PRECIPITATION KINETICS IN Mg-Gd ALLOY AFTER NATURAL AGEING

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Abstract

Annealing at ambient temperature connected with a substantial degree of strengthening (natural ageing) is well known and investigated in Al-based alloys. Clustering of solute atoms at room temperature proven by atom probe tomography is believed to be assisted by vacancies quenched in material from high annealing temperature. This process has often a very deteriorating effect on further precipitation during artificial ageing of Al alloys. Natural ageing is not common in Mg-based alloys contrary to Al hardenable alloys.

Two squeeze cast Mg-Gd alloys with different Gd content were solution heat treated. The increase of solute concentration in the matrix during the treatment was monitored by electrical resistivity measurements. Microhardness decrease during the solution heat treatment corresponds to dissolution of secondary phases combined with solid solution hardening. Electrical resistivity of both alloys measured at 77 K decreases, if the alloys are kept at room temperature immediately after quenching from the solution temperature. These changes are accompanied by a microhardness increase. The process is much slower compared to Al alloys and does not completely saturate even after 2 months. Most probably a solute atoms clustering proceeds during the natural ageing as no secondary phase(s) particles were revealed by transmission electron microscopy in the naturally aged alloys.

The influence of natural ageing on phase changes due to isochronal annealing from room temperature to 500°C and to isothermal annealing at 200°C was studied by electrical resistometry performed at 77 K and microhardness development measured at room temperature. Natural ageing in the studied Mg-Gd alloys does not diminish microhardness increase achieved during artificial heat treatment contrary to Al alloys.

Keywords: MgGd alloys, natural ageing, electrical resistivity, microhardness, phase transformations

1. INTRODUCTION

Natural ageing is well known in Al-based alloys [1]. It is caused by clustering of solute atoms assisted by vacancies when specimen is kept at ambient temperature after quenching from high annealing temperature. Dislocation motion is affected by clusters formed during natural ageing and this effect causes significant strengthening of the material. The model of clusters growth during natural aging [2, 3] assumes that vacancies need to escape from clusters and this is the rate-limiting event of natural ageing. According to the model, all vacancies are bound in clusters at the end of natural aging [3] and clusters have to dissolve before the main precipitation phase develops. In the case of direct artificial aging, mobile quenched-in vacancies and the solute super-saturation control precipitation reactions at temperatures of artificial ageing resulting in more pronounced hardening effect.

Natural ageing is not common in Mg-based alloys. It was reported in Mg-6Zn-2Cu-0.1Mn alloy (in wt.%) [4]. After 8 weeks of natural ageing considerable strengthening was measured and a dense dispersion of planar precipitates and fine prismatic precipitates was observed. Microhardness response to natural ageing was also observed in binary Mg-7Zn alloy (in wt.%) and it is notably accelerated by addition of a trace amount of vanadium [5]. Similarly to many aluminum alloys G. P. zones were found to precipitate at low temperature in the Mg - 0.5 at.% Nd alloy [6]. Natural ageing was described in binary Mg-Gd and Mg-Tb alloys recently [7].

Most probably, quenched-in vacancies facilitate diffusion of Gd, resp. Tb atoms which subsequently agglomerate into small clusters. Significant hardening of Mg-5Gd, Mg-10Gd, Mg-15Gd and Mg-13Tb (in wt.%) was observed after natural ageing of these alloys.

The aim of this work was to compare microstructure development during artificial ageing and its influence on mechanical properties of Mg-15Gd and Mg-10Gd solution treated alloys in two states: a) just quenched and b) naturally aged after quenching.

2.   EXPERIMENTAL PROCEDURE

Binary MgGd alloys were produced by squeeze casting under a protective gas atmosphere of Ar + 1% SF_6. Nominal concentration of Gd is 10 wt.% (Mg-10Gd) and 15 wt.% (Mg-15Gd). The as-cast alloys for electrical resistivity measurement were solution treated at 500 °C for 8 hours and quenched into water at room temperature [8]. The H-shaped specimens machined to dimensions of (3 x 7 x 62) mm^3 (Mg-10Gd), (4 x 4 x 59) mm^3 (Mg-15Gd) were used. Specimens were exposed to ambient temperature for more than two months and electrical resistivity was measured within this time at temperature 77 K. After that performance electrical resistivity was measured during isochronal annealing in the range 20 °C - 500 °C. The annealing was carried out in steps of 20 °C/20 min followed by quenching. This treatment was performed in a stirred oil bath up to 240 °C and the specimen was quenched into liquid nitrogen after each annealing step. At higher temperatures up to 500 °C specimens were heat-treated in a furnace and each heating was followed by water quenching. Resistivity was measured after each heating step. Relative electrical resistivity changes $\Delta\rho/\rho_0$ were obtained within an accuracy of 10^{-4}. The resistivity was measured by means of the dc four-point method with a dummy specimen in series. The influence of parasitic thermoelectromotive force was suppressed by current reversal.

Resistivity annealing curves were compared to measurement of Mg-10Gd and Mg-15Gd alloys prepared the same way without natural ageing [8, 9].

The development of mechanical properties was measured by Vickers microhardness. The as-cast alloys for microhardness measurement were solution treated the same way as specimens for resistivity measurement. A part of materials was subsequently naturally aged for more than two months while the rest of material was stored at temperature 77 K during this time. Specimens of Mg-15Gd were produced by cutting bigger piece of material into two smaller ones and microhardness measurement was performed on originally matching areas (**Fig. 1**). Isothermal annealing of both kinds (just quenched and aged) of alloys at 200 °C was performed. After each annealing step Vickers microhardness HV0.5 was measured at room temperature in Wilson Wolpert 401 MVD microhardness tester. Seven indentations were evaluated and the average together with its standard deviation was determined.
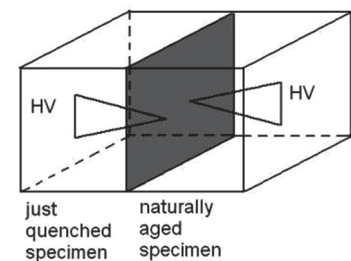

Fig. 1 Scheme of Mg-15Gd specimens for microhardness measurement

The microstructure investigation was realized using transmission electron microscopy (TEM) and electron diffraction (JEOL JEM 2000FX electron microscope).

3. RESULTS AND DISCUSSION

3.1 Electrical resistivity and microhardness measurement during natural ageing

The Mg-10Gd and Mg-15Gd alloys were naturally aged at ambient temperature and Vickers microhardness HV0.1 at room temperature and resistivity changes at temperature 77 K were measured. **Fig. 2** shows microhardness and resistivity development during natural ageing of both alloys. Resistivity was measured during ageing up to 2680 hours (approx. 112 days) and obviously decreases during this time in both alloys. Relative decrease of resistivity after ageing is 0.8 % in the Mg-15Gd alloy and 1.8 % in the Mg-10Gd alloy. Microhardness was monitored for 40 000 hours (approx. 4.5 years) in the Mg-10Gd alloy and for 2800 hours (117 days) in the Mg-15Gd alloy. After this time of ageing microhardness of both alloys significantly increases. While in the Mg-15Gd alloy natural ageing is evident in microhardness development after 10 hours of ageing about 1000 hours was necessary for evidence in the Mg-10Gd alloy. Because no secondary phase(s) particles were revealed by TEM in both naturally aged alloys these changes are caused most probably by clustering of solute atoms during ageing which is enabled by movement of quenched-in vacancies [7].
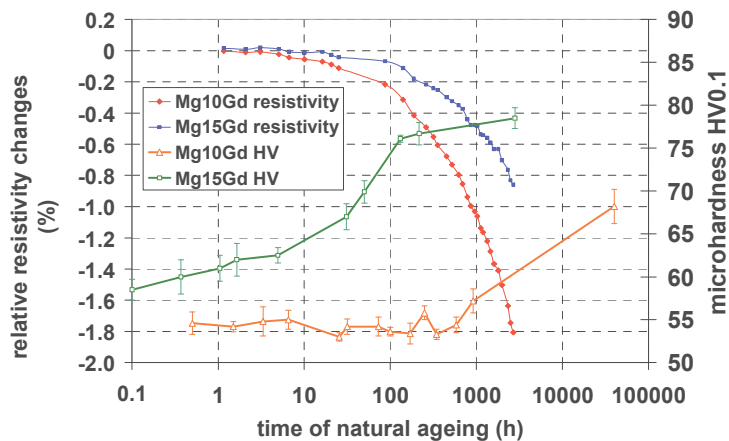

Fig. 2 Development of microhardness and resistivity during natural ageing of Mg-10Gd and Mg-15Gd alloy

3.2 Electrical resistivity measurement during isochronal annealing

The Mg-10Gd and Mg-15Gd alloys - both just quenched and naturally aged - were isochronally annealed from room temperature up to 500 °C (**Fig. 3**). The resistivity of only quenched Mg-10Gd alloy decreases up to annealing temperature 180 °C. This resistivity drop which is connected with matrix purifying due to secondary phase precipitation is followed by an increase (due to precipitate dissolution) that is accomplished at 330 °C. Resistivity development of naturally aged Mg-10Gd is very similar up to annealing temperature 180 °C while subsequent increase is interrupted by a precipitation process between 240 and 260 °C. This process is slightly noticeable also at resistivity curve of Mg-10Gd alloy without natural ageing as a slowdown of resistivity increase. Dissolution of phases precipitated below 260 °C in naturally aged alloy is accomplished at 380 °C and resistivity attains the value slightly exceeding its initial value contrary to just quenched alloy. TEM revealed the β'' (D0$_{19}$ hexagonal structure, a = 0.641 nm, c = 0.521 nm) metastable phase in just quenched alloy after annealing up to 180 °C only in electron diffraction. It showed homogeneous precipitation of very fine coherent particles of this phase.
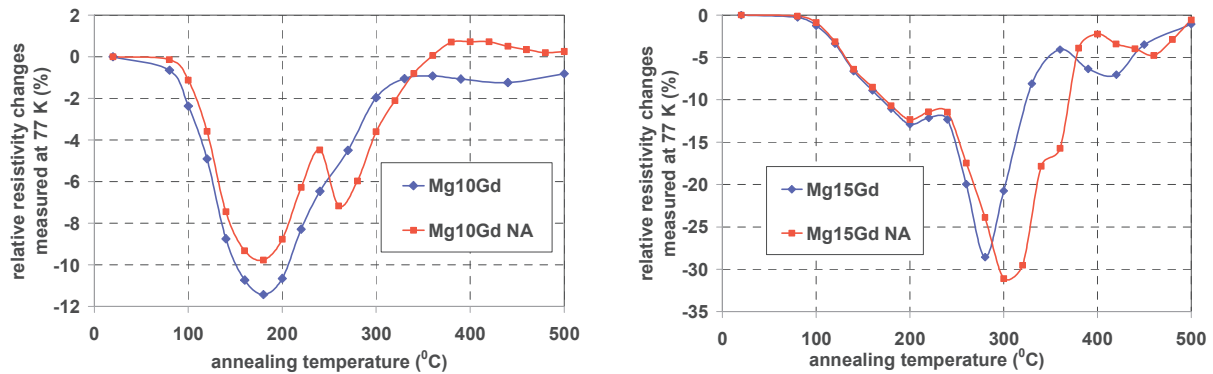
Fig. 3 Resistivity development during isochronal annealing of just quenched and naturally aged Mg10Gd and Mg15Gd alloy

Resistivity development during isochronal annealing of both just quenched and naturally aged Mg-15Gd alloys is almost the same up to annealing temperature 240 °C - resistivity decrease is followed by a slight increase between 200 and 240 °C. Similar to Mg-10Gd alloy TEM revealed β'' ($D0_{19}$) phase in just quenched alloy after annealing up to 200 °C. Subsequent resistivity drop is faster in just quenched alloy and resistivity minimum in this alloy is situated at annealing temperature 280 °C where β' (cbco structure, a = 0.641 nm, b = 2.223 nm, c = 0.521 nm) metastable phase was observed in form of semincoherent prismatic plates having 10 nm - 15 nm in diameter after annealing at 240 °C and growing up to double size at 280 °C. The resistivity minimum is shifted to 300 °C in naturally aged alloy.

Further decrease between 360 and 420 °C in just quenched alloy and between 400 and 460 °C in naturally aged alloy was observed. Development of stable β (Mg_5Gd, fcc structure, a = 2.23 nm) phase was proved after annealing up to 390 °C in the just quenched alloy. Resistivity after annealing at 500 °C is very similar in both alloys and reaches almost the initial value. Naturally aged alloy contrary to just quenched one shows a slowdown of dissolution process around annealing temperature 350 °C.

3.3   Microhardness measurement during isothermal annealing

Both kinds of the Mg-10Gd and Mg-15Gd alloys were isothermally annealed at 200 °C where the T6 (peak hardening) treatment was determined for solution treated Mg-15Gd alloy [8]. Initial values of HV0.5 are 50 ± 1 in just quenched Mg-10Gd alloy and 55 ± 1 in naturally aged one; 61 ± 1 in just quenched Mg-15Gd alloy and 67 ± 2 in naturally aged one (**Fig. 4**). Connecting lines in this and following two figures are for better recognition only. Significant increase of microhardness was observed after first 20 hours of annealing in all alloys studied. Microhardness development of both Mg-10Gd alloys is quite similar, despite of an insignificantly faster HV0.5 increase of just quenched alloy in the first 12 hours (**Fig. 4**). Hardening after 165 hours of annealing is about 30 % (**Fig. 5**).
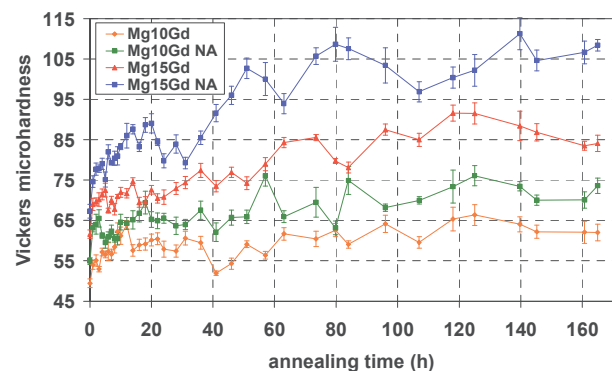

Fig. 4 Microhardness changes due to isothermal annealing at 200 °C in just quenched Mg10Gd, Mg15Gd and naturally aged Mg10Gd and Mg15Gd alloys

Age hardening is more pronounced in naturally aged Mg-15Gd alloy than in just quenched one and relative HV0.5 changes are ~ 60 % in naturally aged alloy and they do not exceed 40 % in just quenched alloy after 165 hours of annealing (**Fig. 5**). The non-monotonic type of both curves especially at the beginning of annealing corresponds to development of early precipitation stages observed in the isochronal annealing curves of electrical resistivity. Kinetics for both alloys is slower than in the Mg-Y-Nd alloy [11], where the best hardening response was achieved after 24 hours of annealing at the same annealing temperature and is also unsurprisingly slower than at 250 °C [8, 10].

The peak hardness in Mg-15Gd naturally aged is comparable to results obtained in the literature [10, 11]. TEM performed at the same specimens as used for microhardness measurements showed existence of the β' metastable phase with cbco structure in both kinds of Mg-15Gd alloy artificially aged at 200 °C/165 hours (**Fig. 6** and **Fig. 7**). This phase has a form of very small plates on {11-20} matrix planes in all three variations. The plates having size ~ 20-25 nm are arranged into a network and its mesh size differs in just quenched and naturally aged Mg-15Gd alloy. The estimated diameter of the mesh is ~ 18 nm in the naturally aged and ~ 23 nm in the just quenched alloy. This arrangement is the most effective obstacle arrangement design for movement of basal dislocations [12] and its parameters explain differences in peak mechanical properties determined in artificially aged Mg15Gd alloys after quenching and after natural ageing. The observed particles have not a homogeneous thickness, a necking can be observed in most of them. These necks are precursors for β_1 phase transformation which develops directly from the β' [10] and it seems therefore that the maximum volume fraction attainable during annealing at 200 °C was reached.
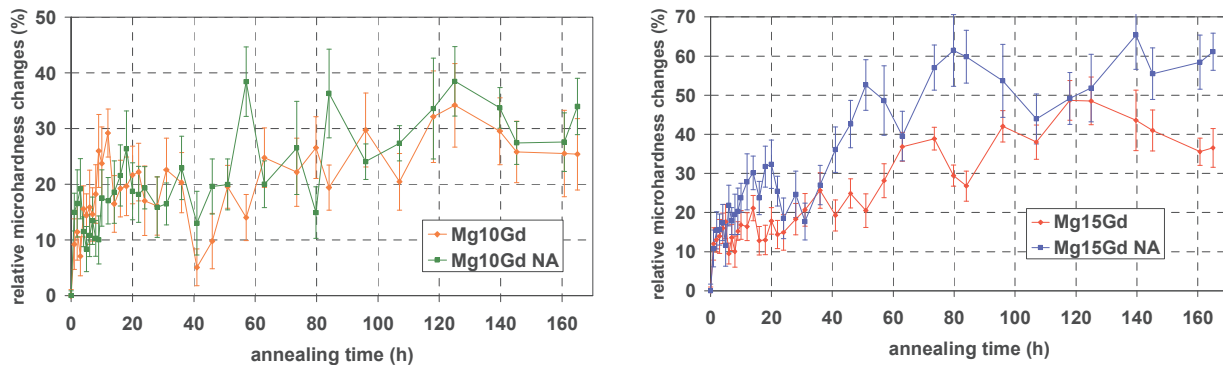

Fig. 5 Relative microhardness (HV0.5) changes due to isothermal annealing at 200 °C in just quenched Mg10Gd, Mg15Gd and naturally aged Mg10Gd and Mg15Gd alloys
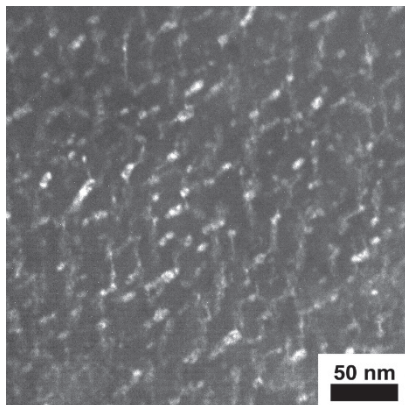

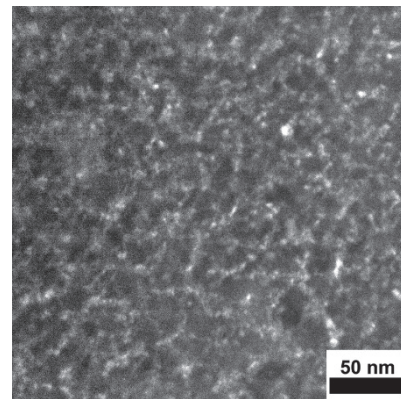**Fig. 6** TEM image of just quenched Mg15Gd alloy after isothermal annealing 200 ºC/165 h

Fig. 7 TEM image of naturally aged Mg15Gd alloy after isothermal annealing 200 ºC/165 h

CONCLUSIONS

Comparison of resistivity changes during isochronal annealing and microhardness development during isothermal annealing between just quenched and naturally aged Mg-10Gd and Mg-15Gd was performed. Solid solution super-saturation is the cause of the following precipitation sequence in Mg-Gd alloys: β'' (DO_{19}) metastable → β' (cbco) metastable → β (Mg_5Gd) stable. The best hardening is achieved, when the β' metastable phase with the cbco structure is embedded in the matrix in a form of thin prismatic plates. These plates were observed in Mg-15Gd alloy after annealing up to 280 °C where resistivity minimum was determined.

Natural ageing preceding isochronal annealing slightly modifies resistivity annealing curves on annealing higher than 200 °C in the Mg-10Gd alloy and on annealing higher than 280 °C in the Mg-15Gd alloy. Natural ageing has no considerable influence on microhardness development during isothermal annealing at 200 °C in the Mg-10Gd alloy, the hardening response is ~ 30 %. Natural ageing causes a pronounced increase of age hardening in the Mg-15Gd alloy (~ 60 % in the naturally aged and ~ 40 % in just quenched alloy). Development of the β' (cbco structure) transient phase in a triangular arrangement preferred as obstacles for basal dislocation motion was found by TEM. A network of these very fine plates is denser in specimen aged at 200 °C after natural ageing.

Natural ageing has a positive influence, contrary to Al alloys, on age hardening in solution treated Mg-15Gd alloy artificially aged at 200 °C. Even though the same transient phase develops after 165 hours of annealing, its number density is higher in naturally aged alloy probably due to a higher concentration of nucleation sites provided by solute clustering during natural ageing.

ACKNOWLEDGEMENTS

REFERENCES

[1]   STULÍKOVÁ, I., FALTUS, J., SMOLA, B. Influence of composition on natural ageing of Al-Mg-Si alloys. *Metallic Materials*, 2007, Vol. 45, pp. 85-90.

[2]   SEYEDREZAI, H., GREBENNIKOV, D., MASCHER, P., ZUROB, H.S. Study of the early stages of clustering in Al-Mg-Si alloys using the electrical resistivity measurements. *Mat. Sci. Eng.* A, 2009, Vol. 525, p. 186.

[3]   ZUROB, H.S., SEYEDREZAI, H. A model for the growth of solute clusters based on vacancy trapping. *Scr. Mater.*, 2009, Vol. 61, p. 141.

[4]   BUHA, J. Mechanical properties of naturally aged Mg-Zn-Cu-Mn alloy. *Mat. Sci. Eng*. A, 2008, Vol. 489, p. 127.

[5]   BUHA, J. Grain refinement and improved age hardening of Mg-Zn alloy by a trace amount of V. *Acta Materialia,* 2008, Vol. 56, p. 3533.

[6]   PIKE, T.J., NOBLE, B. The formation and structure of precipitates in dilute magnesium-neodymium alloy. *J. Less Common Mat.,* 1973, Vol. 30, p. 63.

[7]   ČÍŽEK, J., SMOLA, B., STULÍKOVÁ, I., HRUŠKA, P., VLACH, M., VLČEK, M., MELIKHOVA, O., PROCHÁZKA, I. Natural ageing of Mg-Gd and Mg-Tb alloys. *Phys. Stat. Sol*. A, 2012, Vol. 209, No. 11, p. 2135.

[8]   VOSTRÝ, P., SMOLA, B., STULÍKOVÁ, I., von BUCH, F., MORDIKE, B.L. Microstructure evolution in isochronally heat treated Mg-Gd alloys. *Phys. stat. sol*. *(a)*, 1999, Vol. 175, p. 491.

[9]   SMOLA, B., STULÍKOVÁ, I., PELCOVÁ, J., MORDIKE, B.L. Significance of Stable and Metastable Phases in High Temperature Creep Resistant Magnesium-Rare Earth Base Alloys. *J. Alloys and Compounds,* 2004, Vol. 378, p. 196.

[10] GAO, X., HE, S.M., ZENG, X.Q., PENG, L.M., DING, W.J., NIE, J.F. Microstructure evolution in a Mg-15Gd-0.5Zr (wt.%) alloy during isothermal aging at 250 °C. *Mat.s Sci. Eng*. A, 2006, Vol. 431, p. 322.

[11] VOSTRÝ, P., STULÍKOVÁ, I., SMOLA, B., CIESLAR, M., MORDIKE, B.L. A study of the Decomposition of Supersaturated Mg-T-Nd, Mg-Y and Mg-Nd Alloys. *Z. Metallkde,* 1988, Vol. 79, p. 340.

[12] NIE, J.F. Effects of precipitate shape and orientation on dispersion strengthening in magnesium alloys. *Scripta Mater.*, 2003, Vol. 48, p. 1009.