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Investigation of Precipitation Effects in Mg–Tb and Mg–Tb–Nd Alloys

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Investigation of precipitation effects in solution treated Mg–Tb and Mg–Tb–Nd alloy was performed. Solution treated alloys were compared with samples deformed by high pressure torsion to examine influence of deformation on precipitation effects. Dislocations present in samples processed by high pressure torsion can serve as diffusion channels for atoms and also as nucleation sites for precipitates. Therefore precipitation of some phases in high pressure torsion deformed samples was observed at lower temperatures than in solution treated ones.

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1. Introduction

Mg–Tb is a novel hardenable alloy with good creep resistance at elevated temperatures with promising applications in aerospace and automotive industry. The solubility of Tb in Mg reaches maximum of 24 wt% at eutectic temperature 559 °C [1] and strongly decreases at lower temperatures. Therefore, supersaturated solid solution can be prepared by annealing at solution treatment temperature and subsequent fast quenching.

With increasing temperature, supersaturated solid solution α' decomposes according to the sequence [2]:

$$\alpha'(\text{hcp}) \rightarrow \beta''(\text{D0}_{19}) \rightarrow \beta'(\text{c-bco}) \rightarrow \beta(\text{bcc}, \text{Mg}_{24}\text{Tb}_5). \quad (1)$$

The β'' transient phase exhibits hexagonal D0_{19} structure and is fully coherent with Mg matrix. The semicoherent transition β' has c-base centered orthorombic structure (c-bco). The stable β phase exhibits body centered cubic (bcc) structure and is incoherent with Mg matrix. Lattice mismatch at the interface of semicoherent or incoherent particles and Mg matrix is compensated by open-volume misfit defects.

Addition of Nd to MgTb alloying system modifies the precipitation sequence to [3]:

$$\alpha'(\text{hcp}) \rightarrow \beta''(\text{D0}_{19}\text{ clusters}) \rightarrow \beta''(\text{D0}_{19}\text{ plates}) \rightarrow \beta'(\text{c-bco}) \rightarrow \beta_1(\text{fcc}, \text{Mg}_3\text{Gd type}) \rightarrow \beta(\text{fcc}, \text{Mg}_5\text{Gd type}) \rightarrow \beta(\text{bct}, \text{Mg}_{41}\text{Nd}_5\text{ type}). \quad (2)$$

Industrial applicability of Mg-RE (rare-earth) alloys is limited by their low ductility which can be improved by grain size refinement [4]. Novel techniques for grain size refinement based on severe plastic deformation (SPD) were recently developed [5]. Finest grain size (typically $\approx$ 100 nm) is achievable by high pressure torsion (HPT) [5], where initially coarse-grained material is simultaneously deformed in torsion and compressed by pressure of several GPa.

SPD creates large amount of defects, mainly dislocations and vacancies [5]. In case of age hardenable alloys it is expected that presence of defects induced in the material by SPD will influence decomposition of supersaturated solid solution.

Positron lifetime (LT) spectroscopy [6] is well established technique ideally suited for investigation of open-volume misfit defects created by presence of semicoherent and incoherent phases in Mg matrix and also defects created in material by HPT deformation.

2. Experimental details

Samples of binary Mg–13 wt%Tb alloy (MgTb) were produced by squeeze casting under a protective Ar + 1%SF_6 atmosphere. As-cast samples were solution annealed at 530 °C for 6 h under Ar atmosphere and subsequently quenched into water of room temperature. Composition of solution treated sample was determined by chemical analysis as 13.3 wt% Tb and balance of Mg. The content of Tb is well under the solubility of Tb in Mg at 530 °C, which is 22 wt%.

Samples of ternary Mg–3.6 wt%Tb–2.1 wt%Nd (MgTbNd) alloy were also produced by squeeze casting under Ar + 1%SF_6 atmosphere. Solution treatment at 500 °C for 4 h was finished by quenching into water of room temperature. Selected samples of MgTb and MgTbNd alloys after the solution treatment were deformed by HPT at room temperature using hydrostatic pressure of 6 GPa and 5 revolutions. Both solution treated and HPT deformed samples were subjected to isochronal annealing with steps 20 °C/20 min. Each annealing step was finished by quenching into water of room temperature and then hardness and positron lifetime measurements were performed.

Positron LT measurements were performed using a digital positron LT spectrometer [7] with outstanding time resolution of 145 ps (FWHM ^{22}Na). $^{22}Na_2CO_3$ positron source deposited on a 2 μm mylar foil was used and at least 10^7 annihilation events were accumulated in each

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LT spectrum. Decomposition of LT spectra into individual components was performed by a maximum likelihood code [8]. The goodness-of-fit expressed by the χ^2 value per degree of freedom was always below 1.03.

Vickers hardness (HV) was measured on polished samples using microhardness tester Struers Duramin 300 using a load of 100 g applied for 10 s. Each measurement was repeated at least ten times to improve precision of measurement and estimate statistical uncertainty of the hardness value.

3. Results

Evolution of HV of solution treated and HPT deformed MgTb samples during isochronal annealing is shown in Fig. 1. One can see in the figure that maximal hardness of solution treated samples is reached at (200±40) °C and it is associated with precipitation of β'' phase with $D0_{19}$ structure which was identified in the sample by selected area electron diffraction (SAED) [9]. At 260 °C hardness drops due to coarsening and dissolution of β'' particles. Subsequently hardness increases again and reaches local maximum at 280 °C. This is caused by precipitation of β' phase which was identified in the sample by SAED. Let us note that two stages corresponding to formation of β'' particles and subsequent precipitation of β' phase was found in the temperature dependence of electrical resistivity [9].

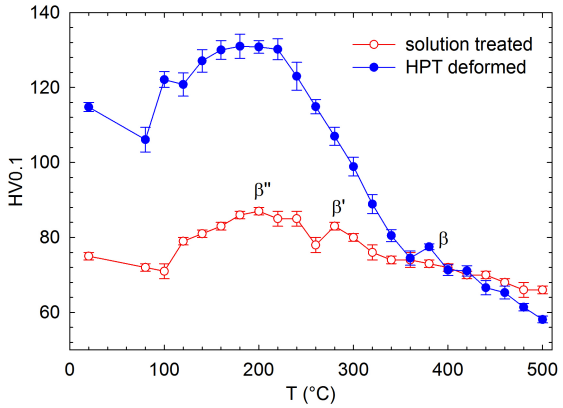

Fig. 1. Temperature dependence of HV for solution treated (open points) and HPT deformed (full points) MgTb alloy.

Initial hardness of HPT deformed samples is significantly higher than that of solution treated samples due to grain refinement and introduction of lattice defects during HPT deformation. Maximum hardness is reached at (180 ± 40) °C and at temperatures above 220 °C hardness decreases due to grain growth and recrystallization. At 360 °C process of recrystallization is finished and hardness is similar as hardness of solution treated samples.

Temperature dependence of the lifetimes resolved in positron lifetime spectra of solution treated samples is plotted in Fig. 2a. After solution treatment the MgTb alloy exhibits a single component spectrum with lifetime which agrees well with the bulk Mg lifetime τ_b = (224.8±0.5) ps [10]. Hence, within sensitivity of LT measurement the sample can be considered as a defect-free material. In temperature range 120–380 °C an additional component with lifetime $\tau_2 \approx 256$ ps appeared in the measured LT spectra. Lifetime of this component agrees well with the lifetime of positrons trapped in vacancy-like misfit defects at interfaces between semicoherent or incoherent precipitates and Mg matrix [10, 11]. The intensity I_2 of this component is plotted in Fig. 2b as a function of annealing temperature. For comparison temperature dependence of HV is plotted in the figure as well.

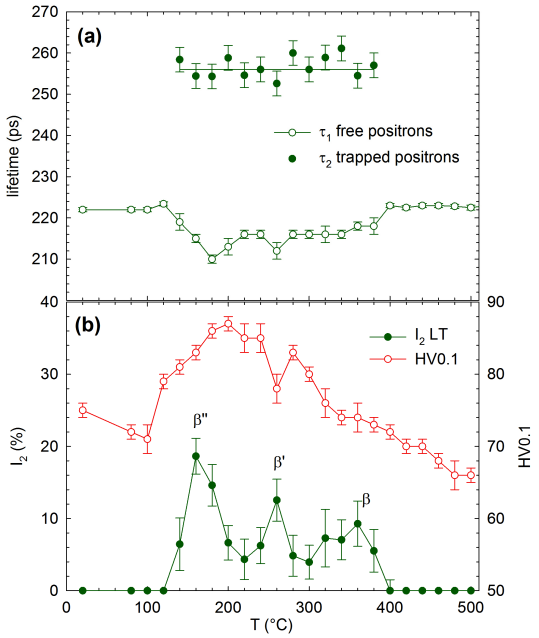

Fig. 2. Solution treated MgTb alloy subjected to isochronal annealing: (a) temperature dependence of positron lifetimes, (b) temperature dependence of HV (open points) and I_2 (full points) for solution treated MgTb alloy subjected to isochronal annealing.

There are two pronounced peaks in the temperature dependence of I_2. The highest value of I_2 is reached after annealing at (160 ± 20) °C. This peak occurs at lower temperature than the temperature of maximum hardening, i.e. (200 ± 40) °C, and it is associated with early stages of precipitation of β'' phase. Although β'' phase is coherent with matrix in early stages of precipitation, the structure of β'' particles is not perfect and contains vacancy-like defects which are trap positrons. When finely dispersed precipitates of β'' with well-defined orientation with respect to the Mg matrix are formed, they contain less vacancy-like defects. Therefore decrease in I_2 is observed. On the other hand, this condition is most favorable for precipitation strengthening mechanism and maximum hardness is achieved. Thus maximum value of I_2 intensity is reached at lower temperature than the maximum hardness although both are associated with the precipitation of β'' phase.

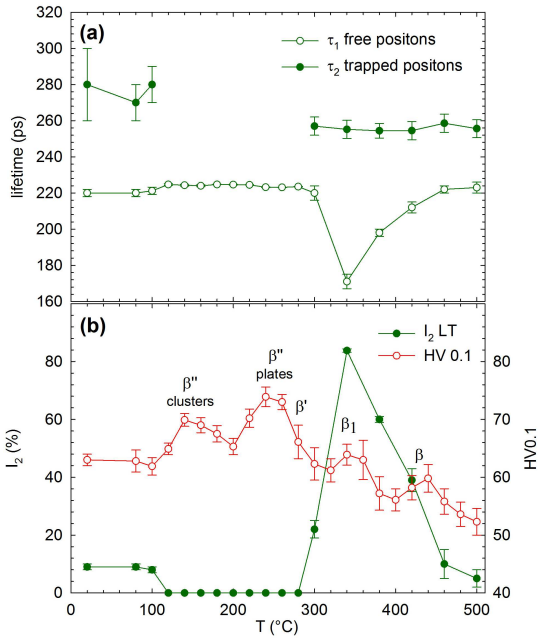

Fig. 3. Solution treated MgTbNd alloy subjected to isochronal annealing: (a) temperature dependence of positron lifetimes, (b) temperature dependence of HV (open points) and I_2 (full points) for solution treated MgTbNd alloy subjected to isochronal annealing.

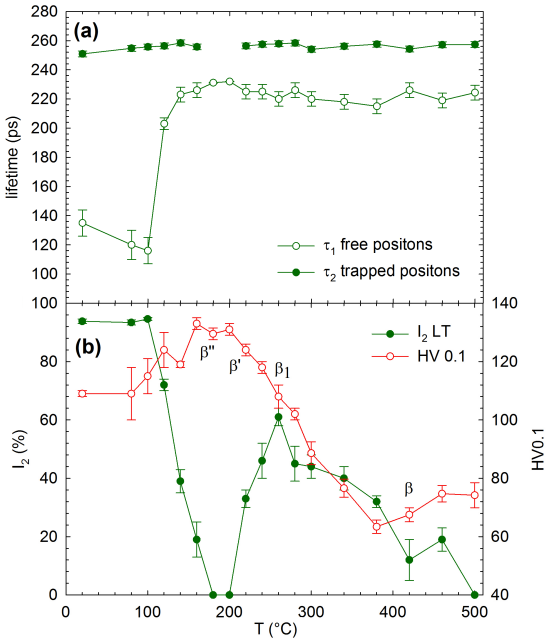

Fig. 4. HPT deformed alloy subjected to isochronal annealing: (a) temperature dependence of positron lifetimes, (b) temperature dependence of HV (open points) and I_2 (full points) for HPT deformed MgTbNd alloy subjected to isochronal annealing.

To examine the influence of addition of Nd to Mg–Tb alloying system, samples of MgTbNd alloy were investigated by HV and LT measurements. Temperature dependence of positron lifetimes, HV and I_2 for solution treated and HPT processed MgTbNd samples are shown in Figs. 3 and 4, respectively. After solution treatment MgTbNd alloy exhibits the lowest hardness. During isochronal annealing HV increases with increasing temperature and reaches maximum at $(220 \pm 20)\,^{\circ}\mathrm{C}$. This hardening peak is associated with formation of plates of β'' phase. At slightly higher temperature particles of β' phase are formed which coexist with plates of β'' phase at temperature around 270 °C [3]. This leads to a decrease of hardness and subsequent annealing up to 500 °C does not produce any further pronounced hardening. Results of LT measurements of solution treated MgTbNd alloy revealed presence of a second component with lifetime of (280 ± 20) ps at temperatures up to 100 °C. This long-lived component can be attributed to positrons trapped at quenched-in complexes of vacancies and Nd or Tb atoms. Since quenched-in vacancies were not observed in the binary MgTb alloy the vacancies are likely associated with Nd atoms. At 120 °C this component disappears because vacancies bound to solutes are annealed out. From 120 °C up to 280 °C there is only one component present in LT spectra and virtually all positrons annihilate in the free state.

Hence, contrary to MgTb alloy particles of β'' particles in MgTbNd alloy exhibit well-defined structure without vacancy-like defects. Second component appears again at temperatures above 300 °C, however, now it has lifetime of (256 ± 5) ps which corresponds to positrons trapped at misfit defects at the precipitate–matrix interface. Presence of misfit defects implies that semicoherent or incoherent precipitates are formed in this temperature range. Maximum intensity of second component is reached at $(340 \pm 20)\,^{\circ}\mathrm{C}$ and is associated with formation of semicoherent β_1 phase. After further annealing Mg_5Gd-type β phase is formed at 390 °C and only few irregular particles of the $Mg_{41}Nd_5$-type phase are present after isochronal annealing up to 500 °C [3]. Although these phases are also not coherent with Mg matrix, they trap significantly smaller fraction of positrons than semicoherent β_1 phase. This decrease of fraction of positrons trapped at misfit defects at interfaces is caused by coarsening of particles at temperatures higher than 340 °C. As precipitates join together, their number density and also the surface area decrease resulting in a significant reduction of concentration of misfit defects at interfaces.

HPT processed samples exhibit significantly higher initial hardness due to grain refinement and lattice defects introduced during deformation. Maximum hardness associated with formation of plates of β'' phase is reached at $(180 \pm 20)\,^{\circ}\mathrm{C}$. At temperatures above 200 °C hardness decreases due to grain growth and minimum hardness is reached at $(380 \pm 40)\,^{\circ}\mathrm{C}$. Possible changes of hardness caused by precipitation of β' and β_1 are difficult to distinguish because they are overwhelmed by the major decrease in hardness due to grain growth occurring in the same temperature range. At temperatures over 380 °C there is slight increase in hardness caused by formation of β phase.

HPT deformation introduces dislocations into the processed material. This is testified by presence of the second component with lifetime of (256 ± 2) ps in the measured LT spectra at temperatures up to 100 °C. Lifetime of this component agrees well with the lifetime reported for positrons trapped at dislocations in Mg [10]. At temperatures below 100 °C range we can observe very high intensity I_2 of the second component since almost all positrons are trapped at defects. This is in agreement with expected high density of defects introduced by HPT processing. Intensity of I_2 starts to decrease at 120 °C and reaches zero at 180 °C where defects introduced by HPT deformation were annealed out. The component with lifetime of (256 ± 2) ps appears again after annealing at 220 °C and higher temperatures. In this temperature range it is associated with misfit defects at interfaces between Mg matrix and semicoherent or incoherent precipitates. Intensity I_2 of this component reaches local maximum at 260 °C and then gradually decreases until it finally disappears at 500 °C. Peak in intensity of the second component is associated with formation of semicoherent β_1 phase. Further annealing leads to coarsening and dissolution of β_1 precipitates followed by formation of coarse β phase particles. These processes cause the decrease of I_2.

4. Discussion

Comparison of temperature dependence of hardness of solution treated and HPT deformed MgTb alloy clearly shows that maximum hardening is achieved at lower temperatures in HPT deformed samples. Deformation during HPT processing introduces high density of dislocations which serves as nucleation centers for formation of second phase particles and also facilitates diffusion of solutes (pipe diffusion). This leads to precipitation of β'' at lower temperatures than in solution treated samples. Although β'' phase itself is coherent with matrix in the early stage of precipitation, β'' particles may contain vacancies. When precipitates of β'' with well defined structure and orientation with respect to the Mg matrix develop, vacancies gradually disappear.

In the binary MgTb alloy the β'' phase particles contain vacancy-like defects while in the ternary MgTbNd alloy no vacancy-like defects associated with the β'' phase have been detected. It indicates that in MgTbNd β'' phase particles exhibit well defined $D0_{19}$ structure already in early stages of precipitation while in MgTb β'' particles exhibit more defected structure in the early stages of precipitation. Semicoherent β_1 phase in MgTbNd alloy exhibits exceptionally strong trapping of positrons. Peak in intensity I_2 of the second component in LT spectra, corresponding to misfit defects at the interface between β_1 phase and Mg matrix, was also shifted to lower temperatures in HPT processed alloy. Thus β_1 phase also forms at lower temperatures in HPT deformed samples.

5. Conclusions

Maximal hardening in MgTb alloy is associated with precipitation of coherent β'' phase which is formed by thermally activated long-range diffusion of Tb. In HPT deformed alloy precipitation of β'' phase occurs at lower temperature than in the solution treated alloy due to dislocations introduced by severe plastic deformation. Presence of vacancies associated with β'' phase was confirmed by a rise of a component with lifetime of 256 ps in LT spectra at temperatures corresponding to the early stages of precipitation.

In solution treated and HPT deformed MgTbNd alloy maximum hardness is also associated with precipitation of β'' phase. Similar to MgTb, in HPT deformed MgTbNd alloy precipitation of β'' phase is also promoted by defects introduced by severe plastic deformation and takes place at lower temperatures. However, contrary to MgTb in MgTbNd samples β'' phase is not associated with presence of defects. The semicoherent β_1 phase exhibits exceptionally strong trapping of positrons and its precipitation is also shifted to lower temperatures in HPT deformed samples.

Acknowledgments

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