Acta Materialia 144 (2018) 80–91

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Microstructure and mechanical properties of a precipitation-strengthened Al-Zr-Sc-Er-Si alloy with a very small Sc content

Anthony De Luca [a, *], David C. Dunand [a, b], David N. Seidman [a, b, c]

[a] Northwestern University, Department of Materials Science and Engineering, 2220 Campus Drive, Evanston, IL 60208-3108 USA
[b] NanoAl LLC, Illinois Science + Technology Park, 8025 Lamon Ave, Suite 446, Skokie, IL 60077 USA
[c] Northwestern University Center for Atom-Probe Tomography, 2220 Campus Drive, Evanston, IL 60208-3108 USA

ARTICLE INFO

Article history:
Received 21 August 2017
Received in revised form
16 October 2017
Accepted 16 October 2017

Keywords:
Al-Zr-Sc-Er-Si alloy
Atom-probe tomography
Precipitation strengthening
High-temperature alloy
Mechanical properties

ABSTRACT

The precipitation hardening behavior of an Al-0.08Zr-0.014Sc-0.008Er-0.10Si (at.%) alloy was investigated utilizing microhardness, electrical conductivity, atom-probe tomography (APT), and compressive creep-measurements. This new composition, with a Sc:Zr atomic ratio of less than 1:5 represents a significant reduction of the alloy's cost when compared to the more usual Al-0.06Sc-0.02Zr based alloys with typical Sc:Zr atomic ratios of 3:1. To study the precipitation behavior of this *low-Sc alloy*, isothermal aging experiments between 350 and 425 °C for a duration of up to 6 months were performed. The low concentration of Sc, compensated by the high Zr concentration, permits the alloy to achieve a higher peak microhardness than the corresponding Sc-richer, Zr-leaner alloys. The *low-Sc alloy* also shows better over aging resistance, as anticipated from the smaller diffusivity of Zr when compared to Sc, leading to slower coarsening kinetics. Atom-probe tomography demonstrates that the high microhardness is due to the formation of a high number density of nano-precipitates, ~10^{23} m^{-3} for peak aging conditions, with a mean radius of 1.9 nm, thus yielding a high volume fraction (0.35%) of nano-precipitates. Like alloys with much higher Sc and Er concentrations, the $(Al,Si)_3(Sc,Zr,Er)$ nano-precipitates still exhibit a core-shell structure with a concentration of Zr in the shell of up to 25 at.%, and a Sc- and Er-enriched core. Compressive creep experiments at 300 °C demonstrate that the new alloy, with only 0.014 at% Sc, is as creep resistant as a binary Al-0.08Sc at.% alloy, displaying a threshold stress of 17.5 ± 0.6 MPa at peak aged condition.

1. Introduction

The automotive industry has steadily reduced the environmental footprint of vehicles by making more efficient use of fuel. One way to achieve this goal is to decrease vehicle mass by an increased use of low-density aluminum alloys. Most commercial aluminum alloys are, however, limited to low temperatures (i.e., below ~225 to 250 °C) due to the dissolution or phase transformation of their strengthening precipitates. To deploy aluminum alloys for high temperature applications in automotive and aerospace, one approach is to create coherent $L1_2$ precipitates containing slow-diffusing elements, which strengthen the alloy by impeding dislocation motion and are stable and coarsen only slowly by diffusion at the operating temperature [1].

During the last decade, dozens of $L1_2$ forming Al-alloys have been investigated, with micro-additions of one to five elements [2–30]. These Al-alloys are aimed at optimizing the strength of Al-alloys by achieving higher processing temperatures and maintaining reasonable prices. Building on an alloy studied by Vo et al. [26,29],we engineered a *low-Sc*, high-Zr Al-Zr-Sc-Er-Si alloy [30]. Addition of Zr to Al-Sc alloys improves the coarsening resistance of the $L1_2$ precipitates by forming a Zr-enriched shell around a Sc-enriched core, to form a core/shell precipitates. Al_3Zr however has a smaller lattice parameter mismatch with the Al matrix than Al_3Sc [16]. Replacement of Sc by Zr in this shell reduces the creep strength of the alloy. By contrast, adding Er accelerates the nucleation rate of the $L1_2$ precipitates, forms an Er-enriched core, and since Al_3Er has a larger lattice parameter mismatch with the matrix than does Al_3Sc it markedly improves the creep strength [7,8]. Addition of Er to Al-Sc-Zr alloys thus compensates for the smaller lattice parameter mismatch of the Zr-enriched core [17]. Alternatively, silicon accelerates diffusion and precipitation kinetics of the

* Corresponding author.
E-mail address: anthony.deluca@northwestern.edu (A. De Luca).

https://doi.org/10.1016/j.actamat.2017.10.040
1359-6454/

$L1_2$ formers [20,26,29]. The effect of Si on the $L1_2$ precipitate-matrix lattice parameter mismatch is, however, unknown. The newly investigated Al-0.08Zr-0.014Sc-0.008Er-0.10Si at.% alloy [30], represents a drastic reduction of price, because Sc is extremely expensive. Utilizing the current prices of Sc, Zr, Er and Al (2017) of 15,000, 100, 95 and 0.44 USD/kg, respectively [31,32], the cost of the new alloy is ~6 USD/kg, compared to ~16 USD/kg for the previous Sc-richer composition; this is nearly a threefold decrease in cost. We previously demonstrated that the alloy achieved a similar peak microhardness of 587 ± 20 MPa as the Sc-richer alloy during isochronal aging [30]. The position of the peak shifted 50 °C toward higher temperatures yielding a better coarsening resistance than anticipated. An optimal single-step aging temperature was estimated to lie between 350 and 425 °C.

This article investigates the precipitation hardening behavior of the above *low-Sc alloy* during isothermal aging in the temperature range 350–425 °C. The alloy exhibits increased strength and coarsening resistance at the investigated temperatures compared to Sc-rich alloys, and is as strong as an Al-0.08Sc alloy when crept at 300 °C. APT investigation reveals that the higher strength achieved is due to the presence of a high number density and a high volume fraction of nanometer diameter precipitates.

2. Experimental procedures

An alloy with a nominal composition of Al-0.08Zr-0.02Sc-0.005Er-0.10Si at.% (Al-0.27Zr-0.03Sc-0.03Er-0.10Si wt.%), was melted in alumina crucibles in a resistively heated furnace by adding, to molten 99.99 at.% pure Al, appropriate amounts of Al-8.0 wt% Zr, Al-2 wt.% Sc, Al-3.9 wt% Er master alloys preheated to 640 °C and Al-12.6 wt% Si preheated at 450 °C. The melt was maintained in air for 1 h at 800 °C, regularly stirred, and then cast into a graphite mold. The mold was preheated to 200 °C and placed on an ice-cooled copper platen prior to casting to enhance directional solidification. The chemical composition of the as-cast alloy was measured by direct current plasma mass spectroscopy (DCPMS) at ATI Wah Chang (Albany, OR (Table 1). The iron concentration was less than the detection limit (<100 wt ppm). APT was also utilized to measure alloy chemical compositions, using the average values of ten specimens (cf. Table 1). The LEAP tomography results are in reasonable agreement with the DCPMS measurements. When compared, however, to the nominal composition, the Sc concentration is lower. In this article, we use the DCPMS composition of the alloy, Al-0.08Zr-0.014Sc-0.008Er-0.10Si at.%, and we express all compositions in atomic percent (at.%). For easier reading, and compared with other alloys, this alloy is denoted the *low Sc alloy*.

After quenching, the alloy was homogenized in air for 8 h at 640 °C, which was determined to be the optimized homogenization condition [30]. The alloy was then subjected to isothermal aging at 350, 375, 400 and 425 °C, for durations ranging from 20 min to 6 months. All heat treatments were performed in air and terminated by water quenching.

Vickers microhardness measurements were performed employing a Duramin-5 microhardness tester (Struers) utilizing an applied load of 200 g for 5 s on samples polished to at least a 1 μm surface finish. A minimum of ten and up to twenty indentations, on different grains, were made for each specimen. Electrical conductivity measurements were performed utilizing a Sigmatest 2.069 eddy current instrument (Foerster Instruments, Pittsburgh, PA). For each specimen, five measurements were made at 120, 240, 480, and 960 kHz.

Specimens for three-dimensional (3D) local-electrode atom-probe (LEAP) tomography were prepared by cutting with a diamond saw ~0.35 × 0.35 × 10 mm^3 blanks, which were electropolished at 20–25 VDC using a solution of 10% perchloric acid in acetic acid, followed by electropolishing at 12–18 VDC utilizing a solution of 2% perchloric acid in butoxyethanol, both at room temperature [33,34]. Pulsed-laser atom-probe tomography was performed utilizing a LEAP 4000X Si-X tomograph (Cameca Instruments Inc., Madison, WI) [35,36] at a specimen temperature of 30 K. Focused picosecond ultraviolet (UV) laser pulses (wavelength = 355 nm) with a laser beam waist of <5 μm at the e^{-2} diameter were utilized. Analyses were performed with a pulse frequency of 500 kHz while maintaining a detection rate of 1 or 2%. To reduce the white noise in the mass spectra for the Zr^{3+} ions due to the thermal tail of the Al^{1+} ions, the laser energy was adjusted for each experiment, and ranged between 15 and 24 pJ $pulse^{-1}$. This adjustment was achieved to obtain a compromise between a lower $Al^{1+/2+}$ ratio and low overall white noise in the mass spectra. LEAP tomographic data were analyzed employing IVAS v3.6.1 (Cameca Instruments). The LEAP datasets were reconstructed in the voltage mode and the initial nanotip radius was adjusted in to obtain the correct aluminum atomic interspacing for the observed crystallographic {hkl} planes.

Constant-load compressive creep experiments were performed at 300 °C, with a thermal fluctuation of ±1 °C. Cylindrical creep specimens with a 10 mm diameter and 20 mm height, were placed between boron-nitride-lubricated alumina platens, and heated in a three-zone furnace. Sample displacement was measured with a linear variable displacement transducer (LVDT) with a resolution of 10 μm. Minimum strain rates at a given stress were determined by measuring the slope of the strain vs. time line in the steady-state creep regime. The applied load was increased when a clear steady-state strain rate was observed. The total accumulated creep strain for each specimen was maintained below 10% to guarantee that the shape of the specimens remained cylindrical and the applied stress uniaxial.

Table 1
Composition (at.%) of the investigated alloy, as measured by direct plasma emission spectroscopy (DCPMS) and local-electrode atom-probe (LEAP) tomography.

	Zr	Sc	Er	Si
Nominal	0.08	0.02	0.0045	0.10
DCPMS	0.075	0.014	0.0075	0.094
LEAP	0.060	0.011	0.0025	0.094[a]

[a] Atomic concentration of $^{28}Si^{2+}$ ions in the LEAP tomographic mass spectrum.

3. Results

3.1. Isothermal aging at temperature ranging from 350 to 425 °C

The temporal evolution of the Vickers microhardness and electrical conductivities of the *low Sc alloy*, homogenized for 8 h at 640 °C, and then aged at 350, 375, 400 and 425 °C, are plotted as a function of aging time in Fig. 1. At 350 °C, the microhardness gradually increases from the as-homogenized state (251 ± 7 MPa) and peaks at 639 ± 29 MPa after aging for 40 h. This slow hardening rate is due to the sluggish diffusion of Zr at 350 °C. For longer aging times, the microhardness decreased slowly and stabilized at ~600 MPa between 3 weeks and 3 months. It later decreased to 554 ± 25 MPa after 6 months. The electrical conductivity (Fig. 1b) increased steadily from 30.06 ± 0.09 MS m^{-1} to 33.66 ± 0.07 MS m^{-1} after 40 h, indicating continuous precipitation. Beyond peak aging, the rate of change on the EC curve decreases with increasing aging times and after six months, the measured electrical conductivity was 34.94 ± 0.1 MS m^{-1}. The change in rate after 40 h indicates that the driving force for precipitation has been greatly reduced and the matrix composition is approaching equilibrium.