DEVELOPMENT OF ELECTRICAL RESISTIVITY DUE TO SOLUTION TREATMENT OF SQUEEZE CAST MAGNESIUM-RARE EARTH ALLOYS

IVANA STULÍKOVÁ*, BOHUMIL SMOLA, NAĎA ŽALUDOVÁ, MARTIN VLACH, JITKA PELCOVÁ

Charles University, Faculty of Mathematics and Physics, Ke Karlovu 5, CZ-121 16 Prague 2, Czech Republic

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The solution heat treatment of Mg-Tb and Mg-Tb-Nd alloys with relatively high solute concentration was characterized by electrical resistivity measurements at 77 K and 293 K. Linear concentration dependence of resistivity at 77 K and 293 K was observed for solution treated Mg-Tb alloy. The resistivity contributions of 1 at.% of Tb in magnesium at 77 K and 293 K were determined. Negative deviations from Matthiesen's rule were found in solution treated Mg-Tb and Mg-Tb-Nd alloys. Precipitation of the $D0_{19}$ phase in solution treated Mg-Tb alloy decreases the slope of resistivity-concentration dependence but does not change the sign of deviation from Matthiesen's rule.

K e y w o r d s: Mg alloys, rare earth, terbium, electrical resistivity

1. Introduction

Age hardenable magnesium alloys with rare earth elements (e.g. WE54, WE43 – MgYNdZr [1]) are recognized as commercial light materials for applications at elevated and high temperatures. The necessity of energy consumption reduction in transport, mainly due to environmental requirements, induces the search for new age hardenable magnesium alloys with other rare earth elements (RE) and their combination [2–5]. Successful solution treatment is of eminent importance for effective subsequent age hardening. Most of RE exhibits a reasonable solubility at eutectic temperature and at those near to it [6]. Therefore it is possible to produce a sufficiently supersaturated solid solution by suitable heat treatment and quenching. The measurement of electrical resistivity response to the isothermal annealing at

*corresponding author, e-mail: ivana.stulikova@mff.cuni.cz

high temperatures is very sensitive and reliable method to study solution treatment process [7].

The total electrical resistivity of dilute alloy may be expressed as

$$\rho(T) = \rho_{\mathrm{P}}(T) + \rho_{\mathrm{S}} + \Delta(T), \tag{1}$$

where ρ_{P} is the resistivity of pure solvent crystal, ρ_{S} is the temperature-independent resistivity due to lattice defects (solutes, clusters, etc.) and Δ is a term representing the deviation from Mathiessen's rule (DMR). Mathiessen's rule is obeyed, if $\Delta(T)$ is negligible.

Variety of Mg-RE binary alloys such as Mg-Gd, Mg-Nd and Mg-Sc were studied from the point of view of DMR, for example [5, 8–16]. The validity of Mathiessen's rule as well as positive and negative DMR were reported. The temperature-independent term ρ_{S} of Mg-RE alloys varies linearly with the solute concentration [5, 9, 17]. The slope of this dependence is characteristic for individual RE solutes.

The aim of the present work is to investigate the possibility of successful solution treatment of Mg-Tb binary alloys with higher Tb content and ternary Mg-Tb-Nd alloy, establish the resistivity-solute concentration relations and determine the possible DMR of the alloys.

2. Experimental details

Binary Mg-Tb and ternary Mg-Tb-Nd alloys were produced by squeeze casting. The nominal notation and weight and atomic concentrations are summarized in Table 1. Pure magnesium of 99.9 wt.% and Tb and Nd of commercial purity 99.5 wt.% were used. The alloy compositions were determined by atomic absorption spectroscopy.

Solution heat treatment of as-cast alloys was carried out in argon protective atmosphere at 803 K (binary alloys) and 773 K (ternary alloy). Heat treatment was interrupted at selected time intervals and specimen was water quenched. Electrical resistivity was then measured at 77 K and 293 K by means of the dc four-point method with a dummy specimen in series. Relative electrical resistivity changes $\Delta\rho/\rho$ were obtained to within an accuracy of 10^{-4}. The effect of a parasitic thermo-

Table 1. Composition, measured and calculated density of investigated alloys

Notation	Tb		Nd		Density [kg·m^{-3}]	
	[wt.%]	[at.%]	[wt.%]	[at.%]	measured	calculated
Mg10Tb	9.72	1.62	–	–	1880 ± 2	1885
Mg15Tb	13.39	2.31	–	–	1940 ± 7	1946
Mg4Tb2Nd	3.96	0.64	2.53	0.45	1829 ± 2	1832

-electromotive force was eliminated by a change in polarity. The ratio $RRR = \rho(293\ \mathrm{K})/\rho(77\ \mathrm{K})$ is independent of specimen form and it generally indicates the purity of the majority conducting phase in alloys (mainly solid solution matrix).

The specimens were H-shaped with dimensions 6 × 5 × 86 mm; the length represents the gauge length for resistivity measurements. The accuracy of specimen dimensions to about 1 % limits that of absolute resistivity values. The deformation of electrical field in the vicinity of contacts was estimated yielding the total accuracy better than 3 %. Microstructure of alloys was monitored by optical metallography and phase composition was determined by electron transmission microscopy (TEM) and electron diffraction (ED) (JEOL JEM 2000FX).

3. Results and discussion

The grain size in as-cast alloys is dependent on the solute concentration. It is about 50 μm for the Mg15Tb, 100 μm for Mg10Tb and Mg4Tb2Nd alloys. Squeeze casting ensures the low porosity of alloys – cf. measured and calculated values of density in Table 1. The ratio RRR of as-cast alloys decreases with increasing total solutes concentration – see Table 2. Figure 1 shows the normalized resistivity isothermal annealing curves of alloys measured at 77 K for the corresponding temperatures of solution heat treatment (803 K and 773 K). Normalized resistivity increases rapidly after 30 minutes annealing about 40 % for binary alloys and about 50 % for ternary alloy (maximum value). The increase slows down for binary alloys reaching a maximum after two hours annealing. The prolonged annealing leads to the insignificant decrease of the normalized resistivity for all alloys studied. This decrease may be ascribed to the observed grain size growth. Grain size reaches approx. 80 μm and 450 μm after 24 h annealing of the Mg15Tb and Mg10Tb, respectively. Grain size in the Mg4Tb2Nd was found to be over 500 μm after the annealing for 4 h. The increase of resistivity is caused by dissolution of phases present after casting into solid solution matrix. The decrease of RRR values compared to those measured in as-cast alloys confirms this interpretation – see Table 2. Again, the RRR values correspond to the total solute concentration.

Table 2. $RRR = \rho(293\ \mathrm{K})/\rho(77\ \mathrm{K})$ ratio for alloys: as-cast, solution treated and isochronally annealed up to 453 K

Notation	Total solutes content	$RRR = \rho(293\ \mathrm{K})/\rho(77\ \mathrm{K})$		
	[at.%]	as-cast	solution treated	solution treated and isochronally annealed to 453 K
Mg4Tb2Nd	1.09	1.553	1.326	–
Mg10Tb	1.62	1.362	1.223	1.260
Mg15Tb	2.31	1.242	1.130	1.160

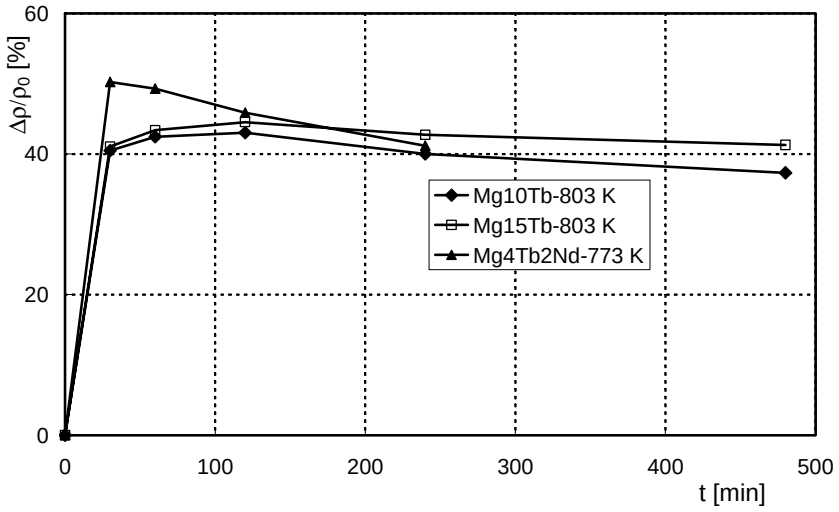

Fig. 1. Normalized resistivity isothermal annealing curves of Mg-Tb and Mg4Tb2Nd alloys. Resistivity was measured at 77 K. ρ_0 is the resistivity of as-cast alloys.

Absolute values of the resistivity both at 77 K and 293 K were determined for binary alloys after annealing at 803 K for 8 h. These values are plotted versus atomic concentration c of Tb in the form of the product $c \times (1 - c)$ in Fig. 2. The concentration dependence obeys Nordheim's concentration rule [18] ($\rho \sim c \times (1-c)$, which yields $\rho \sim c$ for small concentrations c). The contribution of the addition of 1 at.% of Tb to the resistivity of Mg (the slope of $\rho(c)$ linear dependence – $\delta\rho$) is compared to that measured by other authors and to those of some other RE in Table 3. The $\delta\rho$ values are different for different RE solutes contrary to the results of [19, 20]. Comparable values of $\delta\rho$ obtained by [17] for diluted Mg-Tb alloy indicates the successful solution heat treatment.

The negative DMR was found for binary Mg-Tb alloys as the slope $\delta\rho$ is higher for 77 K than for 293 K. Similar result was also found for binary Mg-Tb alloy in [17] and also for other binary Mg-RE alloys listed in Table 3. On the other hand the validity of Mathiessen's rule was observed for Mg-Nd and Mg-Gd alloys in [9]. Using $\delta\rho$ values obtained for Mg-Tb and Mg-Nd alloys the absolute resistivity values of ternary Mg4Tb2Nd alloy were calculated. They agree very well with the measured resistivity – see Table 4.

Decomposition of supersaturated solid solution can influence the value and sign of deviations from Matthiessen's rule. The isochronal annealing of Mg-Tb alloys up to 453 K, which resulted in the precipitation of maximum volume fraction of $D0_{19}$ phase plates in the specimens, did not change the DMR sign. The value of $\delta\rho$

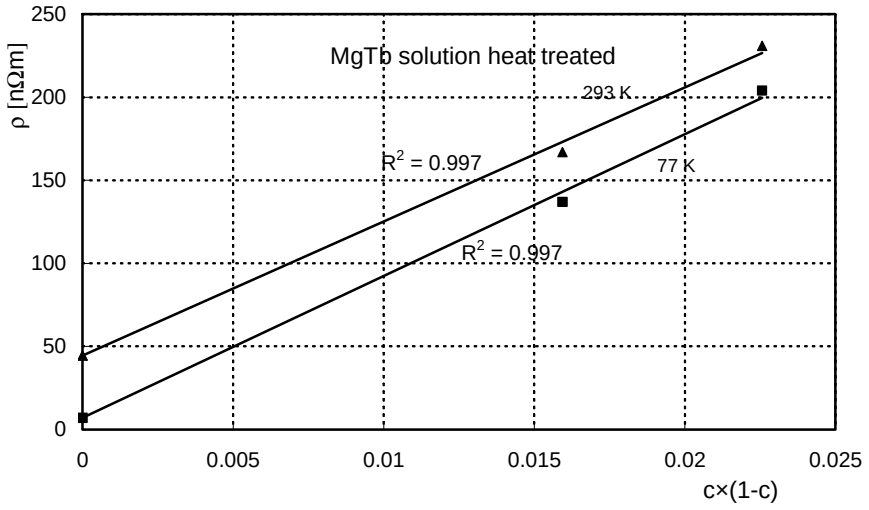

Fig. 2. Dependence of electrical resistivity of Tb solid solution in Mg on product $c \times (1-c)$, where c is atomic concentration of Tb.

Table 3. Contribution of 1 at.% of solute to the resistivity of Mg

Alloy	$\delta\rho$ [nΩm/at.%] 77 K	$\delta\rho$ [nΩm/at.%] 293 K	$\delta\rho$ [nΩm/at.%] 273 K	Ref.
Mg-Tb	83.6	79.1	–	this work
Mg-Tb	88.2	–	74.8	[17]
Mg-Sc	50.9	47.0	–	[5]
Mg-Gd	87.2	80.8	–	[5]
Mg-Gd	91.3	–	86.7	[17]
Mg-Gd	82	–	82	[9]
Mg-Nd	77.0	74.4	–	[5]
Mg-Nd	79.4	–	65.9	[17]
Mg-Nd	95	–	95	[9]
Mg-Nd	115	–	–	[16]

at 293 K (71.09 nΩm/at.%) after this annealing is lower than that at 77 K (74.69 nΩm/at.%) again. These values are significantly lower than corresponding ones for solution treated alloy – Fig. 3 and Table 3. This indicates that the majority conducting phase, namely solid solution matrix, contains less solutes after this isochronal annealing than originally after solution treatment. The higher *RRR*

T a b l e 4. Measured and calculated electrical resistivity of the Mg4Tb2Nd alloy

Temperature [K]	Resistivity [nΩm]	
	measured	calculated
77	94 ± 2	95.3
293	125 ± 3	128.7

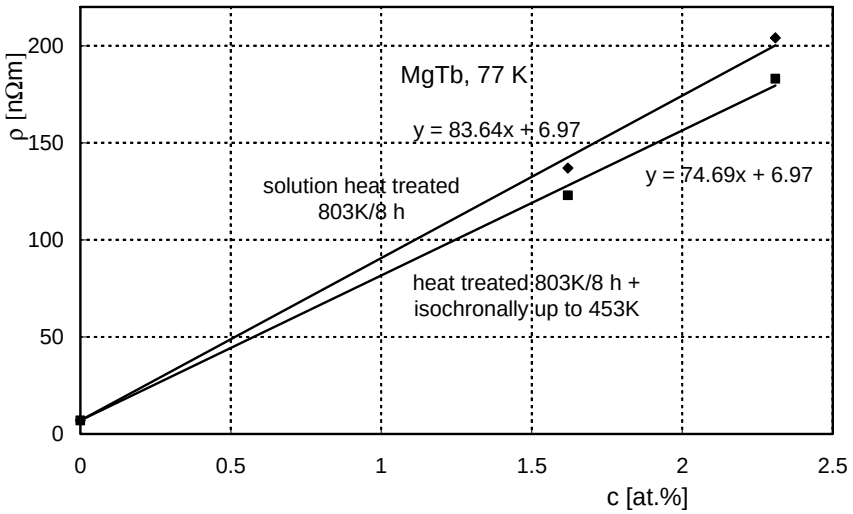

Fig. 3. Dependence of electrical resistivity of Mg-Tb alloys solution heat treated and heat treated to the maximum volume fraction of $D0_{19}$ phase on atomic concentration c of Tb.

values confirm this conclusion – see Table 2. Supposing that this interpretation is valid, the volume fraction of the $D0_{19}$ phase precipitated can be estimated as ~ 0.008. Similar behaviour was found in Mg15Gd alloy isochronally annealed after solution treatment up to the temperature where the maximum volume fraction of the $D0_{19}$ phase precipitated [5].

Temperature coefficient of resistivity α of Mg varies within three orders of magnitude in the temperature range of 4.2–300 K [10]. The magnitude of average α_A coefficient calculated from the resistivity values at 77 K and 293 K of this published dependence agrees very well with that measured in the present work. In the case of validity of Matthiessen's rule the product $\rho(T) \times \alpha(T)$ for an alloy at particular temperature T should be independent of solute concentration and equal to that for pure Mg. The concentration dependence of $\rho(77) \times \alpha_A$ for all alloys studied is presented in Fig. 4 together with those calculated from [17] and those measured in [5]. The product $\rho(77) \times \alpha_A$ decreases with increasing concentration distinctly

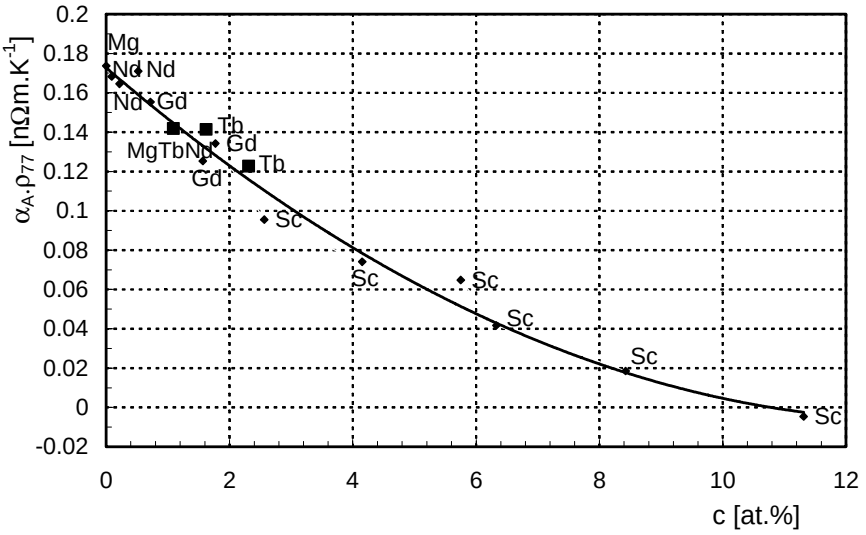

Fig. 4. Dependence of product $\rho(77) \times \alpha_A(77)$ on solute concentration of variety RE solid solutions in Mg.

showing the deviations from Matthiessen's rule. Both measured and calculated values follow common concentration dependence regardless of the solute type, which could indicate similar conductivity electron scattering processes at Tb and other RE atoms in Mg.

4. Conclusions

Isothermal resistivity annealing curves at 803 K for Mg-Tb binary alloys and at 773 K for ternary Mg4Tb2Nd alloy measured at 77 K approach the saturated resistivity values for reasonable times showing the possibility to quench in the supersaturated solid solutions.

Nordheim's concentration rule is obeyed in Mg-Tb binary alloy similarly to Mg-Gd, Mg-Nd and Mg-Sc alloys at 77 K and 293 K. The resistivity contribution of 1 at.% of solute was determined for Tb in Mg at 77 K and 293 K. These values fall into the range of those reported in literature for Mg-RE alloys.

Negative deviations from Matthiessen's rule were observed in solution treated Mg-Tb and Mg-Tb-Nd alloys studied. Ageing of Mg-Tb alloys which produced two phase structure $\alpha' + D0_{19}$ does not change the sign of the deviation.

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