The γ” Phase in Mg-RE-TM Alloys

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In magnesium–rare earth–transition metal (Mg-RE-TM) alloys, the γ” phase (with a hexagonal structure with the space group $P\bar{6}2m$) is a critical strengthening phase that can significantly improve their mechanical properties. However, compared to other phases in Mg-RE-TM alloys, research on the γ” phase is less documented, and an understanding of the γ” phase is not well established

Keywords: Mg-RE-TM alloys ; phase ; stability

1. Introduction

Magnesium–rare earth–transition metal (Mg-RE-TM) alloys have been developed to be superior-strength and age-hardenable alloys [1][2]. They have potential applications in the aerospace and aviation industries, the weapon and defense industries, as well as the auto industry and other civil industries [1]. RE elements (i.e., Gd, Y, etc.) are added to improve the mechanical properties of Mg alloys [1][2]. TM elements (i.e., Zn, Ag, etc.) are micro-alloyed together with the RE elements to constitute different strengthening phases. The main strengthening phases in Mg-RE-TM alloys include prismatic β series precipitates [3][4][5][6] and basal-plate-like precipitates that include the γ’ [7][8]/long-period stacking ordered (LPSO) phase [9][10][11][12][13] and γ” phases [7][14][15][16][17]. These strengthening phases play a critical role in determining the mechanical properties of these alloys [18]. Research on the γ” phase in Mg-RE-TM alloys is relatively less documented when compared to the extensive work on the γ’/LPSO phase and β series phases. In addition, the γ” phase has not been unambiguously distinguished from the Guinier–Preston (G.P.) zone in the literature [7][14][15][16][19][20][21][22][23][24][25][26][27][28][29][30].

2. Structure of the γ” Phase

The structure of the γ” phase has been inconsistently documented in the literature. In 1980, Nuttal et al. [26] observed basal-plate-like precipitates (they had designated the precipitated phase γ”) during aging in a dilute Mg-Nd-Zn alloy. The aging sequence was as follows: supersaturated solution→low temperature reaction→γ”→γ [26]. Here, the γ” phase exhibited a hexagonal structure with lattice parameters of $a = 3-\sqrt{3}a_{Mg}$, $c = 3c_{Mg}$ ($a = 0.556$ nm, $c = 1.563$ nm). The orientation relationship between the γ” phase and Mg matrix was $(0001)_{\gamma''}$ $[10\underline{1}01\bar{0}]_{\gamma''}$//$(0001)_{Mg}$ $[2\underline{1}\underline{1}01\bar{1}\bar{0}]_{Mg}$. In their opinion, the low-temperature reaction in the aging sequence was caused by the formation of either short-range order or a G.P. zone before the ordered γ” phase. In other words, they regarded the G.P. zone as the phase prior to the γ” phase. It was claimed in their paper that no evidence for G.P. zone formation could be found via electron microscopy or selected area diffraction at that time due to the technical limitations of electron microscopy [26].

In contrast to the studies by Nuttal et al. [26], Ping et al. [27] proposed that the basal-plate-like precipitates (typically less than 10 nm in diameter and 1 nm in thickness) in a Mg-RE-Zn-Zr alloy exhibited an ordered G.P. zone structure (hexagonal, $a = 0.556$ nm) as shown via a three-dimensional atom probe (3DAP) and TEM at that time. Note that the γ” phase and the G.P. zone were also not regarded as the same phase here.

The atomic arrangement of the plate-like precipitates observed by Ping et al. is similar to that of the G.P. zone found by Nishijima et al. [19][20]. From the experimental observations of Mg-Gd-Zn alloys, Nishijima et al. proposed a model of the G.P. zone [19], in which a closed-packed plane of Mg atoms was sandwiched by two close-packed planes with Gd and/or Zn atoms occupying ordered positions. In addition, the G.P. zone had an ABAB stacking sequence of close-packed planes, the same as that of the Mg matrix, and had no strain field at the termination with the Mg matrix [19]. Additionally, Saito et al. [20][31] found microstructural changes of the G.P. zones during aging.

Regarding the previously mentioned basal-plate-like precipitates, Gao and Nie [32] thought it might not be appropriate to define the thicker basal plates as ordered G.P. zones. Based on HAADF-STEM images and the Z-contrast principle [33], Nie et al. [7] pointed out that the γ” phase was not the ordered G.P. zone reported by Ping et al. [27] and could not be

described by Nishijima's model [19]. They found that the γ" phase had an ordered hexagonal structure (space group $P\underline{6}\bar{6}2m$, a = 0.560 nm) with a single unit cell height (c = 0.444 nm), leading to a negative misfit (−0.16) between the γ" phase and Mg matrix along $[0001]_{\gamma''}//[0001]_{Mg}$ and a composition of approximately $Mg_{70}Gd_{15}Zn_{15}$ measured by 3DAP in a Mg-Gd-Zn alloy [7]. Additionally, the middle layer of the three-layered γ" plate was not pure Mg but enriched with Zn in their model [7]. In other words, the γ" phase was composed of Gd-enriched layers and Zn-enriched layers.

Similar to Nie's opinion, Zhu et al. [34] also distinguished the γ" phase from the G.P. zone. Specifically, they proposed that the G.P. zone had a single atomic layer on $(0001)_{Mg,}$ while the γ" phase had three atomic layers in a Mg-6Y-2Ag-1Zn-0.6Zr (wt.%) alloy with the help of HAADF-STEM observations and DFT calculations. In their model, the γ" phase had an ordered hexagonal structure (P6/mmm, a = 0.556 nm, c = 0.450 nm), and the atomic positions in the central layer were displaced when observing not only along the $<10\underline{1}01\bar{}0>_{Mg}$ direction, but also along the $<11\underline{2}2\bar{}0>_{Mg}$ direction. The γ" phase in their model was enriched with Ag instead of Zn, and the atomic positions in the central layer were not unambiguously determined.

Note that in Nie's model, the position of Zn in the Zn-enriched middle layer of the γ" structure was also not determined. To address this issue, Li et al. [15] proposed a model of the γ" structure that was conformed with the HAADF-STEM observations in a Mg-Gd-Zn alloy (viewed from both the $[11\underline{2}2\bar{}0]_{Mg}$ and $[10\underline{1}01\bar{}0]_{Mg}$ directions by displacing a $(0001)_{Mg}$ plane along $[11\underline{2}2\bar{}0]_{Mg}$ with a distance of 0.80 Å (i.e., $a_{Mg}/4$)). In their model, the Zn atoms occupy certain atomic sites in the middle layer of the γ" structure. However, the displacement in their model will cause projections of the atomic structure that are inequivalent along three $<10\underline{1}01\bar{}0>_{Mg}$ or $<11\underline{2}2\bar{}0>_{Mg}$ directions, as claimed by Gu et al. [16].

Gu et al. [16] considered the γ" phase and the G.P. zone to be the same phase and determined the structure of the γ" phase in a Mg-Gd-Zn alloy by atomic resolution HAADF-STEM viewed from different directions, i.e., $[11\underline{2}2\bar{}0]_{Mg}$, $[10\underline{1}01\bar{}0]_{Mg}$ and $[0001]_{Mg}$, and for the first time directly observed the ordered Gd structure in the $(0001)_{Mg}$ plane. They found that the γ" phase exhibits a hexagonal structure (a = 0.556 nm, c = 0.39 nm), and Zn atoms were centered between Gd atoms in the Zn-enriched middle layer. Since the Zn content in the composition of the γ" phase measured by a 3DAP was lower than the nominal value ($Mg_2Zn_3Gd_1$) [16], they assumed that Mg atoms substituted part of the Zn atoms in the middle layer.

Similar to Gu's model of the γ" phase in a Mg-Gd-Zn alloy, Sha et al. [22] proposed an atomic model of the γ" phase in a Mg-Gd-Y-Ag alloy using atomic resolution HAADF-STEM viewed from three independent directions, i.e., $[0001]_{Mg}$, $[2\underline{1}\underline{1}1\bar{}1\bar{}0]_{Mg}$ and $[01\underline{1}1\bar{}0]_{Mg}$, and the γ" phase was also found to exhibit a hexagonal structure with lattice parameters of a = 0.55 nm and c = 0.42 nm.

As mentioned in Gu's model, the measured composition of the γ" phase by a 3DAP was not consistent with the nominal value. Considering this, Xie et al. [23] tried to clarify the issue and proposed a topologically close-packed (TCP) structure for the γ" phase in the Mg-Gd-Zn alloy. In Xie's model [23], the γ" phase has a hexagonal structure with the space group P6/mmm and lattice parameters of a = 0.556 nm and c = 0.521 nm. Moreover, the γ" phase in their model is composed of monolayer atomic icosahedral clusters with five $(0001)_{\gamma''}$ layers, with a composition of $Mg_2Gd_2Zn_3$ that is consistent with the previous 3DAP results [16]. They also treated the γ" phase and the G.P. zone as the same phase.

Note that the previously reported lattice constants (a and c values) and specific configuration of the γ" phase show discrepancies; in other words, the fine crystal structure of the γ" phase has many variants. To clarify this phenomenon, Bai et al. [24] studied the anomalous structure of the γ" phase in Mg-RE-Zn(Ag) alloys by using first-principle calculations. They verified a new quasi-five-layer structure for the γ" phase, with the middle layer composed of Mg and Zn (Ag) atoms, in accordance with the experimental HAADF-STEM observations [23]. The ordered extent of the atoms in the middle layer increases with decreasing atomic ratio of RE: Zn (Ag) and/or increasing solute content in the alloys. Additionally, they found that the variants (diverse Zn (Ag) fractions in the middle layer of the γ" phase) change with the RE: Zn (Ag) atomic ratio of alloys. For example, when the atomic fraction of Zn in the middle layer increases to 0.43, the related structure is the same as that in Gu's model. They also claimed that Zhu's model is thermodynamically unstable, since the formation energy for the Mg-Y-Ag alloy is positive. The dependence of the c value on the RE: Zn (Ag) atomic ratio could explain the different c values in different Mg-RE-Zn(Ag) alloys.

As mentioned above, there is also no consistent definition of the γ" phase, i.e., whether the G.P. zone and the γ" phase are the same phase or not. Some researchers [15][16][22] believe that the γ" phase and the G.P. zone are the same, while Nie et al. [7] believe that the γ" phase is not the G.P zone reported by Ping et al. [27]. By using Cs-corrected HAADF-STEM [14], researchers observed in a Mg-Gd-Y-Zn-Ni-Mn alloy that the G.P. zone and the γ" phase were on the same plate, and

the subtle difference between them was reflected in their different extents of segregation of Mn atoms. 3. Stability of the γ” Phase

Yasuhara et al. [35] pointed out that the G.P. zone was preferentially formed when the composition ratio of Gd/Zn was 1~1.5; in particular, exclusive formation of G.P. zones without other precipitates was found in alloys with Gd/Zn = 1 and Gd/Zn = 1.5 by annealing at 200 °C for 100 h [31].

The stabilities of the G.P. zone and γ” phase can be reflected by their morphologies. Saito et al. [20] reported that the G.P. zones in Mg-Gd-Zn alloys changed morphology during aging as follows: wavy→planar→band-shaped (multilayered) [20]. The γ” phase in Mg-Gd-Zn alloys shows a saucer shape when viewed along $[0001]_{Mg}$ [23], while it shows a streak shape when viewed along $[11\underline{2}\bar{2}0]_{Mg}$ and $[10\underline{1}01\bar{0}]_{Mg}$ [15]. As reported by Xie et al. [23], the γ” phase has a diameter of 30~50 nm and a thickness of less than 1 nm lying on the basal plane of Mg.

The stability of the γ” phase at different aging temperatures has been studied. For instance, Choudhuri et al. [17] reported that the γ” precipitates in a Mg-Nd-Zn alloy were stable at about 177 °C for around 4800 h during a creep test. Also, researchers found that the γ” phase in a Mg-Gd-Y-Ag-Zr alloy was thermodynamically stable at room temperature, and no transformation behavior of the γ” phase was found up to 200 h during isothermal aging at 200 °C [36]. In addition, Bai et al. [25] claimed that the γ” phase remains at its single-unit-cell height during aging at 200 °C.

The reason for this extreme thermal stability of the γ” phase has been regarded by Nie [28] as one of the four unsolved issues in precipitation-hardened magnesium alloys. To explain the origin, Bai et al. [25] employed a ledge-thickening model and found that it was challenging for the solute atoms to jump into the nearest basal plane adjacent to the γ” phase, rendering ledge nucleation extremely difficult. Moreover, the almost totally coherent α-Mg/γ” heterointerface, which lacked stable sites to capture solute atoms, and the lower aging temperature (~200 °C) also led to the nucleation of extremely hard ledges on the heterointerface. Therefore, the γ” phase maintains its thermal stability during the aging process.

Note that the previously reported γ”→γ’→γ [34] precipitation sequence with the progress of aging at 200 °C and/or above 200 °C in a Mg-Y-Ag-Zn-Zr alloy was not found in researchers' investigation into a Mg-Gd-Y-Zn-Mn alloy [3].

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