Magnesium Technology 2008 *Edited by Mihriban O. Pekguleryuz, Neale R. Neelameggham, Randy S. Beals, and Eric A. Nyberg*
TMS (The Minerals, Metals & Materials Society), 2008

LOCAL-ELECTRODE ATOM-PROBE TOMOGRAPHIC INVESTIGATION OF STRENGTHENING PRECIPITATES IN A Mg-7Zn-3Al ALLOY AT PEAK HARDNESS

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Keywords: Precipitation Strengthening, Mg Alloys, LEAP Tomography

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Abstract

The precipitates in the Mg–7Zn–3Al (in wt. %) alloy aged to peak hardness at 150°C have been characterized by local-electrode atom-probe (LEAP) tomography. The chemical compositions of the matrix and the precipitates were measured and compared with the results calculated using the COST2 database by the Thermo-Calc software. Ternary nanoscale precipitates have been found consistent with the predicted φ phase demonstrating a metastable composition. The measured particle size at peak hardness, corresponding to an equivalent sphere radius of 17 nm, provides an important calibration point for quantitative modeling of precipitation strengthening for alloy design.

Introduction

While typical Mg-Al-Zn casting alloys such as AZ91 are Al-rich, Zn rich alloys associated with the Zn-rich lower ternary eutectic can provide low melting compositions with the potential for greater precipitation strengthening. A previous study demonstrated that ZA143 alloy aged to peak hardness at 150°C for 100 hrs could reach a yield strength of 190 MPa.

While details of precipitation strengthening in Mg-Al-Zn alloys are not well known, the precipitation strengthening in binary MgZn alloys has been well studied. The precipitation sequence in Mg-Zn is well documented starting from G. P. zone formation, followed by the formation of β_1' and β_2' metastable precipitates before reaching the formation of equilibrium β phase [1-7].

In the present work, the Mg–7Zn–3Al (in wt. %) was investigated. Its microhardness after precipitation heat-treatments at 150°C was measured. The precipitates aged to peak hardness were characterized by a local-electrode atom-probe (LEAP) tomography (Imago Scientific Instruments (Madison, WI)) at the atomic level as the basis for calibration of precipitation strengthening models for Mg alloys design. According to the size, shape and composition of the precipitates, the interfacial energy between the matrix and the precipitates was determined.

Experiment

A ZA73 alloy (Mg–7Zn–3Al, wt. %) was induction melted under an Ar atmosphere and cast into ingots. The samples were encapsulated together in a pyrex tube in vacuum to prevent oxidation of the magnesium and then backfilled with argon to prevent vaporization of the zinc. These samples were heated in a furnace at a solution treatment temperature of 358 °C for 24 hours and then quenched in oil to retain a super-saturated solid solution. Samples were then encapsulated individually and aged in a furnace for 100 hours at 150 °C corresponding to the peak hardness conditions identified in a previous study [8]. Vickers microhardness was measured using a 200 g weight and 10 seconds load time ground to a 1 μm surface finish.

In order to make the LEAP tomographic sample, square bars having a dimension of 0.5 mm×0.5 mm×12 mm were cut from the bulk specimens and electropolished to make sharp needle specimens. The electropolishing electrolyte was a solution of 2 vol. % perchloric acid in 2-butoxyethanol and the voltage was initially set at 25 V and reduced to 5 V when pulsing. The sharpened specimens were rinsed carefully in ethanol after electroplishing.

LEAP tomographic analyses were performed at a tip temperature of about 40 K to minimize atomic motion in an ultrahigh vacuum condition (residual pressure < 10^{-8} Pa) with an applied high voltage pulses at a frequency of 200 kHz and a pulse fraction (ratio of pulse voltage to the steady-state voltage) of 0.2. The voltage levels required for field evaporation are dependent on the radius of curvature of each specimen tip, with the standing DC voltage ranging from 500V for very sharp tips (diameter < 10nm) to 15,000V for larger tips (~100nm diameter). Steady field evaporation rates of 400-10,000 atoms/second were maintained through software-controlled manipulation of the voltage levels, with applied voltage steadily increased to account for tip blunting with continued specimen evaporation.

Both voltage-pulse and laser-pulse modes of field evaporation were applied in this study. One tip sample was investigated using the common voltage-pulse mode. Another tip sample was investigated using the alternative laser-pulse mode. The alternative mode of operation of pulsed-laser evaporation reduces the frequency of nanowire fracture by eliminating the voltage pulses in favor of more localized laser excitation, which does not produce a repetitive stress on the sample. In addition to reducing specimen fracture, laser pulsing generally produces sharper mass spectra and fewer unidentified peaks.

Three-dimensional tomographic reconstructions were obtained, using Imago's computer program IVAS 3.0 and proximity histograms (proxigrams) [9] were calculated employing IVAS 3.0

and Apex software [10], utilizing an isoconcentration surface of 20 at.% Zn. The average precipitate and matrix concentrations were calculated by employing the fraction of total atoms in the pertinent volume. Standard deviations (σ) of measured compositions through the LEAP analysis were calculated using Eq. 1 [11]:

$$\sigma_c = \sqrt{c(1-c)/N} \qquad (1)$$

where c is the measured composition of the particular element, N is the total number of atoms detected.

Results and discussion

Fig. 1 displays the Vickers microhardness as a function of aging time at 150 °C for the ZA73 alloy studied. It shows that the Vickers microhardness increases a lot after aging for 100 hrs comparing with that after solution treatment. Corresponding to the peak hardness conditions identified in a previous study [8], it is believed the peak hardness was achieved after aging at 150 °C for 100 hrs.

Fig. 2 (a) displays LEAP tomographic reconstructions for the ZA73 alloy aged at 423 K for 100 hours using the voltage-pulse mode. A proximity histogram (proxigram) showing the concentration of Mg, Zn, Al and Ca as a function of radial distance from the precipitate interfacial is also presented in Fig. 1 (b). It is apparent that both Zn and Al partition to the precipitates. The Zn and Al contents are very low in the matrix. The approximate chemical compositions of the matrix and the precipitates can be read in this proximity diagram. The average chemical compositions of the matrix and the precipitates are reported in Table. 1.

Fig. 2 (a) displays LEAP tomographic reconstructions for a second equivalent specimen using the laser-pulse mode. A proxigram showing the concentration of Mg, Zn, Al and Ca as a function of radial distance from the precipitate interfacial is also presented in Fig. 2 (b). It is again apparent that both Zn and Al partition to the precipitates, while the Zn and Al contents are very low in the matrix. The average chemical compositions of the matrix and the precipitates are reported in Table. 1. Equilibrium thermodynamic calculations were carried out using the alloy nominal composition. The COST2 database [12] and Thermo-Calc software [13] were used. The calculation shows that hcp and φ phases ($Mg_6(Zn, Al)_5$) are in equilibrium. The calculated chemical compositions of the matrix and the precipitates are also listed in Table. 1. Compared with the experimental data, the equilibrium calculations show a higher Mg content, lower Zn and Al contents in the matrix and a lower Mg content, higher Zn and Al contents in the precipitates. This discrepancy indicates that the precipitates observed in experiments might be a metastable phase, not an equilibrium phase.

The calculated isothermal section at 423 K is shown in Fig. 4 with equilibrium and experimental lines. The composition point of ZA73 alloy locates in the two phase region which says the precipitates are the phase. However, the experimental composition points of precipitates locate in the three phase region. It is believed that the precipitates are the metastable phase since the precipitates composition points near the extrapolated line of the phase. The detected matrix composition is much more Mg-lean which can be caused by the capillarity effect.

Conclusions

In summary, a study of the precipitation hardening nanostructure of Mg-7Zn-3Al (in wt .%) aged to peak hardness at 423 K for 100 hrs was performed. The chemical compositions of the alloys as well as the matrix and the precipitates were measured by LEAP tomography and compared with the results calculated by the Thermo-Calc software based on the COST2 database. Ternary nano-sized precipitates have been found. The precipitates have compositions consistent with the ternary φ phase including its metastable extention. The precipitate size at peak hardness corresponds to an equivalent sphere diameter of 17 nm.

Acknowledgment

This research was supported by the US Department of Energy, under the grant DE-AC05-00OR22725 with subcontract No. 4000054701, titled "Center for Virtual Design and Manufacturing" at Mississippi State University. Matching funds were provided by General Motors. The LEAP tomograph was purchased with funding from the NSF-MRI (Grant DMR-0420532) and ONR-DURIP (Grant N00014-0400798) programs. We thank Dr. Michele Manuel for supplying alloys and help during the sample preparations. We also thank Dr. Dieter Isheim for helpful discussions on quantitative microanalysis.

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Table 1. Composition of the matrix and the precipitates in ZA73 alloy as measured by LEAP spectrometry and by equilibrium calculations using Thermo-Calc and COST2 database.

at. %		Matrix			Precipitates		
Elements		Mg	Zn	Al	Mg	Zn	Al
LEAP analysis	I	91.81±0.30	2.98±0.19	5.21±0.23	51.79±3.45	38.08±3.40	10.13±2.02
	II	94.48±0.14	2.63±0.07	2.89±0.12	54.91±2.21	32.39±2.16	12.70±1.34
Thermo-Calc calculation		98.57	0.64	0.79	54.55	23.85	21.61

I: voltage-pulse mode; II: lase-pulse mode.

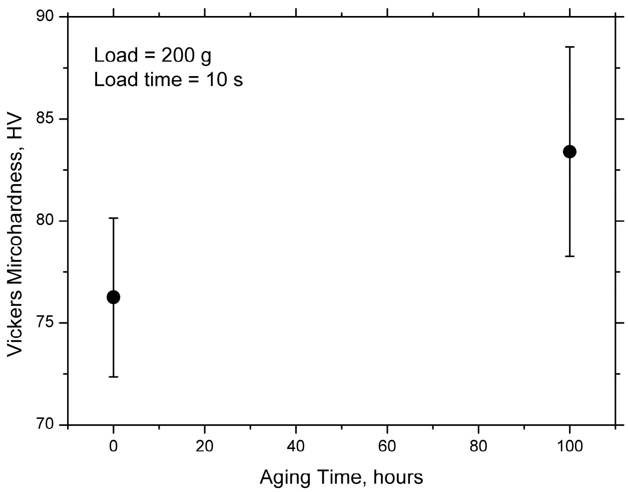
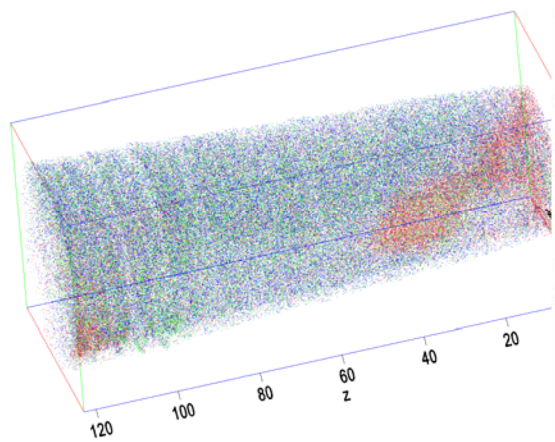
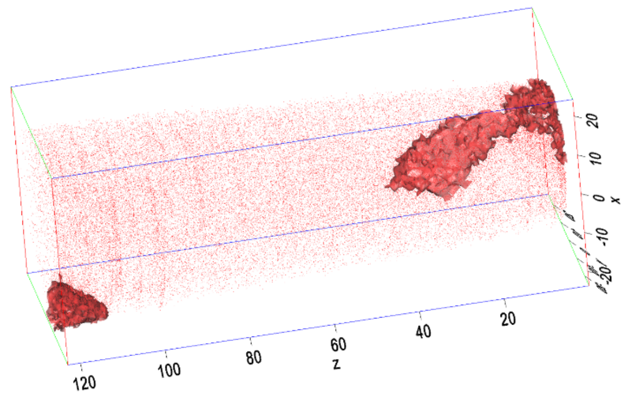


Fig. 1. Vickers microhardness vs. aging time at 150 °C for Mg-7Zn-3Al. Error bars are one standard deviation from the average.



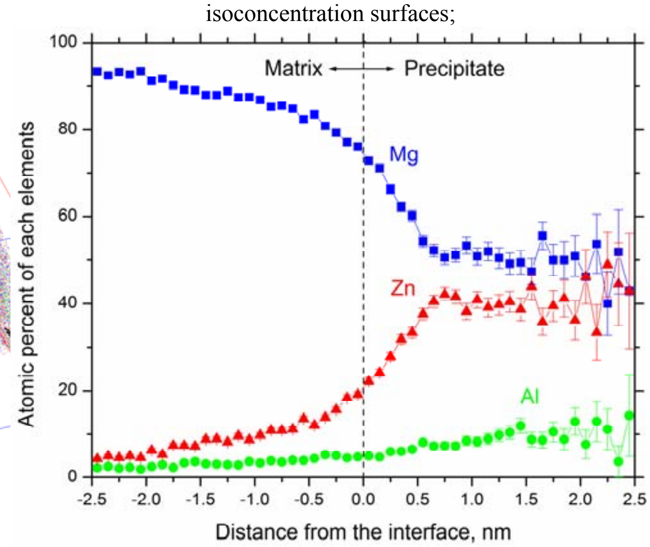
(a)

Fig. 2. (a) LEAP tomographic reconstructions of Mg-7Zn-3Al using the voltage-pulse mode;



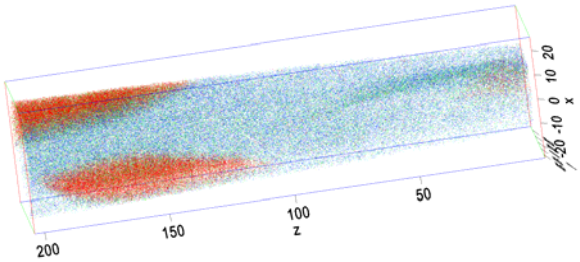
(b)

Fig. 2. (b) LEAP tomographic reconstructions of 20 % Zn isoconcentration surfaces;

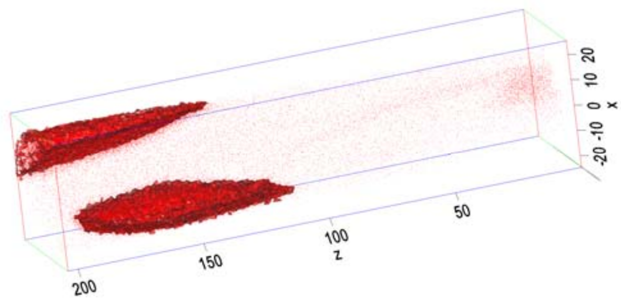


(c)

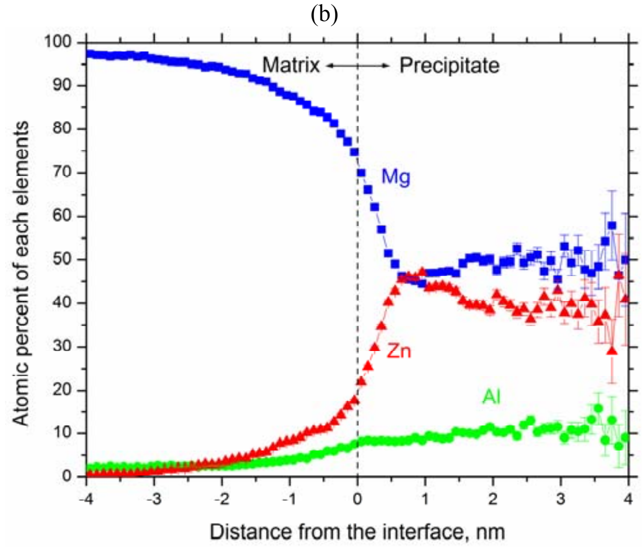
Fig. 2. (c) Proximity histogram for the LEAP tomographic reconstructions displayed in Fig. 2 (a) showing the average concentration of Mg, Al, Zn and Ca as a function of distance from the Mg-Zn-Al ternary heterophase interfacial, as defined by a 20 at. % Zn isoconcentration surface.



(a)



(b)



(c)

Fig. 3. (a) LEAP tomographic reconstructions of Mg-7Zn-3Al using the laser-pulse mode; (b) LEAP tomographic reconstructions of 20 % Zn isoconcentration surfaces; (c) Proximity histogram for the LEAP tomographic reconstructions displayed in Fig. 3 (a) showing the average concentration of Mg, Al and Zn as a function of distance from the Mg-Zn-Al ternary heterophase interfacial, as defined by a 20 at. % Zn isoconcentration surface.

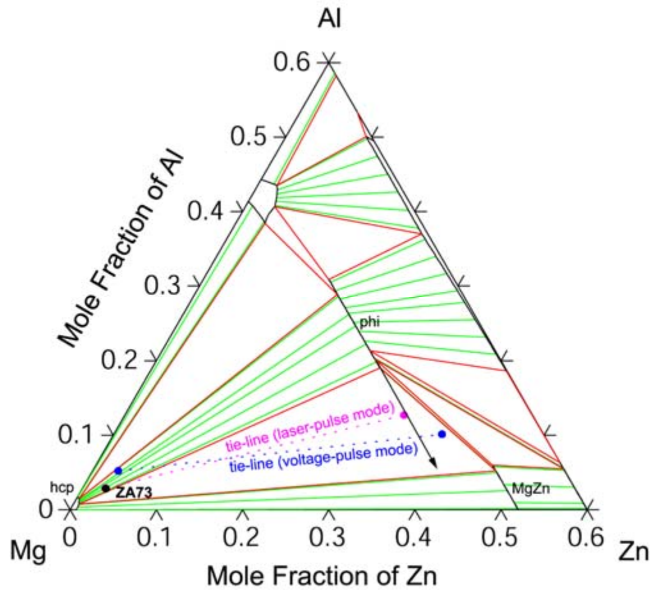


Fig. 4. Calculated isothermal section of the Mg-Zn-Al system at 423 K using the COST2 database. The green lines are the equilibrium tie lines which indicate the two phase regions. The black solid circle is the nominal composition of ZA73 alloy. The blue dashed line is the experimental tie-line using voltage-pulse mode with two solid circles at the both ends. The purple dashed line is the experimental tie-line using laser-pulse mode with two solid circles at the both ends. The line with an end arrow is the extrapolate φ phase in the equilibrium three phase region (hcp + MgZn + φ).