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Comprehensive study of phase transformation in age-hardening of Mg–3Nd–0.2Zn by means of scanning transmission electron microscopy

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Abstract—Effects of thermal history on precipitation behavior and precipitation kinetics in Mg–3Nd–0.2Zn (wt.%) alloy were studied. Microstructure analysis of the aged alloys revealed the presence of new phases in the microstructure in addition to the old description: *Super saturated solid solution (SSSS) → G. P. zones → β″ → β′/β$_1$ → β*, reported for Mg–Nd system. In this regard, the sequence of precipitation for the studied alloy was identified as: *Super saturated solid solution (SSSS) → Clusters of atoms → G. P. zones (I, II, III) → β′ → β$_2$ → β$_1$/γ′ → β.* The formation of clusters of solute atoms in this system was confirmed by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and atom probe tomography analysis. In addition, new metastable phases designated as G. P. zones (I, II, III) and β_2 were identified in the microstructure of the aged alloys by means of high resolution HAADF-STEM. The β_2 phase was found to be a transition phase in transformation of β' to β_1. Furthermore, the microstructure analysis revealed that the structure of β_1 phase is indeed a body centered tetragonal structure in spite of face centered cubic structure that has been reported for this phase in the literature.

Keywords: Magnesium alloys; Phase transformation; Age-hardening; Scanning electron transmission microscopy; Metastable phases

1. Introduction

Magnesium alloys have received considerable attention due to their low density and high specific strengths [1,2]. However, poor ductility of magnesium at room temperature due to its hexagonal closed-packed (hcp) structure and low creep resistance and strength at elevated temperatures hinders its applications in critical structural components [1–3]. Modification of texture is reported to significantly improve the ductility of magnesium alloys [2,3]. This is achieved by alloying magnesium with rare-earth elements such as cerium (Ce), gadolinium (Gd), and neodymium (Nd) [4–7]. Addition of rare earth elements also has a significant effect on the hardness and creep resistance of Mg alloys both at room and elevated temperatures [8].

Among the rare earth elements Nd has relatively high solubility in Mg(α) at the eutectic point (0.55 at.%) and low solubility at room temperature (~100 ppm), which make it suitable for potential age hardening [8]. The strength of age-hardened Mg–Nd alloys can be further enhanced through solid solution strengthening by controlled addition of a third element such as zinc (Zn) [9,10–14]. Researches have shown that addition of 0.2 wt.% Zn to Mg–3Nd wt.% alloy improves the mechanical properties through mainly solid solution strengthening mechanism [8,12–19]. However, a higher amount of Zn than 0.5 wt.% degrades the precipitation hardening effect from Nd due to the effect of zinc on the sequence and nature of precipitation [8].

The effect of Zn can be further recognized, as the precipitation sequence in Mg–3 wt.%Nd (Mg–0.5Nd at.%) alloy is drastically different from the ternary Mg–3Nd–1.3Zn wt .% (Mg–0.5 Nd–0.5Zn at.%) alloy. The sequence in Mg-3 wt.%Nd alloy is identified as: *SSSS → G.P. zones → β″ → β′/β$_1$ → β* [7,8,20,21]. This sequence is almost the same for rare earth-containing magnesium alloys, although the kinetics of precipitation varies from one to another.

On the other hand, other researchers have identified that addition of Zn to Mg–3 wt.%Nd alloy alters the nature of precipitation such that for Mg–3Nd–0.5Zn wt .% (Mg–0.5Nd–0.2Zn at.%) and Mg–3Nd–1.3Zn at.% alloys, no β series phase forms during decomposition of super saturated Mg (α) solid solution. In this regard the sequence is identified as: *SSSS → low-temperature reaction → γ″ → γ* [8,9]. Additionally, recent study on a newly designed

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Mg–3Nd–0.2Zn wt.% (Mg–0.5Nd–0.1Zn at.%) alloy showed that at 0.2 wt.% Zn, β series and γ' phases co-precipitate in this alloy, however, γ' is sparsely distributed on grains. It is evident that the addition of a high amount of Zn (higher than 0.5 wt.%Zn) completely changes the nature and sequence of precipitation from Nd enriched β series to Zn enriched γ series. In other words, the addition of high zinc content has a restricting effect on the precipitation of β series, which has been shown to be the most effective precipitation hardening phase in rare-earth containing magnesium alloys [8,22].

The structure of the G. P. zones in Mg–RE alloys has not been evaluated due to the small size of these features and instrumentation limits; hence, information on this phase is limited. However, in a paper by Saito et al., it is reported to be the same as β'' [21]. The structure of β'' is determined as ordered D019 with $a_{\beta''} = 2a_{Mg}$ and $c_{\beta''} = c_{Mg}$. According to the arrangement of atoms in the structure, the composition of β'' was determined as Mg_3Nd [7,8,21]. This phase forms on both prismatic planes type I and II ($(11\bar{2}0)$ and $(10\bar{1}0)$) [8] and is fully coherent with the matrix. Similar structure has been reported for the β'' in alloys containing Gd and Nd [21,23–26]. β' is fully coherent with the matrix and forms on prismatic planes type I $(10\bar{1}0)$ [21,23–25]. The lattice parameters for this phase have been determined from diffraction patterns and high resolution electron microscopy and the results are not consistent. In the research by Pike et al. on Mg–3Nd (wt.%) [7], the structure is determined as hexagonal with $a_{\beta'} = 0.52$ nm and $c_{\beta'} = 1.3$ nm. However, in recent researches on Mg–RE (Gd, and Nd) alloys, a base centered orthorhombic structure with lattice parameters $a_{\beta'} = 0.642$ nm, $b_{\beta'} = 2.223$ nm, $c_{\beta'} = 0.521$ nm is reported for the β' phase. The composition of the β' phase based on BCO structure and proposed structural model for this phase is $Mg_{14}RE$ [23]. However, further STEM analysis which was performed later on Mg–Gd alloy showed a slightly different arrangement of solute atoms in β' [25]. The difference was the presence of an extra layer of solute atoms in $Z = 1/2$ layer and at the same positions as $Z = 0$ layer. Based on the new arrangement, the lattice parameter b is determined to be $b_{\beta'} = 1.11$ nm. In addition, this arrangement of atoms results in a composition of Mg_7RE that is closer to the composition reported for β' from atom probe tomography analysis [23].

The β_1 precipitates are formed on prismatic planes $(10\bar{1}0)$. The structure of this phase was determined from HREM and diffraction patterns to be fcc with $a_{\beta_1} = 0.744$ nm. β_1 precipitates are semi coherent with the matrix. The composition of this phase is reported to be Mg_3Nd [20].

The final precipitate in the sequence of precipitation is the equilibrium β phase. Similar to β', different structures and lattice parameters have been reported for this phase. In a research by Pike et al., this phase was determined as a base centered tetragonal lattice with $a_\beta = 1.031$ nm and $c_\beta = 0.593$ nm. The composition of β was also determined to be $Mg_{12}Nd$ [7]. However, in some research conducted on Mg–RE alloys [8,20], a fcc structure with composition of Mg_5RE has been reported with $a = 2.223$ nm.

In terms of γ series, there are two different reports on the structure of γ'' phase. In the TEM study on Mg–2.8Nd–1.3Zn wt.%, the lattice parameter for γ'' is reported to be an ordered hexagonal closed-packed (HCP) with $a_{\gamma''} = \sqrt{3}a_{Mg}$; $c_{\gamma''} = 3c_{Mg}$ [9]. However, TEM and STEM analyses on a Mg–1Gd–0.4Zn–0.2Zr (at.%) showed the same lattice structure but with $c_{\gamma''} = 0.444$ nm. Also the atom probe tomography (APT) investigation showed a composition of Mg–15Gd–15Zn (at.%) for this phase. γ'' forms as plates on basal planes with a thickness of a single unit cell and aspect ratio of 60:1. The orientation relationship between γ'' and matrix is such that $(0001)_{\gamma''}//(0001)_{Mg}$ and $[10\bar{1}0]_{\gamma''}//[2\bar{1}\bar{1}0]_{Mg}$ [27].

γ' has been reported in Mg–Zn–RE alloys containing Gd and Nd [8,27] and has a disordered hcp structure with $a_{\gamma'} = 0.321$ nm and $c_{\gamma'} = 0.781$ nm. For Mg–Gd–Zn, the closely packed planes in γ' have ‘‘ABCABC’’ stacking sequence with Zn and Gd atoms in B and C planes. The composition of γ' has been reported to be the same as γ''. This phase also forms as plates on basal planes with a thickness of a unit cell height and very large aspect ratio. The orientation relationship between γ' and matrix is such that $(0001)_{\gamma''}//(0001)_{Mg}$ and $[21\bar{1}0]_{\gamma''}//[2\bar{1}\bar{1}0]_{Mg}$ [27]. The thickness of this phase does not change throughout the whole aging process in such way that it remains under 1 nm for prolonged aging times [27]. The last phase in this sequence is the equilibrium phase γ. This phase has an fcc structure similar to β with $a_\gamma = 0.744$ nm. The structure and the lattice parameter of this phase are similar to the ones reported for β_1, however, the high amount of Zn and orientation with respect to the matrix are what make this phase different from β_1 [27].

As was noticed in the above discussion, there is no consistency in the structure of the intermediate phases reported for the Mg–Nd–Zn system. In addition, there is limited information on the precipitates that form during early stages of aging (i.e. G. P. zones). Furthermore, the nature and sequence of precipitation strongly depend on the composition of the alloy and vary by the amount of neodymium and zinc in the system and Nd/Zn concentration ratio. Therefore, in this research, it is aimed to conduct a systematic study of the microstructure of Mg–3Nd–0.2Zn wt.% alloy. Cs corrected atomic resolution HAADF-STEM technique and APT techniques were employed to explore the structure of the precipitates at different stages of precipitation and their relative compositions.

2. Experimental

The as-cast ingot of Mg–3Nd–0.2Zn–0.46Zr wt.% (commercially known as NZ30K) was prepared by mixing of pure Mg, Zn, Zr, and Mg–20 wt.%Nd master alloy in a 200 lb steel crucible under a protective gas mixture of SF_6/CO_2 and cast into a steel mold preheated to 200 °C. The alloy melt was degassed by bubbling pure Argon for about 20 min at 740 °C, following which, the slag was removed prior to casting. The dimensions of the cast ingots were $15 \times 10 \times 3$ cm^3.

Samples with dimensions $10 \times 10 \times 5$ mm^3 were cut from the ingot, polished, and cleaned in ethanol. The samples were then wrapped in tantalum foil (to prevent reaction between the samples and the glass tube) and quickly encapsulated in glass tubes under helium atmosphere to prevent oxidation. Solution treatment of samples was performed at 540 °C for 5 h in a horizontal tube furnace followed by quenching in water at room temperature. Solution-treated alloys were polished after quenching to remove the oxide layer from the surface, cleaned with ethanol, and placed in an oil bath at 200 °C for different lengths