Effects in Mg-Zn-based alloys strengthened by quasicrystalline phase

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Abstract. Magnesium Mg-based alloys are promising lightweight structural materials for automotive, aerospace and biomedical applications. Recently Mg-Zn-Y system attracted a great attention due to a stable icosahedral phase (I-phase) with quasicrystalline structure which is formed in these alloys. Positron lifetime spectroscopy and in situ synchrotron X-ray diffraction were used to study thermal stability of I-phase and precipitation effects in Mg-Zn-Y and Mg-Zn-Al alloys. All alloys containing quasicrystalline I-phase exhibit misfit defects characterized by positron lifetime of ~ 300 ps. These defects are associated with the interfaces between I-phase particles and Mg matrix. The quasicrystalline I-phase particles were found to be stable up to temperatures as high as ~ 370°C. The W-phase is more stable and melts at ~ 420°C. Concentration of defects associated with I-phase decreases after annealing at temperatures above ~ 300°C.

1. Introduction
Mg-Zn-Y system attracts attention due to presence of icosahedral phase (I-phase) with quasicrystalline structure [1]. Quasicrystals exhibit structure with lack of translation symmetry and posses unique combination of physical properties: high hardness, high corrosion resistance and low surface energy [2]. Although they are not directly applicable for structural applications due to their brittleness, they could be used as strengthening agents in Mg alloys. Moreover, I-phase has strong interfacial bonding to the Mg matrix, low friction coefficient and low surface energy which is beneficial for ductility and deformability.

Positron annihilation spectroscopy revealed existence of misfit defects associated with the interfaces between I-phase particles and α-Mg matrix [3]. Thermal stability of I-phase and precipitation effects in Mg-Zn-Y and Mg-Zn-Al alloys were studied in this work using positron lifetime spectroscopy combined with in situ synchrotron X-ray diffraction (XRD). Development of mechanical properties was monitored by microhardness testing.

2. Experimental details
Three groups of alloys were studied in this work: (i) Mg-Y-Nd-Zr (WE43) alloy, (ii) WE43 alloy modified by addition of various amount of Zn, and (iii) Mg-Zn-Al alloys. Both WE43 modified by Zn and Mg-Zn-Al alloys contain quasicrystalline I-phase. The WE43 alloy without Zn does not contain
quasicrystalline phase and was used as a reference material. All alloys were produced by squeeze casting under a protective atmosphere (Ar + 1% SF₆). Chemical compositions of studied alloys are shown in tables 1 and 2.

**Table 1.** Compositions of Mg-Zn-Y-based alloys in wt.%.

|        | Zn  | Y    | Nd  | Zr  | Gd  | Mg          |
|--------|-----|------|-----|-----|-----|-------------|
| WE43   | -   | 2.95 | 2.48| 0.30| 0.15| balance     |
| WE43+11Zn | 10.90 | 1.80 | 0.73| 0.28| 0.12| 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     |

**Table 2.** Compositions of Mg-Zn-Al-based alloys in wt.%.

|        | Zn  | Al  | Ca  | Mg          |
|--------|-----|-----|-----|-------------|
| Mg5Zn3Al | 5.3 | 3.2 | 0.1 | balance     |
| Mg12Zn3Al | 11.9| 3.1 | -   | balance     |

Digital positron lifetime spectrometer [4] with excellent time resolution of 145 ps was used for positron lifetime measurements. The resolution of the spectrometer was calculated as FWHM of resolution function obtained from fitting of positron lifetime spectrum of a well-annealed Mg reference sample. Each measured spectrum consisted of at least 10⁷ annihilation events. The ²²Na₂CO₃ positron source deposited on 2 µm thick mylar foil exhibits source contribution consisting of two components with lifetimes 368 ps and 1.5 ns and relative intensities 7% and 1%, respectively, which was always subtracted from the spectra.

The measurements of Vickers microhardness (HV) were performed using a STRUERS Duramin 300 hardness tester with a load of 100 g applied for 10 s.

In-situ measurement of synchrotron X-ray diffraction during heat treatment was used to monitor evolution of phase composition at elevated temperatures. Sample of as-cast WE43+14Zn alloy was subjected to linear heating from room temperature to 425°C. Subsequently the sample was cooled down back to room temperature. Heating and cooling rates were 5 K/min, wavelength of X-ray radiation was set to λ = 0.142 Å.

3. Results

Results of positron lifetime measurements of as-cast alloys are shown in table 3. The WE43 alloy, which does not contain quasicrystalline I-phase, exhibits single component spectrum with lifetime τ₁ = (223.9 ± 0.3) ps which agrees well with the bulk positron lifetime in well-annealed Mg [5]. All other alloys, which contain quasicrystalline phase, exhibit two component spectra, see table 3. The first component comes from annihilation of free positrons while the second component can be

**Table 3.** Results of positron lifetime measurements of as cast samples.

| State   | τ₁ (ps) | I₁ (%) | τ₂ (ps) | I₂ (%) |
|---------|---------|--------|---------|--------|
| WE43    | 223.9(3)| 100    | -       | -      |
| WE43+26Zn | 192(4) | 56(3)  | 302(4)  | 44(3)  |
| WE43+14Zn | 187(2) | 58(2)  | 302(3)  | 42(2)  |
| WE43+11Zn | 201(2) | 67(3)  | 296(5)  | 33(3)  |
| Mg5Zn3Al | 219(1)  | 96(1)  | 290(10) | 4(1)   |
| Mg12Zn3Al | 217.3(5)| 93.9(5)| 300(10) | 6.1(5) |
attributed to annihilation of positrons trapped at defects. The lifetime of the second component $\tau_2 \approx 300$ ps provides characteristic signature of misfit defects associated with quasicrystalline phase [3].

**Table 4.** Results of positron lifetime measurements of WE43+11Zn samples annealed at 500°C.

| State             | $\tau_1$ (ps) | $I_1$ (%) | $\tau_2$ (ps) | $I_2$ (%) |
|-------------------|---------------|-----------|---------------|-----------|
| WE43+11Zn as-cast | 201(2)        | 67(3)     | 296(5)        | 33(3)     |
| WE43+11Zn 500°C/1 h Q | 219(1)  | 96(1)     | 290(10)       | 4(1)      |
| WE43+11Zn 500°C/1 h SC | 217.3(5) | 93.9(5)   | 300(10)       | 6.1(5)    |

The effect of different cooling rates after isothermal annealing was studied on WE43+11Zn alloy. Two samples were annealed at 500°C for 1 hour, one was quenched into the water (Q) while the second one was slowly cooled down with furnace (SC). Results of positron lifetime measurements presented in table 4 revealed that misfit defects remain present in the alloys after annealing at 500°C. However, the fraction of positrons trapped at defects significantly decreases after annealing, especially in the slowly cooled sample.

**Table 5.** Results of positron lifetime measurements of isochronally annealed WE43+11Zn alloy.

| State             | $\tau_1$ (ps) | $I_1$ (%) | $\tau_2$ (ps) | $I_2$ (%) |
|-------------------|---------------|-----------|---------------|-----------|
| WE43+11Zn as-cast | 201(2)        | 67(3)     | 296(5)        | 33(3)     |
| WE43+11Zn 160°C   | 180(10)       | 48(4)     | 278(9)        | 52(4)     |
| WE43+11Zn 300°C   | 203(9)        | 70(5)     | 298(7)        | 30(5)     |
| WE43+11Zn 440°C   | 210(10)       | 75(5)     | 300(10)       | 25(5)     |

The Mg-Zn-Y-based alloys were isochronally annealed with step 20 K/20 min to monitor the development of physical properties with increasing annealing temperature. The evolution of microhardness during isochronal annealing is shown in figure 1. Hardness has generally decreasing trend but there are two notable hardening peaks at ~ 160°C and ~ 440°C.

Based on the development of hardness, annealing temperatures of 160°C, 300°C and 440°C (indicated in figure 1 by arrows) were selected for positron lifetime spectroscopy measurements.
The results of these measurements for WE43+11Zn alloy are summarized in table 5. After annealing at 160°C, the intensity of the second component increased and its lifetime decreased by roughly 20 ps. It has to be noted that positron lifetime of ~ 260 ps was observed in binary Mg-Zn alloy after annealing at 220°C [6]. This lifetime was attributed to positrons trapped at open-volume misfit defects at the interfaces between precipitates and Mg matrix. Therefore, most likely explanation of shortened lifetime $\tau_2$ in WE43+11Zn alloy is that precipitation occurred after annealing at 160°C and components with lifetimes ~ 260 ps (misfit defect at precipitate-matrix interfaces) and ~ 300 ps (misfit defects associated with I-phase) cannot be separated due to limited experimental resolution. Instead, one component with a lifetime of $\tau_2 = (278 \pm 9)$ ps was observed. Precipitates formed at 160°C dissolve at higher annealing temperatures and the lifetime $\tau_2$ of the second component again has value of ~ 300 ps. However, intensity of the second component is slightly decreased compared to the as-cast state.

Results of in-situ XRD studies of WE+14Zn alloy are presented in figure 2 as a 2D image in which individual XRD patterns for each temperature are shown as horizontal lines and intensity is converted to color. The vertical axis shows evolution of XRD patterns during heat treatment. In the as-cast sample, peaks corresponding to Mg matrix, icosahedral I-phase (Mg₃Zn₆Y), cubic W-phase (Mg₃Zn₃Y₂) and graphite crucible in which the sample was placed were identified. Peaks corresponding to the I-phase disappeared when temperature exceeded ~ 367°C, indicated by the red horizontal arrow in the figure. Diffuse bump in the background, testifying presence of liquid phase, also appeared at this temperature. Peaks of W-phase remained visible up to ~ 416°C, indicated by the blue horizontal arrow in the figure. During the cooling, peaks of W-phase and I-phase appeared at temperature ~ 416°C and ~ 367°C, respectively.

![Figure 2. Results of in situ XRD measurement during linear heat up and cool down from room temperature to 425°C. Each horizontal line represents diffraction pattern at some temperature. Intensity was converted to the color scale and increases from black to red. Most pronounced peaks of Mg matrix (black), I-phase (red), W-phase (blue) and graphite crucible (gray) are marked by colored arrows.](image)

Because of lattice expansion the diffraction peaks shift to lower diffraction angles with increasing temperature their temperature evolution during heating and subsequent cooling in figure 2 forms typical "V" shape. The diffraction peaks corresponding to I-phase show different behavior than other peaks. Contrary to other phases the positions of the peaks corresponding to I-phase do not change linearly with temperature but exhibits nonlinear dependence which can be seen as slightly bent curves in figure 2. The relative lattice expansion with respect to room temperature was calculated from fitted
positions of the diffraction peaks and is plotted in figure 3. Thermal expansion of Mg matrix and graphite is approximately linear with temperature. On the other hand, thermal expansion of I-phase exhibits a strong nonlinearity indicating that the coefficient of thermal expansion of I-phase remarkably changes around 310°C.

![Figure 3. Relative thermal expansion with respect to 25°C calculated from XRD data.](image)

4. Discussion

Results of positron lifetime measurements show that all studied alloys containing quasicrystalline phase exhibit two component spectrum with lifetime of the second component $\tau_2 \approx 300$ ps. This lifetime therefore characterizes misfit defects which are uniquely associated with quasicrystalline phase in Mg alloys. These defects are most likely situated at the interface of quasicrystalline phase and Mg matrix. Due to incommensurability of their lattices, misfit defects must be created at their interface. In order to partially retain the coherency between I-phase and $\alpha$-Mg matrix steps or ledges are introduced periodically along the interface and misfit defects are located at these steps along the interface. Presence of these ledges was confirmed by high resolution transmission electron microscopy [7].

Size of the misfit defects can be estimated by comparison of the $\tau_2 \approx 300$ ps with the positron lifetime for a Mg monovacancy. Theoretically calculated lifetime for a Mg monovacancy is $\approx 300$ ps [5]. This would suggest that misfit defects associated with I-phase are approximately of the same size as Mg monovacancy. On the other hand, the experimental positron lifetime reported for Mg monovacancy is $\approx 255$ ps [8]. Hence, according to these experimental results, the misfit defects associated with I-phase are larger than Mg monovacancy. The discrepancy between experimental results and theoretical calculations of positron lifetime for Mg monovacancy is further discussed in reference [9].

Although annealing at 500°C increased the volume fraction of I-phase in grain boundary phase [10], the intensity of the second component in positron lifetime spectrum decreased after annealing. This is due to the fact, that finely dispersed precipitates of I-phase are present in the in Mg matrix of the as-cast alloy and most of these small precipitates are dissolved during annealing. Hence, the content of I-phase in grain boundary phase is enhanced by annealing at 500°C but its concentration in Mg grains is decreased due to dissolution of the fine I-phase precipitates. This leads to a reduction of the fraction of positrons trapped at misfit defects associated with I-phase. Decrease in the intensity of the second
component in positron lifetime spectra after isochronal annealing at temperatures 300°C and 440°C is caused by the same reason.

In situ XRD investigations were performed to study phase transformations in WE43+14Zn alloy during linear heating. The temperatures of formation, i.e. ~ 367°C for the I-phase and ~ 416°C for the W-phase, determined by XRD differ significantly from the values obtained by differential thermal analysis, which are ~ 450°C [7] and ~ 510°C [11]. Our differential scanning calorimetry measurements of WE+14Zn alloy revealed presence of four endothermic peaks at temperatures 330-360°C, ~ 420°C, ~ 445°C and ~ 505°C. First two peaks could be attributed to melting of I-phase and W-phase respectively. The most pronounced peak located at 445°C might be due to melting of whole grain boundary region. However, using this interpretation, the origin of the last peak located around 505°C remains unknown. Further investigations are clearly needed to definitively assign phase transitions observed by X-ray diffraction to peaks measured by differential scanning calorimetry.

Thermal lattice expansion of I-phase shows significant nonlinearity with increase of the thermal expansion around 310°C. This is most likely linked to some structural changes in I-phase occurring in this temperature range. Additional work is needed to elucidate the cause of this effect.

5. Conclusions
Misfit defects associated with interfaces between I-phase and Mg matrix were observed in Mg-Zn-Y and Mg-Zn-Al alloys. Density of defects decreases after annealing at 500°C due to decrease of density of precipitates in Mg matrix and grain growth.

Nonlinear thermal expansion of I-phase lattice was observed above 310°C, which indicates some structural change in the I-phase. Temperatures of phase transformations occurring in WE43+14Zn alloy were determined by in situ XRD during linear heating.

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