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Atomic scale investigation of a novel metastable structure in aged Mg–Nd alloys

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ABSTRACT

Aged Mg-3.0 wt% Nd alloys were investigated by high angle annular dark-field scanning transmission electron microscopy. A hitherto unreported metastable phase designated β_3 can always emerge at the endpoints of β_1 particles. The crystal structure of β_3 phase is determined to an orthorhombic lattice (space group *Cmcm*). With the $\{111\}_{\beta_1}$ planes acting as the basal plane of growth, β_3 phase has three types of variants, which are related by a 120° rotation with respect to each other around the same $[001]_{\beta_3}$ axis. In addition, several peculiar morphologies and further evolution of β_3 phase were also analyzed.

Mg-based alloys containing rare-earth (RE) elements have received extensive attentions owing to their excellent higher specific strength at room and elevated temperatures, as well as remarkable creep resistance [1–8]. This category of Mg-RE alloy is the potential light-weight substitute to materials used in the automotive and aeronautical industries [9]. Relative studies show that solid solution and precipitation strengthening mechanisms are considered as the two significant mechanisms [10,11]. In this respect, Nd has been proven to be very efficient rare-earth elements. The precipitate sequences in aged Mg–Nd alloys is commonly agreed to be: SSSS (supersaturated solid solution) → ordered Guinier–Preston (GP) zones → β'' → β' (β'_F) → β_1 → β → β_e [12–17]. Generally, the GP zone is not regarded as a precipitated phase without a three-dimensional periodic structure [18–20]. Among other intermediate metastable or equilibrium phases, the key strengthening precipitates are β' and β_1 phases.

At present, structural characteristics of β' and β_1 phases have been investigated accurately by high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). In Mg–Nd alloy, the β' phase with the composition of Mg_7Nd, has a base-centred orthorhombic lattice with parameters $a = 0.640$ nm, $b = 1.140$ nm and $c = 0.521$ nm. The orientation relationships (ORs) between β' phase and α-Mg matrix are reported to be $[001]_{\beta'}//[0001]_\alpha$ and $(100)_{\beta'}//\{11\bar{2}0\}_\alpha$ [19,21]. The β_1 phase has a composition of Mg_3Nd and a face-centred cubic lattice with a parameter $a = 0.740$ nm [22]. The ORs between β_1 phase and α-Mg matrix are reported as $\langle 110\rangle_{\beta_1}//[0001]_\alpha$ and $\{112\}_{\beta_1}//\{10\bar{1}0\}_\alpha$. However, the evolution from β' to β_1 and the growth of β_1 phase are controversial. Especially, some transient metastable phases or substructures need to be further clarified, which makes it easy to understand the factors that control the formation and distribution of β_1 particles. Recently, a linear-chain configuration of β_1 precipitate has been found in a Mg-3.0 wt% Nd alloy [23]. The connection regions are composed of the β_2 phase with a hexagonal lattice (space group $P\bar{6}$), whose parameters are $a = 0.5230$ and $c = 0.9630$ nm. It is fully coherent with both α-Mg matrix and β_1 phase. The ORs among β_2, β_1 phases and α-Mg matrix were such that $\langle 11\bar{2}0\rangle_{\beta_2}//\langle 110\rangle_{\beta_1}//[0001]_\alpha$ and $(0001)_{\beta_2}//\{111\}_{\beta_1}//\{11\bar{2}0\}_\alpha$. Furthermore, the β_2 phase can hardly exist independently and always forms in connection points of two β_1 particles. In this study, a hitherto unreported metastable precipitate in aged Mg-3.0 wt % Nd are characterized using HAADF-STEM, and then its three variants and structural evolution are discussed.

Mg-3.0 wt% Nd alloys were prepared by melting the pure Mg (99.9 wt%) and Mg–30Nd (wt%) master alloys in the induction furnace with protection of the argon atmosphere. The molten alloys were stirred and kept at 760 °C for 5 min and poured into a steel mold preheated to 300 °C. As-cast samples were solution treated at 520 °C for 12 h, and then quenched into water. Afterward, a series of samples was aged at 200 °C for 2, 4, 8, 24, 82, 168 and 240 h in sequence. The age-hardening responses were measured by a Vickers hardness tester (WOLPERT 401MVD) with a load of 1 kg and a loading time of 15 s.

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Samples for STEM characterization were prepared by twin jet electropolishing at −40 °C in mixture solution of 5.3 g lithium chloride, 11.2 g magnesium perchlorate, 500 ml methanol and 100 ml 2-butoxy ethanol. Subsequently, Gatan PIPS ΠmodeI 695.O ion milling was used for the thinning and cleaning of specimens with low energy electron beam. HAADF-STEM observations were carried out on JEM-ARM200F, which is fitted with an aberration correctors for correction of C_s and associated parasitic aberrations of the pre-field (STEM). The convergence semi-angle was set to a conservative 25 mrad, which yields a diffraction limited (Gaussian) probe diameter of 0.1 nm. Incident beam is parallel to $[0001]_\alpha$ and $\langle 11\bar{2}0\rangle_\alpha$ directions of α-Mg matrix respectively. Schematic diagrams of unit cell and perspective views were built by VESTA software.

Fig. 1(a) shows an aging-hardening response of Mg-3.0 wt% Nd alloy aged at 200 °C. The hardness of the alloy undergoes a typical three-stage evolution: under-aged stage, peak-aged stage and over-aged stage. When the aging time equals to zero, the alloy is as-solutioned and the hardness value is 49.8 HV. With increasing aging time, the alloy exhibits a significant increase in its hardness and reaches its peak-age condition with a peak hardness of 65 HV. As the aging time is longer than 24 h, the hardness decreases gradually. Fig. 1(b) shows a general morphology of Mg-3.0 wt% Nd alloy aged at 200 °C for 24 h. Incident beam is parallel to $[0001]_\alpha$. Some precipitates were distributed uniformly in α-Mg matrix in the shape of "rod-shape", "V-shape" and "trident", whose sizes are about 50 nm in length and 5 nm in width. A representative HAADF-STEM micrograph of single rod-shape precipitates is presented in Fig. 1(c), showing a typical linear-chain distribution of β_1 precipitates. The β_1 precipitates in the linear configuration were connected to each other according to a distinct contrast in the connection regions. Different from that reported by Nie [23], many junctions between two adjacent β_1 precipitates are some broad regions with different breadth rather than the connection points. The magnified images of the regions enclosed by the red and yellow dashed rectangles in Fig. 1(c) are shown in Fig. 1(d) and (e), respectively. As we know, the brightness of the HAADF-STEM image is approximately proportional to the square of the atomic number. Since the atomic number of Nd (60) is much higher than that of Mg (12), the two enlarged images can provide directly the distribution of Nd atoms in the precipitate. Except the known β_1 particles and β_2 substructure, a hitherto unreported phase can be observed clearly between two adjacent β_1 particles. As shown in Fig. 1(d) and (e), we designated it as β_3 phase here in order to distinguish it from the known metastable phases. Meanwhile, for sake of convenient discussion, it is necessary to define the crystal planes perpendicular to rod axis as the basal plane. In basal planes of β_3 lattice, the intensity of imaging dots varies alternately. Its structural characteristics are different from the β_2 lattice, where the intensity is different in two adjacent basal planes and is uniform in the same basal plane, as provided in Fig. 1(e).

The atomic-resolution $[0001]_\alpha$ HAADF-STEM image of β_3 phase is presented in Fig. 1(f). It is noticeable that the interplanar spacings of basal planes are very close in β_2 and β_3 lattices. Furthermore, the configurations of imaging dots in both phases are uniform if ignoring their intensities, revealing that the structural frameworks of β_3 and β_2 phases should be nearly identical. Assuming that the bright dots represent pure Nd atomic columns and the weak dots denote Mg/Nd mixed atomic columns, the β_3 phase can be described tentatively as a hexagonal lattice with parameters of $a_H \approx 2 \times a_{\beta_2} = 1.0420\ nm$ and $c_H \approx c_{\beta_2} = 0.9610\ nm$. With the aid of model of β_2 unit cell given in the inset of Fig. 1(e), a hexagonal unit cell and three typical perspective views of β_3 phase can be proposed and demonstrated in Fig. 1(g). In the perspective view along $[11\bar{2}0]_{\beta_3}$ ($[0001]_\alpha$) direction, the zigzag lines composed of pure Nd atomic columns can match well with the brighter zigzag lines composed of the brighter dots in Fig. 1(f), and then the Mg/Nd mixed atomic columns in model corresponds to the weaker dots in experimental image. In brief, the $[11\bar{2}0]_{\beta_3}$ HAADF-STEM images fit well with the idealized projection inset in the experimental images, as demonstrated in Fig. 1(f). Additionally, it is necessary to point out that the ratio of Nd to Mg is fixed at 1:1 in mixed columns other than that of β_2 unit cell.

The linear arrangement of β_1 particles can also be observed in Fig. 2 (a) and (b), showing the low magnification $[\bar{1}100]_\alpha$ HAADF-STEM images of Mg-3.0 wt% Nd alloy aged at 200 °C for 24 h. Fortunately, as marked by white arrows in Fig. 2(b), we discovered some connection regions with weaker contrast and different breadth. Fig. 2(c) and (d) demonstrate the enlarged image of the regions enclosed by red and yellow rectangles in Fig. 2(b), respectively. In Fig. 2(c), a red dashed rectangle points out an abnormal rhombic lattice with brighter dots, which is supposed to be the β_3 substructure. On the one hand, Fig. 2 (e) provides the atomic-resolution $[\bar{1}100]_\alpha$ HAADF-STEM image, where the configuration of bright dots in experimental image can match well with the pure Nd atomic columns in $[\bar{1}100]_{\beta_3}$ projection. On the other hand, the rhombic lattice is located between two β_1 particles with the orientation of $\langle 112\rangle_{\beta_1}$, suggesting that the results agree with the observation along $[0001]_\alpha$ direction. Except for the β_3 lattice, the β_2 lattice with alternating bright and weak basal planes can be observed in Fig. 2(d) and (f).

Although the β_3 lattice can be described based on hexagonal lattice, it should be assigned to the orthorhombic structure with space group *Cmcm* in term of crystallography. Its lattice parameters should be $a_{\beta_3} = a_H = 1.0420$ nm, $b_{\beta_3} = \sqrt{3} \times a_H = 1.8047$ nm and $c_{\beta_3} = c_H = 0.9610$ nm. Schematic diagrams of the orthorhombic unit cell and the projections along *a*, *b* and *c* axis are demonstrated in Fig. 3(a). Both 36 Mg and 12 Nd atoms in orthorhombic unit cell, occupy six general equivalent positions, which are (0,0,0) and (1/2,0,0) for Nd, and (0,0,1/3), (1/2,0,1/3), (1/4,1/4,0) and (1/4,1/4,1/3) for Mg. Based on the relationships of orthorhombic and hexagonal basis vectors, the ORs among β_3, β_1 phases and α-Mg matrix can be drawn: $[100]_{\beta_3}//\langle 110\rangle_{\beta_1}//[0001]_\alpha$ and $(001)_{\beta_3}//(111)_{\beta_1}//\{11\bar{2}0\}_\alpha$. Fig. 3(b) provides two perspective views of interface between β_3 and β_1 phases along $[0001]_\alpha$ and $\langle\bar{1}100\rangle_\alpha$ directions. Experimental images indicate that the interface (the basal plane of β_3 phase) between β_3 and β_1 lattices is always flat and coherent. It hints that the initial formation and growth of β_3 phase are dependent of $(111)_{\beta_1}$ plane. On the boundary, schematic diagrams of the atomic configurations on $(111)_{\beta_1}$ and $(001)_{\beta_3}$ planes are shown in Fig. 3(c) and (d), respectively. Since the three $\langle 110\rangle_{\beta_1}$ directions are equivalent in any $\{111\}_{\beta_1}$ basic plane, it is possible that there exist three kinds of the orthorhombic variants with the initial formation of β_3 lattices. In Fig. 3(d), three rectangles in $(001)_{\beta_3}$ plane manifest the relationships among the three orthorhombic variants, from which the three variants are related by a 120° rotation with respect to each other around the same $[001]_{\beta_3}$ axis. Schematic diagrams of $(100)_{\beta_3}$ and $(010)_{\beta_3}$ planes of each variant are also given in Fig. 3(d). For the three variants (V_1, V_2 and V_3), the transformation matrix of basic vectors (*a*, *b* and *c*) can be described as:

$$T = \begin{pmatrix} -0.5 & -0.5 & 0 \\ 1.5 & -0.5 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

namely, $\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{V1} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{V2} \times T = \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{V3} \times T^2 = \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{V1} \times T^3$, indicating that the matrix T^3 should be an identity matrix *I*.

However, it need be pointed out that the V_3 variant has not been observed yet in our experiments. Here, a subtle difference between V_3 variant and other two variants can be perceived from their schematic diagrams of $(100)_{\beta_3}$ and $(010)_{\beta_3}$ planes. First, the lines (black lines) composed of pure Nd atomic columns are the zigzag lines with the smaller angle in $(100)_{\beta_3}$ plane of V_1 and V_2 variants, whereas, the zigzag lines with the larger angle (red lines) appears in $(100)_{\beta_3}$ plane of V_3