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Positron annihilation study of the Mg-Zn-Y alloys with long period stacking ordered (LPSO) structures

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Abstract. The Mg-Zn-Y alloys with long period stacking ordered (LPSO) structures have been studied by positron annihilation lifetime (PAL), coincidence Doppler broadening (CDB) and atom probe tomography (APT). The positron lifetime for all the Mg-Zn-Y alloys is in a range of 221~225 ps, very close to the positron lifetime for pure Mg bulk, 222 ps. Low temperature measurements of the positron lifetime also give no evidence for shallow positron trapping sites in the LPSO phases. The CDB shows that most of the positrons are annihilated with electrons of Mg. These results suggest that sub-nano scale open volumes, which were expected to exist in the Zn/Y enriched layers synchronized with stacking faults of the LPSO phases by the first principles calculations, are not present.

1. Introduction

Recently, long period stacking ordered (LPSO) structures formed in the Mg-Zn-Y alloys have attracted more attention, which are believed to play a critical role in improving the mechanical properties of the Mg-Zn-Y alloys [1-7]. The LPSO structures (four polytypes: 10H, 14H, 18R, 24R) are long period stacking variants of hcp-Mg by introducing the Zn/Y enriched layers synchronized with stacking faults periodically. The Zn/Y atoms are located on four close-packed layers, which have an ABCA stacking sequence and form a local face centered cubic (fcc) structure. Preceding first principles calculations [7] suggested that sub-nano open volumes with mono-vacancy size may be present in these Zn/Y enriched layers of the LPSO phases due to the large displacements of the constituent atoms. Thus it is necessary to confirm experimentally whether such open volumes exist or not in the LPSO phases, because these open volumes may affect the stability of the LPSO phases.

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However, the local structure of the Zn/Y enriched layers of the LPSO phases is difficult to be observed even by using high resolution TEM and STEM.

Positron annihilation spectroscopy (PAS) is well known to detect open volumes in materials. Since the open volumes act as positron attractive centers with negative charge and low electron density, positrons can easily get trapped by the open volumes and show differences in annihilation characteristics, such as increased positron lifetime and annihilation ratio with electrons having low momentum. Positron annihilation lifetime (PAL) could provide us information on the open volumes. Coincidence Doppler broadening (CDB) could identify the chemical environment around the positron annihilation sites [8-11].

In order to confirm whether the open volumes as expected by the calculations exist or not in various types of the LPSO phases in the Mg-Zn-Y alloys, The PAL and CDB measurements were employed at a temperature range from 10 K to 300 K in the present study.

2. Experimental procedure

At present, it is very difficult to prepare the single crystal Mg-Zn-Y alloys, and the formation of the LPSO polytypes depends on the heat-treatments, thus the $Mg_{97}Zn_1Y_2$ and $Mg_{85}Zn_6Y_9$ alloys subjected to the present study are polycrystalline alloys going through various heat-treatments. Their master alloy ingots were prepared either by high-frequency induction melting or by conventional furnace melting. $Mg_{97}Zn_1Y_2$ ingots were solution-treated at 823 K for 8 h, followed by quenching into water and annealed at 473 K for 120 h, 573 K for 120 h and 673 K for 48 h, respectively, in order to obtain various types of the LPSO phases. The $Mg_{85}Zn_6Y_9$ ingot was extruded and annealed at 673 K for 72 h to obtain near single 18R-LPSO phase for giving a direct comparison. Details of the preparation procedure are described elsewhere [4,7]. The LPSO phases in each sample have already been confirmed by TEM [4] or STEM [7] and the results are listed in Table 1.

Atom probe tomography (APT), a powerful method for elemental mapping of materials in three dimensional real space with nearly atomic-scale resolution [12], was employed on the $Mg_{85}Zn_6Y_9$ in order to explore whether the chemical order of the 18R-LPSO phase is consistent with the structural model proposed by STEM [7].

The PAL measurements for all the specimens were performed by using a digital oscilloscope. The ^{22}Na positron source was sandwiched between two pieces of identical pellets. The time resolution is about 190 ps in full width at half maximum (FWHM) and each spectrum contains more than 2×10^6 counts.

The CDB measurements for all the specimens were performed by using two HP-Ge detectors. The overall energy resolution is 1.0 keV in FWHM, which corresponds to a momentum resolution of 3.91×10^{-3} m_0c, where m_0 is the electron or positron rest mass and c is the speed of light. The difference in energies of two γ-rays is cp_L, where p_L is the longitudinal component of the positron-electron momentum along the direction of the γ–ray emission [10-11]. Each spectrum contains more than 3×10^7 accumulated events. The CDB ratio curves were obtained by normalizing the momentum distribution of each spectrum to pure Mg. The peak to background ratio is more than 10^5, which enables us to observe positron annihilation with core electrons [8-11].

3. Results and discussion

3.1 Atom probe study of 18 R in the $Mg_{85}Zn_6Y_9$

Atom map of Zn and Y in the 18R LPSO structure in the $Mg_{85}Zn_6Y_9$ was shown in Figure 1. The Zn/Y enriched layers of the 18R in the $Mg_{85}Zn_6Y_9$ alloy with an interval distance of ~1.6 nm are observed clearly, which is consistent with the 18R-LPSO structural model [6] proposed basing on STEM observation. The

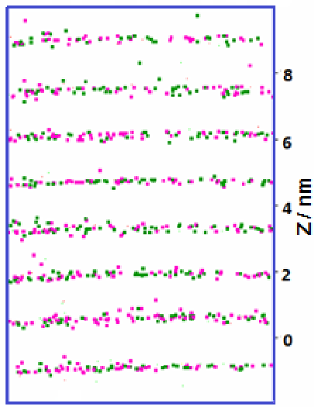

Figure1. Atom map of the Zn/Y enriched layers of the 18R in the $Mg_{85}Zn_6Y_9$. Pink and green dots represent Y and Zn atoms, respectively.

ratio of Y to Zn within four closed packed Zn/Y enriched layers was 1.33 from AP, in good agreement with that value for Zn_6Y_8 clusters 1.33 proposed by the first principles calculations [7].

3.2 Positron annihilation lifetime of the Mg-Zn-Y alloys

Table 1 shows the positron lifetime of the Mg-Zn-Y alloys measured at 300 K. After subtracting the contribution from source component (τ_s=391 ps, I_s=14.8%) and background, all the positron lifetime spectra of the Mg-Zn-Y alloys comprised only a single lifetime component (τ_1: 221~ 225 ps), very close to that for pure Mg bulk (τ_b ~ 222 ps). This result indicates positrons are not trapped by open volumes in the LPSO phases of the Mg-Zn-Y alloys.

Table 1. The positron lifetime of the Mg-Zn-Y alloys

Sample	Mg	$Mg_{85}Zn_6Y_9$ extruded	$Mg_{97}Zn_1Y_2$ cast bulk			
Heat treatment	—	673 K,72 h	As quenched	473 K,120 h	573 K,120 h	673 K,48 h
Phase	α	18R	α+18R+10H	—	α+18R	α+14H+18R
Positron Lifetime/ps	221.5±0.2	222.8±0.2	221.0±0.3	222.4±0.2	225.5±0.2	222.4±0.3

If open volumes in the Zn/Y enriched layers of the LPSO phases are shallow trapping sites for positron, they could be detected by low temperature measurements, therefore the positron lifetime and CDB measurements were performed as a function of temperature (from 10 K to 300 K) for the $Mg_{85}Zn_6Y_9$ alloy. However, the positron lifetime of this alloy measured at 10 K, 100 K and 300 K was 224.2 ps, 228.0 and 222.8 ps, respectively. Nearly no shallow trapping effect is seen in this alloy, which suggests the LPSO phases in the Mg-Zn-Y alloy are free from the open volumes.

In addition to the PAL, the CDB measurements of the Mg-Zn-Y alloys were performed to study the chemical environment where the positrons are annihilated. Figure 2 (a) shows the CDB results of pure Y, pure Zn and the Mg-Zn-Y alloys performed at 300 K. Figure 2 (b) shows the CDB results of the $Mg_{85}Zn_6Y_9$ alloy performed at a temperature range from 10 K to 300 K.

(a) Mg-Zn-Y alloys (b) $Mg_{85}Zn_6Y_9$ alloy

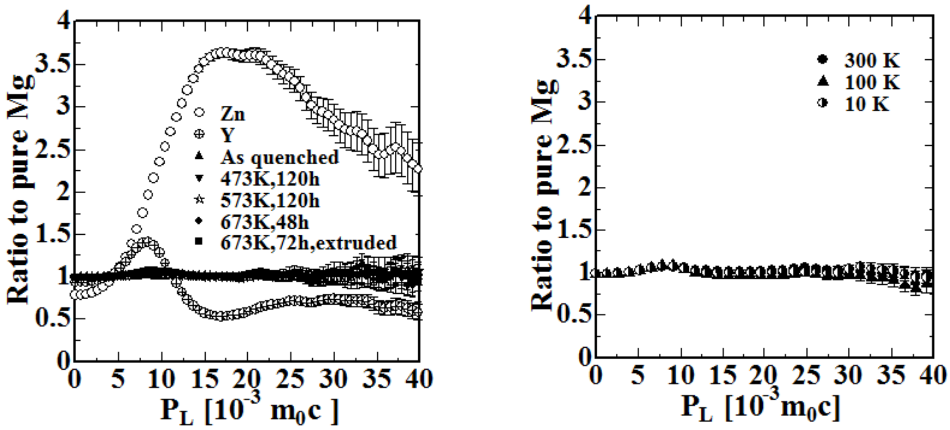

Figure 2. (a) The CDB ratio curves of pure Y, Zn and the Mg-Zn-Y alloys measured at 300 K to pure Mg, (b) The CDB ratio curves of the $Mg_{85}Zn_6Y_9$ alloy measured at 10 K, 100 K and 300 K to pure Mg.

As seen from Figure 2 (a), Zn showed a very high and wide annihilation peak located at 10~ 35×10^{-3} m_0c, which was ascribed to the annihilation of positrons with 3d electrons of Zn. Y showed an annihilation peak and valley located at 10×10^{-3} m_0c and 16×10^{-3} m_0c, respectively. Although the Mg-Zn-Y alloys went through different heat-treatments and hot-extrusion process, their ratio curves obtained at 300 K exhibited common features: no difference either in shape or in height for each other over the whole momentum region, neither Zn nor Y annihilation peak/valley was found. From figure 2 (b), the ratio curves obtained at 10 K, 100 K and 300 K for the $Mg_{85}Zn_6Y_9$ alloy was quite similar to each other either. The CDB measurements show that most of positrons are annihilated with electrons of Mg and no other elements are detected by positrons in the Mg-Zn-Y alloys.

Positron annihilation results suggest that the LPSO phases are free from open volumes, in contrast to the prediction of the first principles calculations [7]. Very recently, another group [13] speculate that the clusters in the Mg-Zn-Y alloys become stable by introducing extra atoms to the sites where the open volumes were expected to form based on the first principles calculations, thus the open volumes should not exist by the occupation of extra atoms, consistent with the present positron annihilation result.

As very qualitative discussion, another possibility that the LPSO phases have open volumes but not detected by positrons is not completed excluded, because the positron affinity of Mg is ~1 eV lower than Zn and Y [14]. The positrons may preferably annihilate with electrons of Mg locating in intervals of the Zn/Y enriched layers, thus the open volumes within the Zn/Y enriched layers can not trap positrons. However, it is very difficult to estimate quantitatively, further study including the first principles calculations of the positron state in the LPSO phases is necessary to explain in the future.

4. Conclusions

The $Mg_{97}Zn_1Y_2$ cast bulk alloys and $Mg_{85}Zn_6Y_9$ extruded alloy with the LPSO phases were studied by positron annihilation spectroscopy. The Mg-Zn-Y alloys employed in this study went through different heat-treatments and hot-extrusion, and consequently various types of the LPSO phases were obtained. However, there are no differences between each Mg-Zn-Y alloy and pure Mg either in positron lifetime or in CDB curve, which suggest the LPSO phases in the Mg-Zn-Y alloys are free from open volumes.

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