Early stages of precipitation in Mg-RE alloys studied by positron annihilation spectroscopy

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Introduction

Natural aging is a process where solute atoms and vacancies cluster at room temperature in materials quenched from high annealing temperature. It is well known effect and was thoroughly investigated in Al-based alloys [1-4]. Significant strengthening occurs because solute clusters developed during natural aging hinder movement of dislocations. Contrary to Al-based alloys, natural aging of Mg-based is not common. So far, natural aging was observed in Mg-Zn-based alloys [5] and, recently, in our work in Mg-Gd and Mg-Tb alloys [6].

Samples

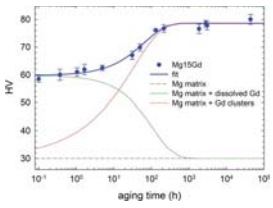
Binary Mg-Gd and Mg-Tb were produced by squeeze casting under a protective atmosphere (Ar + 1% SF_6) with following concentrations in wt. %:

	Gd	Tb	Mg
Mg4Gd	4.48	-	balance
Mg9Gd	9.24	-	balance
Mg15Gd	14.58	-	balance
Mg13Tb	-	13.39	balance

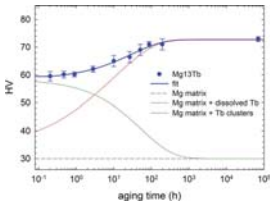
The as-cast Mg-Gd and Mg-Tb alloys were subjected to solution treatment at 500 and 530°C, respectively, for 6 hours finished by quenching into water at room temperature. Samples were subsequently naturally aged at ambient temperature (20°C).

Results (1)

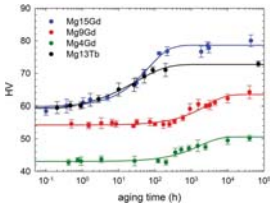
Microhardness of all studied alloys increases with increasing aging time. The time dependence of microhardness plotted in the logarithmic time scale exhibits characteristic S-shaped curve typical for natural aging.



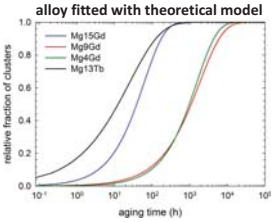
Measured microhardness of Mg15Gd alloy fitted with theoretical model



Measured microhardness of Mg13Tb alloy fitted with theoretical model



Comparison of microhardness evolution during natural aging of studied alloys



Time development of relative fraction of clusters obtained from the fit

The hardness of alloy aged for time t can be expressed as:

$$\mathrm{HV}(t) = \mathrm{HV}_0 + \Delta\mathrm{HV}(t)$$

where HV_0 = 30 ± 2 is the hardness of pure Mg matrix and $\Delta\mathrm{HV}(t)$ denotes hardening caused by solute elements:

$$\Delta\mathrm{HV}(t) = \left(\mathrm{HV}_{ss}^2 + \mathrm{HV}_{cl}^2\right)^{1/2}$$

The symbols HV_{ss} and HV_{cl} denote contribution to the hardening caused by solid solution hardening and by clusters of alloying elements, respectively. Let f denote the relative fraction of solute atoms present in clusters. The hardening caused by clusters HV_{cl} is then proportional to $f^{1/2}$ while the solid solution hardening HV_{ss} is proportional to $(1\text{-}f)^{2/3}$ [1]. Hence, the evolution of the hardness during aging can be written as:

$$\mathrm{HV} = \mathrm{HV}_0 + \left[\left(h_{ss}c^{2/3}(1-f)^{2/3}\right)^2 + \left(h_{cl}\left(\frac{c}{N_{cl}}\right)^{1/2} f^{1/2}\right)^2\right]^{1/2}$$

where c is the net concentration of alloying element (Gd or Tb), h_{ss} and h_{cl} are hardening coefficients for solid solution hardening and hardening by clusters, respectively, and N_{cl} is the average number of atoms per cluster.

The clusters in aged alloys develop by nucleation and subsequent growth. Since the studied alloys are coarse grained and exhibit low dislocation density, it is reasonable to assume that heterogeneous nucleation in limited number of suitable nucleation sites takes place. These sites are used at the early stage of clustering and so called site saturation occurs. Under these assumptions, the relative fraction of clusters is given by expression:

$$f = 1 - \exp\left[-(k(T)t)^n\right]$$

where $k(T)$ is the kinetic rate at temperature T and n is the kinetic exponent [1]. Results obtained by fitting the measured data with proposed model of hardening are shown in following table:

	c	h_{ss}	$h_{cl}/(N_{cl})^{1/2}$	k (s^{-1})	n
Mg4Gd	2.57	342(8)	301(3)	4.5(7) × 10^{-6}	0.8(1)
Mg9Gd	1.55	390(5)	269(5)	1.5(4) × 10^{-7}	0.7(1)
Mg15Gd	0.72	340(10)	243(8)	1.8(7) × 10^{-7}	0.8(3)
Mg13Tb	2.23	360(10)	286(4)	1.1(2) × 10^{-5}	0.52(8)

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement N° 289163.

Experimental details

Positron source
- $^{22}Na_2CO_3$ deposited on 2 μm thick mylar foil
- 1 MBq activity

Positron lifetime spectroscopy
- digital positron lifetime spectrometer
- time resolution 145 ps (FWHM)
- at least 10^7 annihilation events in each spectrum
- source contribution from $^{22}Na_2CO_3$ and mylar foil consists of two components with lifetimes 0.368 and 1.5 ns with relative intensities 8% and 1%, respectively.

Coincidence Doppler broadening spectroscopy
- two HPGe detectors
- resolution 1.0 keV at 511 keV (FWHM)
- at least 10^8 annihilation events in each spectrum

Microhardness measurement
- STRUERS Duramin 300 hardness tester
- 100 gf load applied for 10 seconds
- samples were polished using polishing cloths and 3 μm diamond suspension

Results (2)

Diffusion of alloying elements (Gd or Tb) can be facilitated by quenched-in vacancies. Positron annihilation measurements were performed on quenched and aged alloys to study this hypothesis. Results obtained by positron lifetime spectroscopy testify presence of quenched-in vacancies in quenched alloys. The lifetime of the second component $\tau_2 \approx 300$ ps is comparable to that for a monovacancy in Mg [7]. On the other hand, aged alloys exhibit single component spectra with lifetime $\tau_1 \approx 225$ ps which agrees well with the bulk positron lifetime in Mg [7]. Therefore, they are defect free within the sensitivity of positron lifetime spectroscopy.

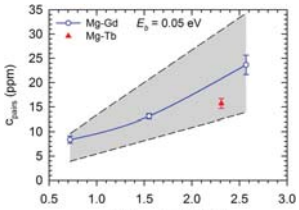
	quenched alloys				aged alloys	
	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_1 (ps)	I_1 (%)
Mg4Gd	219.7(5)	92.5(5)	290(10)	7.5(5)	225.5(2)	100
Mg9Gd	218.6(5)	88.4(5)	300(5)	11.6(5)	225.2(2)	100
Mg15Gd	214.6(7)	80.5(6)	295(5)	19.5(6)	225.4(2)	100
Mg13Tb	214.0(8)	84.3(7)	280(15)	15.7(7)	225.5(2)	100

The concentration of quenched-in vacancy-Gd (or Tb) pairs can be calculated from positron lifetime measurements according to the simple trapping model [8]:

$$c_{pairs} = \frac{1}{\nu_V} I_2 \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right),$$

where ν_v = 1.1 × 10^{13} s^{-1} is the specific positron trapping rate for vacancy in Mg [9]. Values calculated according to this expression can be compared to the equilibrium concentration of vacancy-Gd (or Tb) pairs at solution treatment temperature T given by expression:

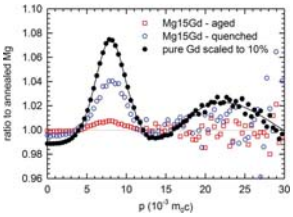
$$c^*_{pairs} = c \exp\left(\frac{S_{v,f}}{k_B}\right) \exp\left(-\frac{E_{v,f} - E_b}{k_B T}\right)$$



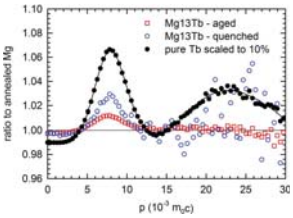
Measured and calculated concentration of quenched-in vacancy-Gd (or Tb) pairs

where k_B is the Boltzmann constant, $S_{vf} \approx 2k_B$ is the vacancy formation entropy [10]. The values of vacancy formation enthalpy E_{vf} reported in literature fall into the range 0.79-0.85 eV [11-13] which is shown in the figure by shaded band. E_b is the binding energy between vacancy and Gd or Tb. The latter quantity is not known, but putting E_b = 0.05 eV, i.e. assuming small attractive interaction between vacancy and Gd or Tb atom, results in agreement of theoretical values with experimental data.

Ratio curves of quenched alloys show peak located at $p \approx 8\ m_0c$ which testifies enhanced concentration of Gd or Tb around quenched-in vacancies and therefore presence of vacancy-Gd (or Tb) pairs. Amplitude of this peak significantly decreases after aging due to disappearance of quenched-in vacancies.



CDB ratio curves for Mg15Gd alloy



CDB ratio curves for Mg13Tb alloy

Conclusions

Natural aging of Mg-Gd and Mg-Tb alloys associated with clustering of solute atoms was observed in this work. Theoretical model of hardening during natural aging showing good agreement with experimental data was developed.

Quenched-in vacancy-Gd (or Tb) pairs are present in solution treated alloys after quenching. Quenched-in vacancies facilitate diffusion of Gd or Tb atoms in Mg matrix and disappear when the formation of clusters is finished.

References

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