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Monodisperse $Al_3(LiScZr)$ core/shell precipitates in Al alloys

V. Radmilovic,[a,*] A. Tolley,[a,b] E.A. Marquis,[c] M.D. Rossell,[a] Z. Lee[a] and U. Dahmen[a]

[a] *National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, University of California, One Cyclotron Road, Berkeley, CA 94720, USA*
[b] *Centro Atomico Bariloche, CNEA, CONICET, 8400 San Carlos de Bariloche, Argentina*
[c] *Department of Materials, Oxford University, Parks Road, Oxford OX1 3PH, UK*

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We demonstrate a way of producing monodisperse $Al_3(LiScZr)$ core/shell inclusions using solid-state reactions. A uniform distribution of particles with a Li- and Sc-rich core surrounded by Li-rich shell a few nanometers thick with Zr segregating at the core/shell interface can be made reproducibly by exploiting kinetic and thermodynamic parameters. This approach to generating precipitate distributions can be applied to a range of alloys and could lead to new types of dispersion-strengthened materials.
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Binary aluminum alloys based on dispersion strengthening by $L1_2$ precipitates of the type Al_3B are known to yield high-strength materials of scientific as well as technological interest. The binary systems Al–Li, Al–Zr and Al–Sc all form $L1_2$ phases under different thermodynamic conditions. Precipitation of Al_3Li occurs immediately upon quenching [1–3], whereas Al_3Zr [4–6] and Al_3Sc [7,8] form metastable and stable phases after quench-aging treatments. Additions of Zr (<0.08 at.%) and Sc (<0.2 at.%) inhibit recrystallization and control grain size through the presence of the coherent cubic Al_3Zr and Al_3Sc particles [4,5], improve toughness and stress corrosion cracking resistance [4,5], control quench rate sensitivity [5,9] and offer preferential nucleation sites for other strengthening precipitates [10,11]. It was shown recently that Al_3Sc precipitates can serve as heterogeneous nucleation sites for metastable Al_3Zr, resulting in the formation of core/shell coherent precipitates in Al-rich Al–Sc–Zr alloys [12,13].

Additions of Sc and Zr to binary Al–Li alloys have led to Al_3Li precipitates enveloped by coherent Al_3Sc and Al_3Zr phases. These composite core/shell precipitates are thought to be due to a reduction in strain energy, surface energy and growth rate [4,5,14,15].

The formation of core–shell nanoparticles was first observed in Al–Li–Zr alloys [16] and has subsequently been reported for other Al rich alloys [12,13]. However, the formation of core/shell structure precipitates in Al–Li–Sc–Zr alloys has not been reported before. The aim of this paper is to demonstrate that such a structure can be obtained via a solid-state reaction. By combining atom probe tomography and transmission electron microscopy with spectroscopy and diffraction techniques, we investigate the underlying mechanisms that control the formation of these unusual structures.

The chemical composition of the Al–Li–Sc–Zr alloy used in this study is listed in Table 1. The material was heat treated in two stages. After annealing for 18 h at 450 °C, the material was heated for 4 h at 190 °C.

The Al–Li–Sc–Zr ingot processed alloy was produced in an electric arc furnace in an Ar atmosphere at $\sim$15 Torr, following by fast cooling in a Cu water-cooled mold. The ingots were re-melted three times to ensure homogeneous distribution of Zr and Sc. The as-cast rods were homogenized and solution heat treated by annealing for 67 h at 640 °C in an Ar atmosphere inside a quartz tube, and then quenched in water. Transmission electron microscopy (TEM) samples were prepared by cutting slices with a slow-speed diamond saw, punching 3 mm discs from these slices, followed by electrolytic thinning using a double jet electropolishing technique in a solution of 1/3 nitric acid 2/3 methanol at -25 °C in the range between 12 and 14 V. The TEM specimens were examined by electron microscopy at 200 and 300 kV operating voltages. Atom probe samples were prepared using conventional electropolishing

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* Corresponding author. Tel.: +1 510 4865663; fax: +1 510 4865888; e-mail: vrradmilovic@lbl.gov

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Table 1. Chemical composition of AlLiScZr alloy

[%]	Zr	Li	Sc	Al
Mass	0.46	1.69	0.62	Balance
Atomic	0.13	6.30	0.36	Balance

methods [17]. Using a LEAP-3000X microscope, the specimens were held at 25 K, and field evaporation was performed using 20% pulse fraction and 200 kHz pulse repetition rate.

Figure 1 shows a typical distribution of monodisperse core/shell precipitates in the Al–Li–Sc–Zr alloy under investigation after heating for 18 h at 450 °C followed by 4 h at 190 °C. The dark field image (Fig. 1a) was taken using a 1 1 0 superlattice reflection in an orientation near the [0 0 1] zone axis. Characteristic $L1_2$ superlattice reflections from the precipitates are clearly visible in the selected area diffraction pattern shown in Figure 1b. The precipitates exhibit a dark core surrounded by a brighter shell. The mean outer diameter of the particles was 30.3 ± 1.5 nm, and the number density was $2.5 \pm 0.3 \times 10^{-6}\ \text{nm}^{-3}$, resulting in a volume fraction of 3.6%. The mean core diameter was 14.0 ± 0.7 nm.

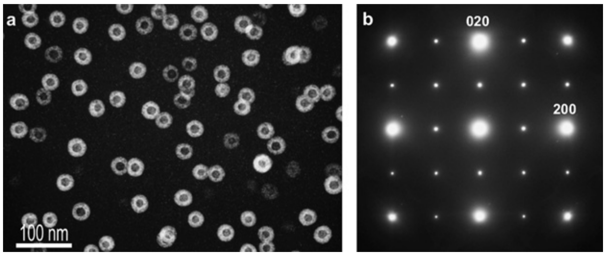

Figure 1. (a) Dark field image of an Al–Li–Sc–Zr alloy aged for 18 h at 450 °C and 4 h at 190 °C, recorded using 1 1 0 superlattice reflection; (b) selected area diffraction pattern in the [0 0 1] zone axis. Cubic $Al_3(LiScZr)$ forms a thin shell between the $Al_3(ScLi)$ core and the metastable cubic Al_3Li outer shell.

Figure 2 presents the results of atom probe tomography (APT) in a specimen subjected to the same double-stage heat treatment. Three-dimensional (3-D) reconstructions indicating the distribution of Li, Sc and Zr atoms are shown in Figure 2a, b and c, respectively. Three precipitates are clearly observed. Figure 2d shows a representative concentration profile across one of the precipitates. All the precipitates that were analyzed showed a core containing Sc and Li, surrounded by a Li-rich shell. An increase in Zr concentration at the Sc-rich core/Li-rich shell interface was also observed. The core composition is 12 ± 1 at.% Sc, 10 ± 1 at.% Li and 75 ± 5 at.% Al. The composition of the shell is 20.0 ± 3 at.% Li and 78 ± 5 at.% Al. The Zr content at the core/shell interface is between 0.2 and 0.8 at.%, up to five times the Zr content in solid solution. It should also be noted that a concentration of approximately 5 ± 1 at.% Li is measured remaining in solid solution. Some of the features visible in Figure 2 are artifacts due to data reconstruction. The Sc-rich cores, which evaporate at a higher field [18], appear elongated in the lateral directions due to a magnification effect. This reconstruction artifact has been observed in many other systems [17].

The distributions of Li and Sc in these precipitates were confirmed by energy filtered imaging using Li and Sc jump ratios, as shown in Figure 3. Figure 4 shows a high-resolution electron microscopy (HREM) image of a precipitate. The core region in the center of the particle shows a contrast that is very similar to that of the Al matrix, whereas the outer shell shows the characteristic contrast corresponding to the $L1_2$ superlattice structure.

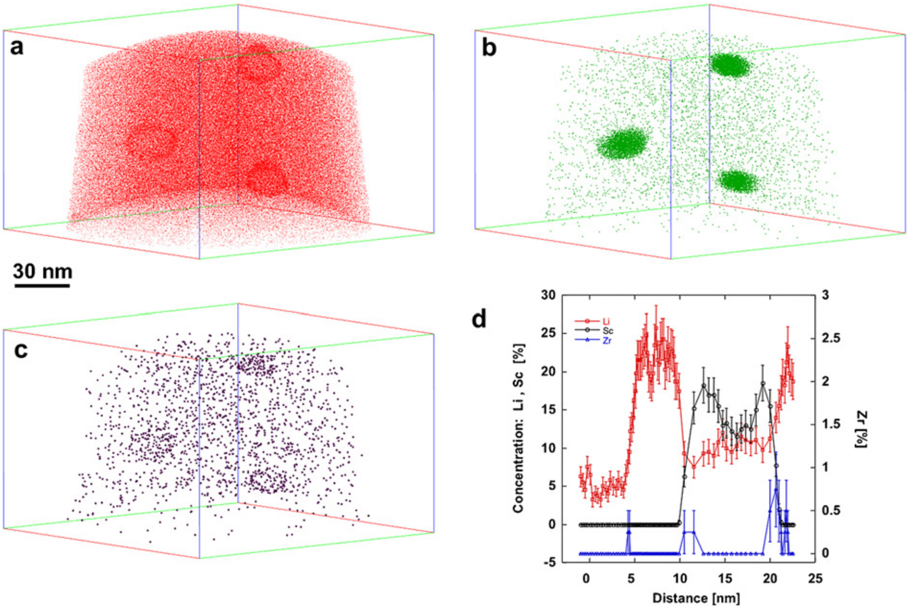

Figure 2. 3-D reconstruction (130 nm × 130 nm × 85 nm) containing three precipitates and showing the Zr-rich and Li-rich regions around the Sc + Li-rich cores: (a) Li atoms; (b) Sc atoms; (c) Zr atoms and (d) concentration profile across the core/shell particle.