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Defects in Mg-Zn-Y-Nd alloys with icosahedral phase

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Abstract

Recently it was reported that icosahedral phase (I-phase) with quasicrystalline structure is formed in some lightweight Mg alloys. It was found that Mg alloys containing I-phase exhibit improved mechanical properties which make them attractive for industrial applications. This work presents microstructure investigations and defect studies of squeeze cast Mg-Y-Nd-Zr (WE43) alloy with addition of 14 wt.% and 26 wt.% Zn. For comparison WE43 alloy without any Zn was investigated as well. Presence of the quasicrystalline I-phase was detected by electron diffraction and X-ray diffraction in both WE43 alloys modified by Zn addition. On the other hand, WE43 without Zn does not contain any I-phase. Mechanical properties of as-cast alloys were examined by Vickers microhardness (HV) testing. It was found that presence of I-phase leads to a significant hardening.

Defects in as-cast alloys were investigated by positron lifetime (LT) spectroscopy combined with coincidence Doppler broadening (CDB). Reference sample WE43 alloy without Zn exhibits a single-component LT spectrum with lifetime of ~ 224 ps which is close to the Mg bulk lifetime. On the other hand, vacancy-like defects characterized by positron lifetime of ~ 300 ps were found in WE43 alloys modified by Zn addition. CDB investigations revealed that chemical environment of these defects is enriched with Zn and Y. Hence, our results indicate the existence of vacancy-like defects connected with the I-phase. We suggest that these defects are located at the interfaces between the I-phase and the Mg-matrix.

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1. Introduction

Quasicrystals exhibit unique structure without translation symmetry. Quasicrystalline materials exhibit attractive properties such as high hardness, high corrosion and wear resistance, low friction and surface energy. Quasicrystalline phases with icosahedral symmetry were recently observed in magnesium alloys with zinc and rare earth elements [1]. It was found that interfaces between the icosahedral phase (I-phase) and the α -Mg matrix are characterized by very low surface energy [2]. Mg-alloys strengthened with I-phase precipitates exhibit promising mechanical properties associated with the unique properties of the quasicrystalline phase.

2. Experimental

Samples of WE43 (Mg-Y-Nd-Zr based alloy) and WE43 modified by addition of 14 wt.% (WE43+14Zn) and 26 wt.% (WE43+26Zn) of Zn were prepared by squeeze casting. Composition of the studied alloys determined by chemical analysis is listed in Table 1. All investigations were performed on the as-cast alloys.

Table 1 Chemical composition (in wt.%) of alloys studied.

Sample	Zn	Y	Nd	Zr	Gd	Mg
WE43	-	2.95	2.48	0.30	0.15	balance
WE43+14Zn	13.80	3.06	1.04	0.29	0.10	balance
WE43+26Zn	25.82	3.02	1.16	0.27	0.17	balance

Scanning electron microscopy (SEM) was performed on the FEI Phenom microscope equipped with a detector of backscattered electrons. Since the cross-section of electron backscattering increases with the increasing atomic number, heavier elements are represented by the lighter areas in resulting SEM images (so called Z-contrast).

Positron lifetime (LT) measurements were performed using a digital positron lifetime spectrometer equipped with BaF₂ scintillators coupled to photomultipliers (PMT) Hamamatsu H3378. Anode signal from PMTs is digitized with sampling rate of 4 GHz by a pair of fast 8-bit digitizers Acqiris DC211. Sampled waveforms are stored in a personal computer and analyzed off-line by software employing the integral constant fraction algorithm [3]. Detailed description of the spectrometer is given in Refs. [4,5]. Resolution of the spectrometer expressed as full width at half maximum of resolution function is ~150 ps.

Coincidence Doppler broadening (CDB) spectroscopy of annihilation radiation was performed using a spectrometer equipped with two high purity germanium detectors. The spectrometer exhibits resolution of ~1.0 keV expressed as full width at half maximum of the resolution function at 511 keV.

3. Results and discussion

A representative SEM image of WE43 alloy is shown in Fig. 1(a). Lighter pattern observed along the grain boundaries testifies presence of heavier elements. Moreover, isolated prolonged particles of the eutectic are located at the grain boundaries. Two phases were identified in WE43 sample by XRD in addition to Mg matrix: (i) larger precipitates of β_1 face-centered cubic (fcc) Mg₃Nd_{0.4}Y_{0.6} phase giving sharp reflections to XRD pattern and (ii) fine particles of tetragonal Mg₄₁Nd₅ phase resulting in broad and reflections with low intensity.

The SEM images of WE43 modified with Zn are shown in Fig. 1 (b-d). Both alloys modified with Zn exhibit typical pattern consisting of grains of the α -Mg phase separated by Zn enriched grain boundary

eutectic (GBE). The GBE volume fraction f_E determined from the SEM images is given in Table 2. Obviously, the f_E increases with increasing Zn content. Fig. 1(d) shows the morphology of GBE in WE43+26Zn alloy in higher magnification. The eutectic exhibits lamellar structure with very high surface-to-volume ratio. This is in striking contrast with the morphology of the eutectic phase in WE43 alloy where the fine lamellar structure is absent; see Fig. 1(a).

The quasicrystalline I-phase with composition $Mg_3Zn_6Y_1$ was detected by XRD in both WE43 alloys modified by Zn addition. Moreover, the fcc W-phase ($Mg_3Zn_3Y_2$) was found in WE43+14Zn, while WE43+26Zn contains the fcc Mg_7Zn_3 phase. This is in agreement with Lee et al. [6] who found that presence of the W-phase is typical for Mg-Zn-Y alloys with low Zn/Y ratio, while in the alloys with higher Zn/Y ratio the Mg_7Zn_3 phase is formed.

Table 2 Results of LT investigations: lifetimes τ_i and relative intensities I_i of the exponential components resolved in LT spectra; the quantity τ_f calculated from Eq. (1) to check the consistency of decomposition with the two state simple trapping model, the concentration of vacancy-like defects c_D calculated from LT data using simple trapping model; Vickers hardness HV0.1; the volume fraction of eutectic f_E determined by SEM.

Sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_f (ps)	c_D (ppm)	HV0.1	f_E (%)
WE43	223.9(3)	100	-	-	-	-	87 ± 2	1.8 ± 0.1
WE43+14Zn	187(2)	55(2)	302(3)	45(2)	226(4)	9.1(1)	94 ± 2	9.8 ± 0.7
WE43+26Zn	192(4)	56(3)	302(4)	44(3)	228(5)	8.3(2)	125 ± 4	25.1 ± 0.8

Results of LT measurements are shown in Table 2. WE43 alloy exhibits a single component spectrum with lifetime $\tau_1 \approx 224$ ps which agrees well with the Mg bulk positron lifetime of $\tau_B = 225$ ps [7]. Therefore, we can conclude that the concentration of positron traps in WE43 alloy is lower than detection threshold of positron lifetime spectroscopy. LT spectra of WE43 alloys modified by Zn addition consist of two components. The lifetime τ_1 of the first component is shortened below τ_B due to the positron trapping in defects. The lifetime of the second component $\tau_2 \approx 302$ ps agrees well with the lifetime of positrons trapped in Mg vacancy ($\tau_V = 299$ ps) calculated in Ref. [8]. Hence, the second component represents a contribution of the positrons trapped at vacancy-like defects. Interestingly, vacancy-like defects were detected only in WE43 alloy modified by Zn addition and not in the original WE43 (without Zn). This indicates that the vacancy-like defects are associated with quasicrystalline I-phase which is present in both WE43 alloys modified by Zn addition (WE+14Zn and WE43+26Zn) but is absent in the original WE43 alloy.

Results of LT investigations were analyzed by application of simple trapping model. Consistency of the decomposition of LT spectra with the two state trapping model can be checked using the quantity [9]

$$\tau_f = \left(\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1}. \quad (1)$$

If assumptions of the two state simple trapping model, i.e. a single type of homogeneously distributed positron traps, no detrapping and no trapping of non-thermalized positrons, are fulfilled, then the quantity τ_f obtained from Eq. (1) equals to the bulk positron lifetime τ_B . One can see in Table 2 that in both WE43 alloys modified by Zn addition τ_f indeed agrees well with the Mg bulk lifetime testifying that the simple trapping model assumptions are fulfilled and the concentration of vacancy-like defects can be calculated using the equation [9]

$$c_D = \frac{1}{\nu_D} \frac{I_2}{I_1} \left(\frac{1}{\tau_B} - \frac{1}{\tau_2} \right), \quad (2)$$

where ν_D is the specific positron trapping rate. For vacancies in metals ν_D falls into the range $10^{14} - 10^{15} \text{ s}^{-1}$ [9]. Here we used $\nu_D \approx 10^{14} \text{ s}^{-1}$ since Mg exhibits low electron density in interatomic regions which

makes the positron binding energy to vacancy lower than in dense metals and, thereby, ν_D is expected to be close to the lower limit of the aforementioned interval. The concentration of vacancy-like defects obtained from Eq. (2) is listed in Table 2. Obviously, both WE43 alloys modified by Zn addition exhibit comparable concentration of vacancy-like defects, despite the fact that GBE volume fraction in the WE43+26Zn alloy is significantly higher than in the WE43+14Zn sample. Furthermore, the lifetime $\tau_2 \approx 302$ ps is substantially longer than lifetimes reported for positrons trapped at defects in single-phase quasicrystals (~ 210 ps) reported by Sato et. al. [10]. These results suggest that vacancy-like defects are most probably located not inside of the I-phase but at the interface between the I-phase and Mg matrix.

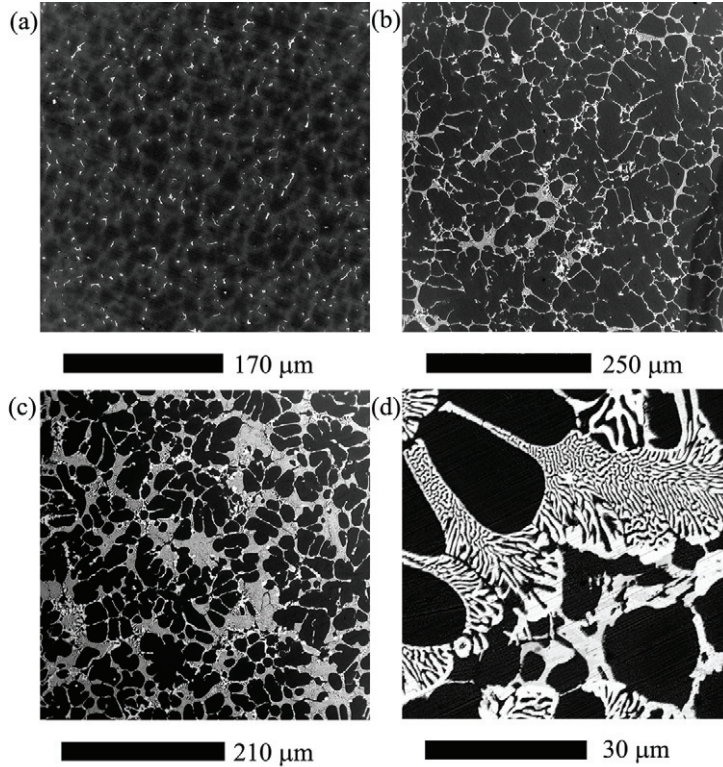


Figure 1 SEM images of: (a) WE43 alloy; (b) WE43+14Zn; (c) WE43+26Zn alloy; (d) WE43+26Zn alloy (detail in higher magnification).

Measured CDB ratio curves (related to well-annealed Mg) are shown in Fig. 2. All studied samples exhibit a peak in the ratio curves at 8×10^3 m₀c which represents a contribution of positrons annihilated by electrons belonging to rare Earth elements, i.e., Y, Nd and Gd. In addition WE43 alloys modified by Zn addition exhibit also a broad peak centered at 18×10^3 m₀c which comes from positrons annihilated by 3d Zn electrons. In the high momentum region, where the contribution of positrons annihilated by core electrons dominates, the ratio curve ρ related to well-annealed Mg can be expressed as linear combination

$$\rho = (1 - F_V) \left(\xi_{Mg,B} + \xi_{Zn,B} \rho_{Zn,B} + \xi_{Y,B} \rho_{Y,B} + \xi_{Nd,B} \rho_{Nd,B} + \xi_{Zr,B} \rho_{Zr,B} + \xi_{Gd,B} \rho_{Gd,B} \right) + F_V \left(\xi_{Mg,V} \rho_{Mg,V} + \xi_{Zn,V} \rho_{Zn,V} + \xi_{Y,V} \rho_{Y,V} + \xi_{Nd,V} \rho_{Nd,V} + \xi_{Zr,V} \rho_{Zr,V} + \xi_{Gd,V} \rho_{Gd,V} \right) \quad (3)$$

where $\rho_{Zn,B}$, $\rho_{Y,B}$, $\rho_{Nd,B}$, $\rho_{Zr,B}$ and $\rho_{Gd,B}$ are the ratio curves of free positrons annihilated by Zn, Y, Nd, Zr and Gd electrons, respectively. These curves were obtained by the measurement of the well-annealed reference sample of corresponding pure metals. The symbols $\rho_{Mg,V}$, $\rho_{Zn,V}$, $\rho_{Y,V}$, $\rho_{Nd,V}$, $\rho_{Zr,V}$ and $\rho_{Gd,V}$ denote

the ratio curves for positrons trapped at vacancy-like defects and annihilated by Mg, Zn, Y, Nd, Zr and Gd electrons, respectively. These curves were obtained by the measurement of cold rolled reference samples of corresponding pure metals which exhibit saturated positron trapping at defects. The fraction F_V of positrons trapped at the vacancy-like defects was calculated from LT data using the two state simple trapping model [9]

$$F_V = I_2 \frac{\tau_2 - \tau_1}{\tau_2} \tag{4}$$

The coefficients $\zeta_{Mg,B}$, $\zeta_{Zn,B}$, $\zeta_{Y,B}$, $\zeta_{Nd,B}$, $\zeta_{Zr,B}$ and $\zeta_{Gd,B}$ represent the fraction of free positrons annihilated by Mg, Zn, Y, Nd, Zr and Gd electrons, respectively, and always fulfill the normalization condition $\zeta_{Mg,B} + \zeta_{Zn,B} + \zeta_{Y,B} + \zeta_{Nd,B} + \zeta_{Zr,B} + \zeta_{Gd,B} = 1$. Similarly, the coefficients $\zeta_{Mg,V}$, $\zeta_{Zn,V}$, $\zeta_{Y,V}$, $\zeta_{Nd,V}$, $\zeta_{Zr,V}$ and $\zeta_{Gd,V}$ represent the fraction of positrons trapped at vacancy-like defects and annihilated by Mg, Zn, Y, Nd, Zr and Gd electrons, respectively. These coefficients also fulfill the normalization condition $\zeta_{Mg,V} + \zeta_{Zn,V} + \zeta_{Y,V} + \zeta_{Nd,V} + \zeta_{Zr,V} + \zeta_{Gd,V} = 1$.

Table 3 Results of fitting of CDB curves using model function described by Eq. (3). The fraction $\zeta_{Zn,B}$ was fixed at 0.023 representing the maximum Zn solubility in Mg. Fraction F_V was calculated according to Eq. (4) for WE43 alloys modified by addition of zinc, in case of WE43 alloy it was obtained from fitting of CDB ratio curves by model function described by Eq. (3).

	$\zeta_{Zn,B}$	$\zeta_{Y,B}$	$\zeta_{Nd,B}$	$\zeta_{Zr,B}$	$\zeta_{Gd,B}$	$\zeta_{Zn,V}$	$\zeta_{Y,V}$	$\zeta_{Nd,V}$	$\zeta_{Zr,V}$	$\zeta_{Gd,V}$	F_V
WE43	-	0.008(2)	0.004(1)	0.00	0.00	0.00	0.00	0.30(2)	0.10(2)	0.60(2)	0.14(1)
WE43+14Zn	0.023	0.010(5)	0.002(1)	0.00	0.00	0.19(3)	0.30(3)	0.00	0.00	0.00	0.16(1)
WE43+26Zn	0.023	0.010(5)	0.002(1)	0.00	0.00	0.54(4)	0.46(4)	0.00	0.00	0.00	0.16(1)

The fractions ζ obtained from fitting of CDB ratio curves by the model curve described by Eq. (3) are listed in Table 3 and the model curves which gave the best fit with experimental data are plotted in Fig. 2 by solid lines. Table 3 shows that fraction of positrons annihilated by electrons of rare Earth elements is substantially higher than the concentration of Y, Nd and Gd in the samples obtained from chemical analysis. This testifies that positrons are annihilated in the rare Earth enriched phases.

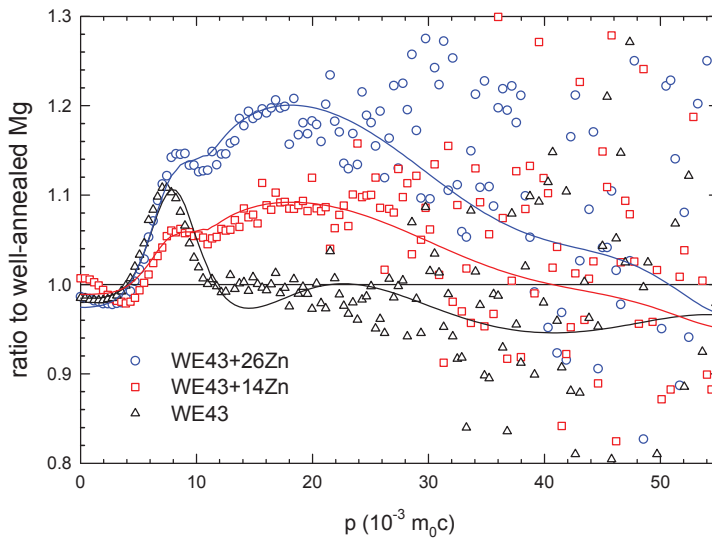


Figure 2 CDB ratio curves (relative to well-annealed Mg). Open circles - measured data; solid lines - fit.

CDB results indicate that in the WE43 alloy positrons annihilate predominantly in Mg matrix but certain fraction of positrons annihilate from localized state at Nd and Gd-rich precipitates. The Nd-rich particles are apparently finely dispersed particles of $\text{Mg}_{41}\text{Nd}_5$ phase identified in WE43 sample by XRD. A high fraction of positrons annihilated by Gd electrons indicate that substantial fraction of Nd atoms in $\text{Mg}_{41}\text{Nd}_5$ phase is substituted by Gd. Since only a single component with lifetime comparable with τ_B was found in LT spectrum of WE43 sample, there are probably no open-volume defects associated with Nd and Gd-rich precipitates but positrons are localized directly inside these particles due to higher absolute value of positron affinity compared to Mg matrix.

It is clear that chemical environment of vacancy like defects in WE43 alloy modified by Zn addition and characterized by lifetime of ≈ 300 ps contain substantially enhanced concentration of Zn and Y as seen from Table 3. This is most pronounced in the case of WE43+26Zn alloy where virtually all positrons trapped at vacancy-like defects are annihilated by Zn or Y electrons. This result supports the picture that vacancy-like defects in WE43 modified by Zn addition are associated with quasicrystalline I-phase $\text{Mg}_3\text{Zn}_6\text{Y}_1$ characterized by high Zn and Y content. Vacancy-like defects are probably situated at interfaces between the I-phase precipitates and the Mg matrix where misfit defects are necessary to accommodate the incommensurable atom spacing in these phases. However, further investigations are needed to support this hypothesis.

4. Conclusions

Samples of WE43 alloy and WE43 alloy modified by addition of 14 wt.% and 26 wt.% of zinc were investigated. Quasicrystalline icosahedral phase $\text{Mg}_3\text{Zn}_6\text{Y}_1$ was identified in the samples of WE43 alloy modified by Zn addition. It was found that the samples containing icosahedral phase contain vacancy-like defects located most probably at the interface between the icosahedral phase and Mg matrix.

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