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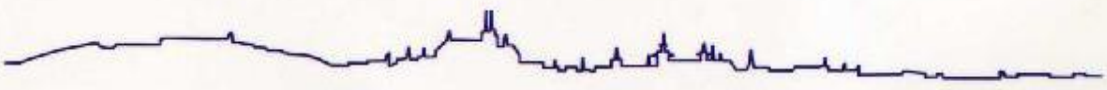

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Defects in Ultra-Fine Grained Mg-Based Alloys Deformed by High-Pressure Torsion

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Abstract. Microstructure of ultra fine grained (UFG) Mg and Mg-9.33wt.%Gd (Mg10Gd) alloy and its development with temperature were studied in this work. The UFG specimens were prepared by high pressure torsion (HPT) and investigated using positron lifetime (PL) spectroscopy combined with transmission electron microscopy (TEM), X-ray diffraction (XRD), and microhardness measurements. It was found that pure Mg has undergone a substantial recrystallization already in the course of HPT treatment which resulted in a binomial type microstructure. On the other hand, a homogenous UFG structure with high density of dislocations was formed in HPT-treated Mg10Gd. Investigations of the development of microstructure with increasing temperature revealed that recovery of dislocations takes place at similar temperatures in both specimens. In pure Mg it is accompanied by grain growth, while Mg10Gd exhibits grain growth only at significantly higher temperatures.

Introduction

Mg-Gd alloys are promising, novel, light hardenable materials with a high creep resistance, even at elevated temperatures [1]. Despite the favorable strength and thermal stability, a disadvantage of Mg-based alloys consists in a low ductility insufficient for industrial applications. It is known that UFG metals with grain size typically about 100 nm can be produced by HPT [2]. A number of UFG metals exhibit favorable mechanical properties consisting in a combination of very high strength and a significant ductility. Hence, it is highly interesting to examine the microstructure and physical properties of UFG Mg-based light alloys. Consequently, microstructure and defect studies of HPT-treated pure Mg and Mg10Gd alloy were performed in the present work. The characterization of lattice defects was undertaken by PL spectroscopy, which is a well developed non-destructive technique with very high sensitivity to open-volume defects such as vacancies, dislocations, etc. [3]. In this work PL spectroscopy was combined with TEM, XRD and microhardness measurements.

Experimental

Specimens of pure Mg (99.95%) and Mg10Gd alloy prepared by squeeze casting were investigated. The as-cast material alloy subjected to a solution annealing at 500^{o}C for 6 hours followed by quenching into water of room temperature. To fabricate the UFG structure, the as-received Mg and the solution treated Mg10Gd alloy were deformed by HPT at room temperature under a high pressure of 6 GPa. The HPT-treated specimens are disk shaped with diameter ≈ 12 mm and

thickness ≈ 0.3 mm. A fast-fast spectrometer similar to that described in [4] with time resolution of 170 ps was used in this work. The decomposition of PL spectra into exponential components was undertaken using a maximum probability procedure [5]. The TEM observations were carried out on a JEOL 2000 FX electron microscope operating at 200 kV. The XRD studies were performed using XRD7 and HZG4 (Seifert-FPM) powder diffractometers with Cu K_α radiation. The Vickers microhardness was measured at a load of 100 g applied for 10 s using a STRUERS Duramin-2 hardness tester.

Results and Discussion

Coarse-grained samples. The microstructure of the initial coarse grained Mg and Mg10Gd (i.e. prior to HPT treatment) has been described in [6]. The coarse grained Mg exhibits dislocation density $\rho \approx 5 \times 10^{12}$ m^{-2} and the mean grain size of about 10 μm. The solution treated Mg10Gd alloy is characterized by large coarse grains and dislocation density below 10^{12} m^{-2} [6].

Table 1. Lifetimes and corresponding relative intensities of the components resolved in PL spectra. The errors (one standard deviations) are given in parentheses.

Sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
HPT-treated Mg	188(5)	39(1)	257(3)	61(1)
HPT-treated Mg10Gd	180(4)	34(2)	256(3)	66(2)

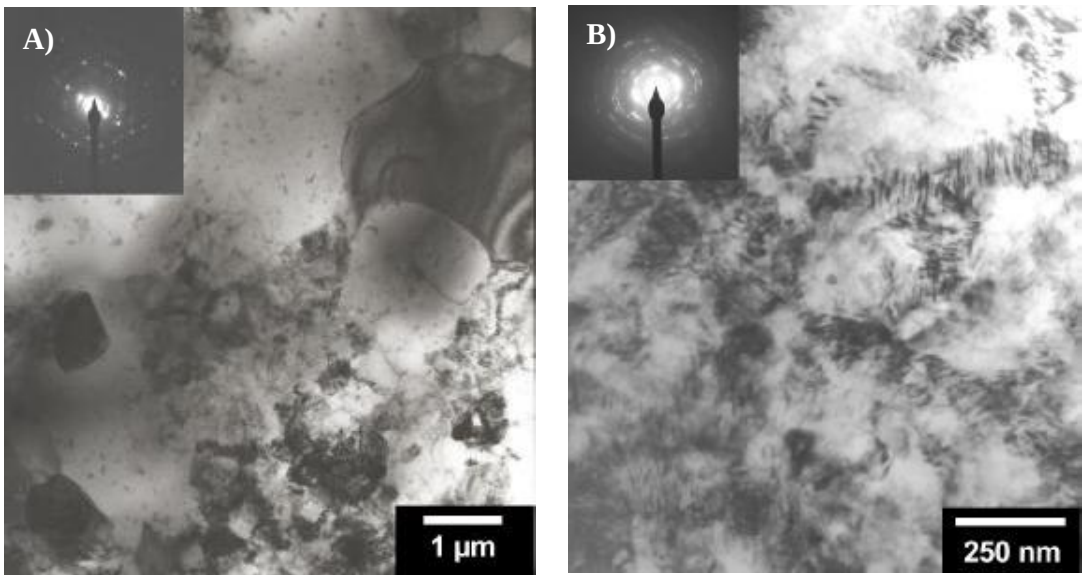

Figure 1 A representative bright-field TEM image and electron diffraction pattern of A) HPT-deformed pure Mg, B) HPT-deformed Mg10Gd.

HPT-deformed samples. A bright-field TEM image and an electron diffraction pattern of HPT-deformed Mg are shown in Fig. 1a. Two different types of region were observed: (i) “deformed regions” with UFG grains (100-300 nm) and a high density of dislocations, and (ii) “recrystallised regions” with substantially larger grains (1-5 μm) and almost free of dislocations. The presence of the “recrystallised regions” indicates an incomplete dynamic recovery of the microstructure during HPT processing. The XRD back-reflection pattern is a superposition of isolated spots and continuous diffraction rings, which testifies co-existence of the two types of regions. The specimen

exhibits (0001) type texture. The PL results for the HPT-deformed samples are shown in Table 1. The HPT-deformed Mg exhibits a two-component PL spectrum consisting of the free positron component with lifetime τ_1 and intensity I_1 and a contribution of positrons trapped at dislocations (lifetime τ_2 and intensity I_2). The lifetime τ_2 of the latter component agrees well with that found in a cold rolled Mg for positrons trapped at dislocations [6]. Hence, we can conclude that positrons in HPT-treated Mg are trapped at dislocations inside the "deformed regions".

A bright-field TEM image for the HPT-deformed Mg10Gd alloy (Fig. 2.) shows uniform UFG microstructure with a mean grain size of about 100 nm, i.e. no dynamic recovery took place during HPT processing. The electron diffraction pattern shows high-angle missorientation of neighboring grains. A high density of homogeneously distributed dislocations was observed. A high dislocation density can be deduced also from a significant broadening of the XRD profiles. Less broadening of (000l) profiles with respect to other peaks indicates the dominating presence of <a> dislocations with the Burgers vector $\vec{b} = 1/3.a.\{2\bar{1}\bar{1}0\}$. A weak (0001) texture was found. The PL spectrum of the HPT-deformed Mg10Gd alloy consists of two components, see Table 2. The first component with a lifetime τ_1 arises from the free positrons. The lifetime τ_2 of the second component corresponds well with the lifetime of positrons trapped at Mg-dislocations [6]. A detailed mapping of the specimen by microhardness measurements at various positions revealed out that there is a slight increase in dislocation density from the centre of the specimen towards the outer edge, see [6] for details. Positron annihilation measurements performed at various distance from the center of HPT-deformed specimens confirmed this conclusion. The observed increase of dislocation density can be expected because of the increasing strain from the specimen center towards the margin. Dislocations in HPT-deformed fcc and bcc metals are situated mostly in layers along grain boundaries, while the grain interiors are virtually free of dislocations [7]. On the other hand, Fig. 1b shows that HPT-deformed Mg10Gd alloy exhibits uniform distribution of dislocations throughout the whole volume of the specimen. Similarly, a high density of equally spaced dislocations is observed in the "deformed regions" in HPT-deformed Mg, see Fig. 1.a

Temperature Development of UFG Structure. After characterization of the as-deformed microstructure, the specimens were subjected to isochronnal annealing in order to study the development of microstructure with increasing temperature. The PL spectra of HPT-deformed Mg and Mg10Gd specimens consisted of the two components with lifetimes τ_1 (free positrons) and τ_2 (positrons trapped at dislocations) at all the annealing temperatures. The lifetime τ_2 did not change with annealing temperature (except of some statistical fluctuations) indicating that the nature of positron traps remains unchanged. Therefore, in order to decrease statistical fluctuations of the fitted parameters, τ_2 was fixed at 256 ps in the final analysis of PL spectra. The relative intensity I_2 of the dislocation component for the HPT-deformed Mg and Mg10Gd is plotted in Fig. 2 as a function of the annealing temperature. Fig. 3 shows the temperature dependence of the microhardness, HV, for the both specimens. The HV of Mg10Gd increases from the specimen centre towards the outer edge. Thus, the minimum and maximum HV values corresponding to the centre and the outer edge of the specimen are shown for each temperature. It is obvious in Fig. 2 that HPT-deformed Mg shows a dramatic decrease in I_2 from the room temperature to 200^{o}C. The regions with UFG structure and high density of dislocations are gradually replaced by dislocation-free recrystallized grains (diameter $\approx$ 5 μm). As mentioned above, the recrystallization process occurs already at room temperature during the HPT processing. Although the HPT-deformed Mg has already undergone a substantial recrystallization in the course of HPT treatment, the TEM observations clearly showed that it still contains a significant volume fraction of "deformed regions" with high density of dislocations. The replacement of the "deformed regions" by dislocation-free recrystallized grains leads to a softening

seen as a strong decrease in HV, see Fig. 3. The largest drop in HV occurs in the temperature range (20-150)^{o}C. Eventually, at T ≈ 200^{o}C the specimen exhibits completely recrystallized structure with a low dislocation density $\rho \approx 1 \times 10^{12}$ m^{-2} and the mean grain size ≈ 5 μm, see Fig. 4a. The recrystallized structure remains essentially the same after annealing to higher temperatures.

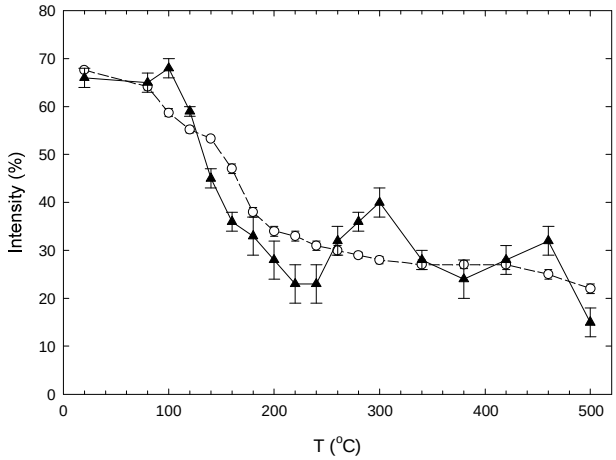

Figure 2 Temperature dependence of the relative intensity I_2 of positrons trapped at dislocations for HPT-treated Mg (open circles) and HPT-treated Mg10Gd (full triangles).

The decomposition of supersaturated solid solutions (sss) and the precipitation effects in solution treated (i.e. coarse-grained) Mg10Gd alloy were studied in details elsewhere [1,8]. The decomposition takes place in the sequence sss → β'' (D019) → β' (cbco) → β (Mg5Gd, cubic). The β'' and β' are metastable phases and β is the high temperature stable phase. It was found that the precipitation effects in HPT-deformed Mg10Gd differ significantly from those in the corresponding coarse-grained material. It is clear from Fig. 2 that a radical decrease in I_2 takes place in the temperature interval (100-220)^{o}C in HPT-deformed Mg10Gd. It indicates a significant recovery of dislocations. A slight local increase in I_2 at 100^{o}C is likely, due to the formation of the β'' phase. However, the β'' phase particles are very fine (10 nm in diameter or less) and were thus not observed by TEM. It should be noted, that the high dislocation density makes TEM observation of fine precipitates very difficult. It can be seen in Fig. 3 that HV for HPT-deformed Mg10Gd falls abruptly after anneal at 80^{o}C, i.e. it precedes the decrease in I_2, see Fig. 2. It indicates that there is a remarkable softening which seems to occur prior to the decrease in dislocation density. It could be connected with some rearrangement of dislocations without a significant change of the net dislocation density or by relaxation of internal stresses introduced by severe plastic deformation. In case of HPT-deformed Mg10Gd the initial drop in HV is reversed at 100^{o}C by a slight increase caused by formation of the β'' phase fine precipitates which cause a weak precipitation hardening. At the same time recovery of dislocations continues which is confirmed by a strong decrease in I_2. Thus, in the temperature range (100–220)^{o}C two competitive processes take place in HPT-deformed Mg10Gd specimen: (i) precipitation hardening, and (ii) softening caused by recovery of dislocations. At higher temperatures the metastable β'' phase dissolves and particles of the stable β phase are formed. The β phase precipitates were identified by TEM in the specimen annealed up to 260^{o}C. Finely dispersed incoherent particles of the β phase cause higher hardening which is reflected by a local maximum of HV at 250^{o}C. Further growth of the β phase precipitates leads to a decrease in HV above 250^{o}C A bright field TEM image of HPT-deformed Mg10Gd annealed to 260^{o}C is shown in Fig. 4b. A significant decrease in the dislocation density inside grains can be seen. However, the grain size does not increase and remains about 100 nm. Thus, contrary to HPT-

deformed Mg, the recovery of dislocations in HPT-deformed Mg10Gd is not accompanied by grain growth. The TEM observations showed that the mean grain size remains about 100 nm up to ≈ 300°C demonstrating very good thermal stability of the UFG structure. A local maximum of I_2 at 300°C is due to the precipitation of the equilibrium β phase in concordance with the HV curve. Coarsening of the β phase particles causes a subsequent decrease in I_2, see Fig. 2. Above 450°C, the β phase particles dissolve and the solid solution is restored.

From our investigations we can conclude that the precipitation sequence in HPT-deformed Mg10Gd differs significantly from that known in the corresponding coarse grained material. Contrary to the coarse-grained alloy, precipitation of the metastable β' phase is absent in HPT-deformed Mg10Gd and the stable β phase is formed at significantly lower temperatures.

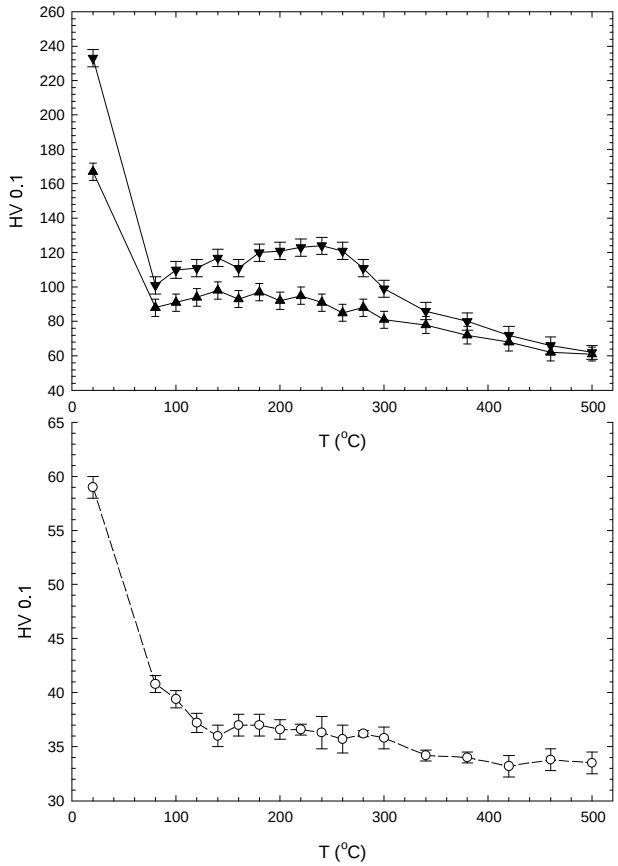

Figure 3 Temperature dependence of microhardness HV. Upper panel - HPT-treated Mg10Gd (full triangles). The triangles oriented up show minimum HV corresponding to the center of the sample, the triangles oriented down show maximum HV corresponding to the edge. Lower panel – HPT-treated Mg (open circles).

Conclusions

The microstructure of HPT-treated Mg and Mg10Gd and its development with temperature were studied. An incomplete dynamic recovery took place during HPT processing of pure Mg. It results in a bimodal kind of structure. The HPT-deformed Mg10Gd exhibits a homogeneous UFG microstructure with a high density of uniformly distributed dislocations and a grain size around 100 nm. Recovery of dislocations occurs already at room temperature in HPT-deformed Mg and is

accompanied by recrystallization. On the other hand, HPT-deformed Mg10Gd exhibits a dramatic decrease in dislocation density in the temperature range (100-220)^{o}C, but no grain growth takes place. The mean grain size in HPT-deformed Mg10Gd remains about 100 nm up to $\approx$ 300^{o}C. There are significant differences of the precipitation sequence in HPT-treated Mg10Gd and corresponding coarse-grained alloy: the formation of the metastable β' phase does not occur and the precipitation of the stable β phase is shifted to lower temperatures.

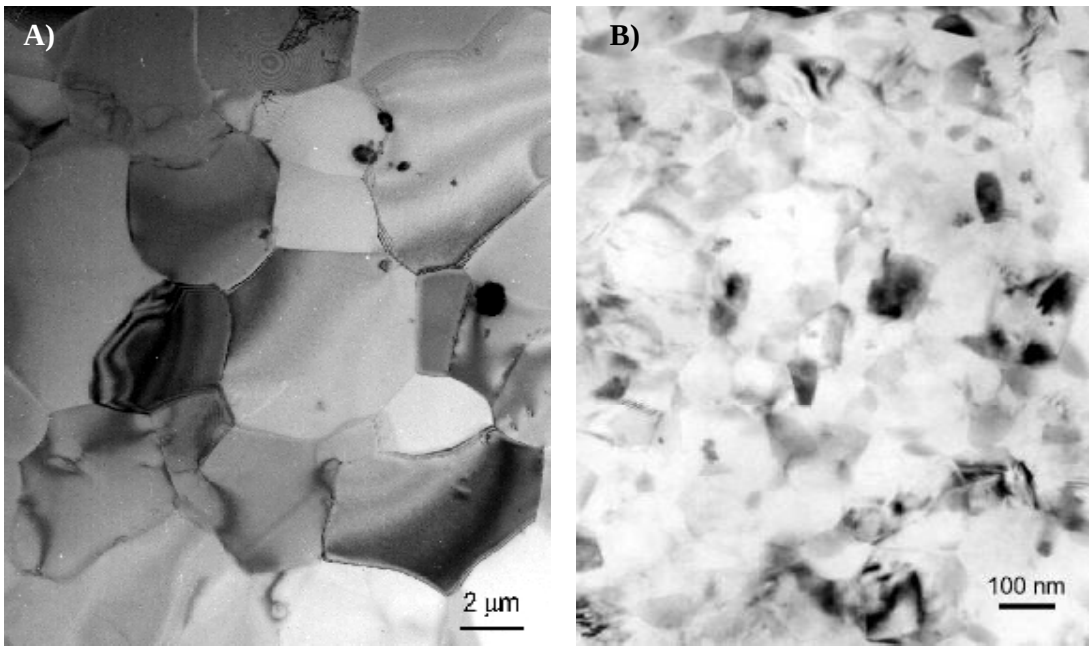

Figure 4 Bright-field TEM image of A) HPT-deformed Mg annealed up to 200^{o}C, B) HPT-deformed Mg10Gd annealed up to 260^{o}C.

Acknowledgement

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References

[1] P. Vostrý, B. Smola, I. Stulíková, F. von Buch, B.L. Mordike: phys. stat. sol. (a) Vol 175, (1999) 491.
[2] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov: Prog. Mat. Sci. Vol 45 (2000), 103.
[3] P. Hautojärvi, C. Corbel, in: A. Dupasquier, A.P. Mills (Eds.), Proceedings of the International School of Physics "Enrico Fermi", Course CXXV, (IOS Press, Varena 1995, p. 491).
[4] F. Bečvář, J. Čížek, L. Lešťak, I. Novotný, I. Procházka, F. Šebesta: Nucl. Instr. Meth. A Vol. 443 (2000) 557.
[5] I. Procházka, I. Novotný, F. Bečvář: Mat. Sci. Forum Vol. 225-257 (1997) 772.
[6] J. Čížek, I. Procházka, B. Smola, I. Stulíková, R. Kužel, Z. Matěj, V. Cherkaska, R.K. Islamgaliev, O. Kulyasova: Mat. Sci. Forum Vol. 482 (2005) 183.
[7] R.K. Islamgaliev, F. Chmelík, R. Kužel: Mat. Sci. Eng. A Vol. 237 (1997) 43.
[8] J. Čížek, I. Procházka, F. Bečvář, I. Stulíková, B. Smola, R. Kužel, V. Cherkaska, R.K. Islamgaliev, O. Kulyasova: phys. stat. sol. (a) Vol. 203 (2006) 466-477.