reconstruction procedure, leading to possible distortions in the reconstructed volumes.

The apparent local atomic density in the 3-D APT reconstruction provides an indication of the severity of local focusing or defocusing effects resulting from ion trajectory aberrations (Blavette et al., 2001; Vurpillot et al., 2004). The differences in the reconstructed atomic density of the α -Al solid solution and $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates are clear in Figure 10, which shows all identified atoms in a thin (3-nm) slice parallel to the analysis direction through the reconstruction in Figure 7. The (111)-type atomic planes in the α -Al matrix are well resolved and with the correct interplanar spacing, indicative of an accurately reconstructed volume using reconstruction parameters appropriate for the α -Al matrix. The same is not true for the reconstructed volume inside the precipitate. The spheroidal precipitates are coherent with the α -Al matrix, and therefore the (111) planes should be continuous through the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate.

Figure 10. A 3-nm-thick slice, cut parallel to the analysis direction, through the reconstruction in Figure 7, showing atomically enriched and depleted regions due to trajectory overlap. This volume contains 6.12×10^5 identified atoms, with all atoms displayed.

The reconstructed precipitate also exhibits a lower atomic density than the surrounding α -Al matrix. At ambient temperature, the lattice parameters of Al and Al_3Zr are similar, 0.405 and 0.408 nm, respectively (Knippling et al., 2006), resulting in a 2% difference in molar volumes. This small difference would be visually indiscernible in a correctly reconstructed volume. It is clear in Figure 10, however, that the reconstructed local atomic density of the α -Al solid solution is significantly greater than that of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate, with a measured density ratio of 3.4. The ratio exhibited in Figure 3 is even greater, 5.9, which is also consistent with the possibly greater fraction of unpositioned solute species (Zr and Ti) in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitate for explaining the substoichiometric compositions observed in Figure 4.

The difference in evaporation fields between the α -Al matrix and $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates is demonstrated quantitatively by considering the mass spectra in Figure 6. As discussed, 95% of the detected Al ions are field evaporated as Al^{1+} from the α -Al solid solution (Fig. 6b), whereas Al^{2+} is predominant from the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates (Fig. 6c), indicative of the higher electric fields required to field evap-

orate ions from the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates. This electric field is estimated from the calculated evaporation fields at 0 K (Brandon, 1964; Tsong, 1978) for the constituent species (Al, Zr, and Ti) in the precipitates (Table 3). Because the Al ions field evaporated from the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates are almost all Al^{2+} , the electric field required to field evaporate ions then must exceed 35 V nm^{-1} ($E_2 = 35 \text{ V nm}^{-1}$; Table 3). This is also consistent with the observed charge states of Zr ions in the precipitates: 93% of the field-evaporated ions are

Table 3. Calculated Evaporation Fields (V nm^{-1}) for Singly (E_1), Doubly (E_2), and Triply (E_3) Charged Al, Zr, and Ti Ions (Tsong, 1978) at 0 K; the Expected Charge States Are Underlined.

Element	E_1 (V nm^{-1})	E_2 (V nm^{-1})	E_3 (V nm^{-1})
Al	<u>19</u>	35	50
Zr	56	<u>28</u>	35
Ti	41	<u>26</u>	43

Zr^{3+} ($E_3 = 35 \text{ V nm}^{-1}$) rather than Zr^{2+} ($E_2 = 28 \text{ V nm}^{-1}$). These results agree with a recent analysis by Sha and Cerezo (2005), who used field-ion microscopy and 3-D APT to estimate an evaporation field of 36 V nm^{-1} for Al_3Zr precipitates in a commercial 7050 Al alloy.

The effect of local magnification aberrations on the measured compositions of nanometer-scale precipitates by 3-D APT has been addressed both experimentally and with modeling (Miller & Hetherington, 1991; Vurpillot et al., 2000, 2004; Blavette et al., 2001). For a one-dimensional atom probe, Miller and Hetherington (1991) showed that, although trajectory overlap leads to significant spatial distortions in the reconstruction, the bulk compositions of the phases are generally unbiased. Recent simulations by Blavette and colleagues (Vurpillot et al., 2000; Blavette et al., 2001) have similarly concluded that the measured compositions from the inner core of precipitates are unaffected by ion trajectory overlap effects occurring at the reconstructed matrix/precipitate interface.

The evaporation field of Al_3Zr ($E_{\text{Al}_3\text{Zr}} = 36 \text{ V nm}^{-1}$) is considerably greater than that of the α -Al solid solution ($E_{\text{Al}} = 19 \text{ V nm}^{-1}$), as measured by Sha and Cerezo (2005) and confirmed presently. The corresponding evaporation field ratio (Vurpillot et al., 2000), $\varepsilon = E_{\text{Al}_3\text{Zr}}/E_{\text{Al}} = 1.9$, represents a greater disparity in evaporation fields than those modeled by Blavette and colleagues ($0.85 \leq \varepsilon \leq 1.15$; Vurpillot et al., 2000; Blavette et al., 2001). Sha and Cerezo (2005) measured directly, however, the extent of ion trajectory overlap for experimental reconstructions and showed that, for Al_3Zr precipitates 3.5–6.0 nm in radius, the experimentally measured ion trajectory overlaps increased from 1.4 to 2.0 nm with increasing precipitate radius. The reconstructed precipitates in Figures 3 and 7 are larger than this, and so the extent of trajectory overlap (and hence the convolution in measured composition at the interface) may be greater for the precipitates discussed herein.

The precipitate composition profiles presented in Figures 4, 5, and 8 are therefore probably less accurate than indicated at the matrix/precipitate heterophase interface. Nevertheless, the reported plateau compositions of the proxigrams (and in particular the solute ratios) at the center of the precipitates are expected to be reliable.

Compositions of the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates

The proxigrams in Figures 4, 5, and 8 are representative of the compositions of all the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates observed by both LEAP tomography and conventional APT. The precipitates are invariably Zr rich, with only a small fraction of Zr replaced by Ti. In all cases, the Ti concentration in the trialuminide is less than 5 at.%, despite the nominally equal concentrations of Zr and Ti initially in the alloys (Table 1). The proxigrams shown in Figure 5, which indicate the temporal evolution of 18 $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates at 375°C, suggest that the Zr:Ti ratio is approximately 10 and varies little with aging time. The proxigram in Figure 4, for a

precipitate formed after 400 h of aging at 425°C, demonstrates that the Zr:Ti ratio is approximately 5, roughly twice that at 375°C, corresponding to a precipitate composition of $\text{Al}_3(\text{Zr}_{0.83}\text{Ti}_{0.17})$. Like the composition of the alloy from which they form (Fig. 2), however, the concentrations of solutes in the precipitates are probably not uniform throughout the volume. Indeed, as shown in Figure 8, the measured Zr:Ti ratio can deviate substantially from those stated above.

The small concentration of Ti observed in the precipitates could be reflective of (1) the substantially higher solid solubility of Ti in α -Al and (2) the smaller diffusivity of Ti in α -Al compared to that of Zr. Figure 9 indicates that the solid solubility of Al_3Zr (L_{12}) in metastable equilibrium with α -Al is 0.008 and 0.016 at.% Zr at 375°C and 425°C, respectively. The solid solubility of Al_3Ti (D_{022}) in α -Al is an order of magnitude greater: 0.101 and 0.163 at.% Ti at 375°C and 425°C, respectively. This greater solubility of Ti would account for the small partitioning of Ti to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates and the residual Ti observed in α -Al solid solution in precipitate-containing 3-D APT analyses (Table 2). The calculated ternary Al-Zr-Ti phase diagram (Fig. 9) indicates, however, that both solutes are supersaturated with respect to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ solvus, especially in the solute-rich dendrites. Thus, the small Ti concentration in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates as well as the residual Ti observed in α -Al solid solution around them are not simply a function of the equilibrium solubilities of Zr and Ti.

The measured tracer diffusivity of Ti in α -Al is smaller than that of Zr in α -Al (Knipling et al., 2006); kinetics, therefore, are probably the dominant influence dictating the observed small concentration of Ti in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates. The diffusivities of Zr and Ti in α -Al are given by an Arrhenius relationship, $D = D_0 \exp(-Q/R_g T)$, where $Q = 242$ and 260 kJ mol^{-1} and $D_0 = 7.28 \times 10^{-2}$ and $1.12 \times 10^{-1} \text{ m}^2 \text{ s}^{-1}$ for Zr (Marumo et al., 1973) and Ti (Bergner & van Chi, 1977), respectively. The root-mean-squared (RMS) diffusion distances, $2\sqrt{Dt}$ of Zr and Ti after 1600 h at 375°C are 228 and 53 nm, respectively; after 400 h at 425°C these distances are 570 and 150 nm, respectively. These calculated RMS diffusion distances are much smaller than the dimensions of the initial dendritic distribution of solute (0.5–4 μm in Fig. 1 and 3–10 μm in Fig. 2). Achieving a homogenous distribution of Ti is therefore impossible for reasonable aging treatments. Even at 375°C, the calculated RMS diffusion distance of Ti is, however, greater than the mean edge-to-edge interprecipitate distance (ca. 10–50 nm) in the precipitate-rich dendrite centers (Fig. 1). The diffusion distance of Ti is also greater than that of a typical 3-D APT reconstruction (ca. $50 \times 50 \times 200 \text{ nm}^3$ as shown schematically in Fig. 1). The growth of the precipitates may therefore be interface limited and not diffusion limited. Additionally, diffusion of a solute in an ordered compound is significantly slower than in the matrix because of the effect of correlation on the diffusivity.

There is only one other study where the composition of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates was measured directly. Using scan-

ning transmission electron microscopy and energy dispersive X-ray spectroscopy, Sato et al. (1996) measured the composition of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates formed after aging an Al-0.09Zr-0.17Ti (at.%) for 168 h at 500°C. Despite the enhanced kinetics at 500°C and the greater supersaturation of Ti as compared to the present study, the estimated Zr:Ti ratio in their precipitates was approximately 10, consistent with our findings that only a small fraction of the available Ti partitions to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ phase. Our results agree also with other 3-D APT studies on Al-Sc-Ti (van Dalen et al., 2005) and Al-Sc-Zr (Fuller, 2003; Forbord et al., 2004; Fuller et al., 2005) alloys, discussed below, where the slower diffusing Ti and Zr atoms are generally a minor constituent in the precipitated trialuminide.

Residual Ti in the α -Al Solid Solution

Table 2 demonstrates that the amount of Ti in α -Al observed locally by 3-D APT can be correlated to the proximity of the 3-D APT analysis to the precipitate-rich and therefore solute-rich regions in the alloy. This is illustrative of how little Ti partitions to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates during aging at both 375°C or 425°C. That the local Ti concentration in α -Al solid solution is sometimes enriched ($C/C_0 > 1$) and other times depleted ($C/C_0 < 1$) relative to the bulk composition is reflective of the initial inhomogeneous distribution of solute atoms shown in Figure 2. In the as-cast alloy, the concentration of Ti, as measured by EDS, is shown to be enriched nearly threefold relative to the bulk alloy composition within the supersaturated dendrites. This is in reasonable agreement with the over twofold enrichment of Ti in solid solution near precipitates measured by 3-D APT (Table 2). That there is only a twofold enrichment of Ti in α -Al in the aged alloys may be explained by the fact that Ti atoms partition to the precipitated $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ phase, as shown in the mass spectra of Figure 6 and the proxigrams in Figures 4, 5, and 8, and hence Ti is depleted from the α -Al solid solution.

As discussed, the solid solubility of Al_3Ti (D_{022}) in α -Al is 0.101 or 0.163 at.% Ti at 375°C or 425°C, respectively, which correspond to the Ti composition of the point in the α -Al + $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}) + Al_3Ti (D_{022}) tie triangle in Figure 9. Because all portions of the alloy are in the α -Al solid solution or the α -Al + $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12}) two-phase field (Fig. 9), any tie line drawn between these two phases must intercept the α -Al solvus at less than 0.101 at.% Ti at 375°C or 0.163 at.% Ti at 425°C. Table 2 shows that the measured Ti concentration in α -Al solid solution for three precipitate-containing analyses performed on Al-0.1Zr-0.1Ti(a) aged at 375°C contain more than 0.101 at.% Ti, the equilibrium maximum solubility at this temperature. Similarly, the α -Al solid solution from one precipitate-containing analysis performed on Al-0.1Zr-0.1Ti(b) aged 400 h at 425°C contained 0.215 ± 0.005 at.% Ti ($C/C_0 = 2.15 \pm 0.10$), well beyond the maximum solubility of 0.163 at.% Ti at 425°C. The fact that concentrations beyond the equi-

librium solubility are measured in the matrix of some precipitate-containing 3-D APT analyses indicates that the alloys have not achieved global thermodynamic equilibrium after 1600 h at 375°C or 400 h at 425°C.

As described in the Introduction, improving the thermal stability of Al_3Zr with ternary or quaternary additions of Ti and/or V has generated considerable interest in the scientific literature. Most of these studies, however, assumed that the ratio of solutes in the precipitated trialuminides was the same as that initially in solid solution (i.e., the bulk alloy composition). This is, at first glance, a reasonable assumption because the transition elements are generally sparingly soluble in α -Al, and all solute atoms should therefore partition to the precipitated phase. In the present study, the alloys had initially the same atomic fraction of solute species (Table 1), yet a Zr:Ti ratio of unity is never observed in the precipitated $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ phase. Moreover, as evidenced by Table 2, the assumption of negligible solubility of solutes in α -Al is invalid; diffusion kinetics in α -Al, which is anomalously slow and varies widely among the transition elements (Rummel et al., 1995; Knipling et al., 2006), is instead the dominant factor dictating the relative amounts of solute atoms in the precipitated phase. The precipitate compositions cited in prior studies (Zedalis & Fine, 1986; Chen et al., 1987, 1990; Lewis et al., 1987; Parameswaran et al., 1989; Lee et al., 1993; Chuang & Tu, 1994; Malek et al., 1994, 1999, 2000a, 2000b, 2000c, 2002; Chung et al., 1995; Han et al., 1995; Tsau & Chen, 2002) are therefore highly speculative. Sato et al. (1996), however, verified the compositions of their $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates by EDS, as noted.

Comparison to 3-D APT Studies on Al-Sc-Ti/Zr Alloys

It is valuable to compare our measured precipitate compositions to those for Al-0.06 Sc-0.06 Ti (at.%) alloys reported in a similar 3-D APT study by van Dalen et al. (2005). Like Al_3Zr , the ordered Al_3Sc phase precipitates from a supersaturated solid solution during aging and also has the L_{12} structure; unlike Al_3Zr , however, Al_3Sc is a thermodynamically stable L_{12} ordered structure. Even after aging at 300°C for 1536 h (64 days), van Dalen et al. (2005) showed that Ti atoms partition weakly to the $\text{Al}_3(\text{Sc}_{1-x}\text{Ti}_x)$ phase, forming precipitates with the average composition $\text{Al}_3(\text{Sc}_{0.94}\text{Ti}_{0.06})$, corresponding to a Sc:Ti ratio of 16, with Ti remaining primarily in α -Al solid solution. The amount of Ti measured in α -Al solid solution by 3-D APT decreased continuously with aging time at 300°C, yet still exceeded the calculated equilibrium value in α -Al after 1536 h, indicating that global thermodynamic equilibrium had not yet been reached.

The higher coarsening resistance of Al_3Zr compared to Al_3Sc , due to the slower diffusion kinetics of Zr (Knipling et al., 2006), allows higher aging temperatures (up to 425°C vs. 300°C for the Al-Sc-Ti alloys; van Dalen et al., 2005).

This amounts to a significant difference in diffusion kinetics, with the calculated diffusivity of Ti being 1.8×10^4 times greater at 425°C than at 300°C. Accordingly, the proxigram shown in Figure 4 indicates that the composition of a precipitate formed after 400 h at 425°C is $\text{Al}_3(\text{Zr}_{0.83}\text{Ti}_{0.17})$. Figure 5, for precipitates formed at 375°C, indicates compositions of $\text{Al}_3(\text{Zr}_{0.91}\text{Ti}_{0.09})$. Both of these represent a larger fraction of Ti compared to $\text{Al}_3(\text{Sc}_{0.94}\text{Ti}_{0.06})$ observed after 1536 h at 300°C (van Dalen et al., 2005). This may be explained in terms of diffusion kinetics: The calculated RMS diffusion distance for Ti in α -Al after 1536 h at 300°C is 3 nm, whereas it is 7 nm after 20 h at 375°C (corresponding to one of the proxigrams in Fig. 5).

The distribution of Ti in the $\text{Al}_3(\text{Sc}_{1-x}\text{Ti}_x)$ precipitates studied by van Dalen et al. (2005) is inhomogeneous, with the precipitates consisting of an Al_3Sc core surrounded by a spherical Ti-enriched outer shell. Similar cored composite precipitates are well documented for Al-Sc-Zr alloys, as observed by 3-D APT (Fuller, 2003; Forbord et al., 2004; Fuller et al., 2005; Clouet et al., 2006), analytical high resolution electron microscopy (Tolley et al., 2005; Clouet et al., 2006), small angle X-ray scattering (Clouet et al., 2006), and atomic-scale simulations (Clouet et al., 2005, 2006). Both Ti and Zr reduce the lattice parameter of Al_3Sc (L_{12}) (Harada & Dunand, 2002, 2003), thus reducing the lattice parameter mismatch with α -Al. The enriched outer shell of the mismatch-reducing solutes (Ti or Zr) within the precipitate should therefore minimize the elastic strain energy of the coherent precipitate (Forbord et al., 2004; Fuller et al., 2005; Tolley et al., 2005; van Dalen et al., 2005; Clouet et al., 2006). It has also been suggested (Fuller, 2003; Forbord et al., 2004; Clouet et al., 2005, 2006; Fuller et al., 2005; Tolley et al., 2005) that, because of the much faster diffusion rate of Sc compared to Ti or Zr, only Sc atoms are kinetically able to participate in the early stages of nucleation and growth. These preexisting clusters then act as heterogeneous nucleation sites for the less mobile Ti or Zr atoms, accounting for the observed cored precipitate compositions.

In the Al-Zr-Ti system, Ti is the slowest diffuser and has also been shown to reduce the lattice parameter mismatch with α -Al of the metastable Al_3Zr (L_{12}) phase (Malek et al., 1999). By analogy with the Al-Sc-Ti or Al-Sc-Zr systems, therefore, one might expect segregation of Ti to the matrix/precipitate interface. Nevertheless, our results provide no evidence for such segregation at the α -Al/ $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ interface after extended aging times at 375°C or 425°C. The lattice parameter mismatch of Al_3Zr (L_{12}) with α -Al at room temperature, $\delta = +0.75\%$, is less than that of Al_3Sc (L_{12}), $\delta = +1.32\%$ (Knippling et al., 2006), which means the elastic strain energy density of the precipitates (proportional to the square of the mismatch; Eshelby, 1957, 1961) of the coherent heterophase interface is also less. There is also the possibility that interfacial segregation of Ti may be veiled by the significant local magnification for this system, as discussed earlier.

CONCLUSIONS

Atom probe tomography was applied to measure directly the chemical compositions of $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ (L_{12} structure) precipitates formed in conventionally solidified Al-0.1Zr-0.1Ti (at.%) alloys during extended aging times at 375°C (to 1600 h) or 425°C (to 400 h). The following results were obtained and discussed:

- Dendritic solidification results in nonuniform distributions of Zr and Ti, which segregate to the dendrite centers and are enriched by a factor of 2 and 3, respectively. The interdendritic regions are concurrently solute depleted. During subsequent aging, $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates are similarly nonuniformly distributed in a dendritic manner.
- The Zr:Ti atomic ratio in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates, as measured by atom probe tomography, is 10 ($x = 0.09$) at 375°C and 5 ($x = 0.17$) at 425°C, indicating that Ti partitions weakly to the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ phase. The precipitate compositions are almost invariant with aging time.
- Residual Ti is observed in analyzed volumes (10^4 – 10^6 nm³) of the α -Al solid solution near the precipitates, which is greater than the calculated solid solubility. The small concentration of Ti in the $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ precipitates as well as the enriched Ti concentration beyond the calculated solubility in α -Al, indicate that global thermodynamic equilibrium has not been achieved after 1600 h at 375°C or 400 h at 425°C. This is consistent with 3-D APT studies on Al-Sc-Ti alloys aged at 300°C (van Dalen et al., 2005).
- There is a correlation between the measured Ti concentration in α -Al solid solution (within the volume of a typical 3-D APT analysis, ca. 10^4 – 10^6 nm³) and proximity of the analysis to the precipitate-rich dendrites, which is reflective of the initial nonuniform distribution of solute atoms.
- There is no indication of Ti segregation at the α -Al/ $\text{Al}_3(\text{Zr}_{1-x}\text{Ti}_x)$ heterophase interface. However, ion trajectory overlap at the reconstructed matrix/precipitate heterophase interface (due to the disparity in evaporation fields between both phases) increases uncertainties for the measured composition at this interface. The measured compositions in the center of the precipitates should, however, be unaffected by trajectory overlap effects and are therefore reliable.

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