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Crystal structures of highly-ordered long-period stacking-ordered phases with 18*R*, 14*H* and 10*H*-type stacking sequences in the Mg–Zn–Y system

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ABSTRACT

The crystal structures of highly-ordered Mg–Zn–Y long-period stacking-ordered (LPSO) phases with the 18*R*-, 14*H*- and 10*H*-type stacking sequences, which are constructed by stacking structural blocks composed of six, seven and five close-packed atomic layers, respectively, have been investigated by atomic-resolution scanning transmission electron microscopy (STEM) and transmission electron microscopy. The in-plane order characterized by the periodic arrangement of Zn_6Y_8 atomic clusters on the lattice points of a $2\sqrt{3}a_{Mg} \times 2\sqrt{3}a_{Mg}$ two-dimensional primitive hexagonal lattice (a_{Mg}: the lattice constant of Mg) is developed in the central four consecutive atomic layers in each of the structural blocks for the 18*R*-, 14*H*- and 10*H*-type Mg–Zn–Y LPSO phases. The random occupation of the central site of each Zn_6Y_8 atomic cluster with Mg, Zn, Y or vacancy is suggested through the analysis of the ultra-high resolution annular-bright field STEM images. The space groups of the most stable polytypes of the 18*R*-, 14*H*- and 10*H*-type Mg–Zn–Y LPSO phases at 500 °C are determined to be *C*2/*c*, *P*6$_3$22 and *Cmce*, respectively.

1. Introduction

Recent development of new light-weight structural alloys in Mg – transition metal (TM) – rare earth (RE) based systems has opened up new possibilities in endowing structural materials with high strength and good ductility simultaneously [1–4]. Extensive studies have been carried out so far in order to elucidate the underlying principles for the simultaneous achievement of both high strength and good ductility [5–7]. The Mg–TM–RE alloys commonly contain a precipitation phase with a long-period stacking-ordered (LPSO) structure [2–7], which has been considered to play essential roles for their attractive mechanical properties. However, there are still many unsolved fundamentals of the Mg–TM–RE alloys, mostly because the crystal structures of the LPSO phases have not been fully understood yet.

Various types of the LPSO phases expressed as 10*H*, 14*H*, 18*R* and 24*R*-types, which are formed by stacking structural blocks composed of five, six, seven and eight close packed atomic layers, respectively, have been reported in various Mg–Zn–RE systems [8–16]. The crystal structures of the Mg–TM–RE LPSO phases have been generally characterized by the periodic stacking faults associated with the enrichment of TM and RE atoms in two consecutive atomic layers [9,12]. It should be noted that the Ramdell's notations used to describe the LPSO structures are assigned under an assumption that all close-packed atomic layers are identical, which are in fact not adequate in a strict crystallographic sense because of the RE and TM enrichment in some of the close-packed atomic layers [9,12–18]. However, the above mentioned Ramsdell notations have been utilized because no atomic ordering in any close-packed atomic layers was considered to exist originally. When no atomic ordering in any close-packed atomic layers is considered, only three different stacking positions, A, B, and C, are defined in describing the stacking of close-packed atomic layers in the LPSO structures. The stacking sequences for the 18*R* and 14*H* LPSO structures are described as ABA/CBCBCB/ACACAC/BAB and ABAB/CACACAC/BAB, respectively, where the slash marks indicate the positions of the stacking faults.

Recently, we have studied the crystal structures of highly-ordered LPSO phases with the 18*R*- and 14*H*-type stacking in the Mg–Al–Gd system by TEM and atomic-resolution high-angle

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annular dark-field (HAADF) STEM and have revealed the following features [13,15,17,18]. First, each structural block in the Mg–Al–Gd LPSO phases have a long-range in-plane order, which is characterized by a periodic arrangement of Al_6Gd_8 atomic clusters with the $L1_2$-type atomic arrangement in the Gd and Al-enriched four consecutive atomic planes. Second, although the Mg–Al–Gd LPSO phases have the perfectly ordered structure in each structural block, they generally exhibit one-dimensional disorder in the stacking of the structural blocks and consequently, their crystal structures are best described with the crystallographic concept of the order–disordered (OD) structure [13,15,18–23]. The Mg–TM–RE LPSO phase with an OD structure is hereafter designated as the Mg–TM–RE LPSO/OD phase.

On the other hand, no apparent long-range in-plane order has been confirmed so far for the other Mg–TM–RE LPSO phases, especially for Mg–Zn–Y LPSO phases coexisting with hcp Mg [9,12–14,16]. However, the diffuse streaks extending along stacking direction in selected area electron diffraction (SAED) patterns has suggested some kind of atomic ordering in the Mg–Zn–Y LPSO phases [12–16]. Thus, various approximate crystal structure models for the Mg–Zn–Y LPSO phases have been proposed [12,16]. Zhu et al. proposed crystal structure models assuming that the enrichment of Zn and Y atoms occurred only in two consecutive atomic layers with a stacking fault in between, however, their atomic resolution STEM images were not sufficient to validate their crystal structure models [12]. In our previous study [13], we confirmed the formation of the Zn_6Y_8 atomic clusters with the $L1_2$-type atomic arrangement, i.e. the enrichment of Zn and Y in four consecutive atomic planes, in the structural block of the Mg–Zn–Y LPSO phase coexisted with hcp Mg [13]. We suggested that the degree of the in-plane order should be closely related to the number density of the Zn_6Y_8 atomic clusters in the Zn, Y-enriched atomic layers, considering the fact that the chemical compositions of the previously studied Mg–Zn–Y LPSO phases were relatively poor in Zn and Y compared with those calculated for the ideal crystal structures based on the results of the Mg–Al–Gd LPSO/OD phases [13]. Alternatively, Egusa and Abe [16] pointed out that the 18*R*-type LPSO phase exist in a wide compositional range and proposed crystal structure models of some polytypes for the 18*R*- and 14*H*-type LPSO phases in the Mg–Zn–Y systems assuming a periodic arrangement of Zn_6Y_8 atomic clusters with the $L1_2$-type atomic arrangement. However, they did not fully describe how they deduced the atomic ordering in the structural blocks and the space groups based on their experimental results obtained from the imperfectly ordered LPSO phases [16]. Their proposed in-plane order and space groups for two crystal structure models of the 18*R*-type LPSO phase are well consistent with our crystal structure models for the two MDO polytypes designated as 1*M* and 3*T* of the Mg–Al–Gd LPSO/OD phases [13,16,18]. However, there is no apparent reason why the Mg–TM–RE LPSO/OD phases in the different ternary systems should possess the same crystal structures. Thus, studies on crystal structures of the Mg–Zn–Y LPSO phases with the perfect in-plane order in each structural block are essential in order to fully understand the characteristics of the crystal structures of the Mg–Zn–Y LPSO phases.

In the present study, the Mg–Zn–Y ternary alloys containing highly-ordered Mg–Zn–Y LPSO phases with Zn, Y-rich compositions have been prepared and the crystal structures of the 18*R*-, 14*H*- and 10*H*-type Mg–Zn–Y LPSO/OD phases with the perfect in-plane order of the TM_6RE_8 atomic clusters identical to that of the Mg–Al–Gd LPSO/OD phases have been investigated by TEM/STEM. The crystal structure models of these Mg–Zn–Y LPSO/OD phases are proposed on the basis on the crystallographic theory of the OD structure (OD theory).

2. Crystal structure description of the Mg–TM–RE LPSO phases based on the order–disorder (OD) theory

In the OD theory, a crystal structure is described with (i) a set of partial symmetry operations (POs) transforming a structural block (an OD layer) into itself (λ-POs) and (ii) a set of POs transforming an OD layer into an adjacent one above it (σ-POs) [13,15,18,21]. In the case of the Mg–TM–RE LPSO/OD phases, a set of λ-POs is described with the layer group of $P(\bar{3})1m$ irrespective of the number of close-packed atomic layers (either 5, 6, 7 or 8), as far as an OD layer is selected so that TM_6RE_8 atomic clusters with the $L1_2$-type atomic arrangement are periodically arranged on lattice points of a $2\sqrt{3}a_{Mg} \times 2\sqrt{3}a_{Mg}$ two-dimensional primitive hexagonal lattice [13,15,18]. The second set of POs, σ-POs depends on the number of close-packed atomic layers in the structural block. When the structural block is composed of an even number of close-packed atomic layers, i.e. six (18*R*-type) or eight (24*R*-type), the stacking relationships between two adjacent structural blocks are described primarily with translation operations. The Mg–TM–RE LPSO/OD phases of this type are hereafter assigned to be those of the *R* (rhombohedral)-type stackings. Here, two adjacent structural blocks containing the central four consecutive atomic layers with the BACB and CBAC stackings are assigned as α- and β-blocks, respectively, where their in-plane lattice points are represented by B and C positions, respectively. The stacking relationships can be characterized by twelve C positions with respect to the B position locating at the lattice point of the in-plane unit cell of the α-block as illustrated in Fig. 1(a). These twelve stacking positions are classified into three types (C_1 – C_3 in Fig. 1(a)), because of the 3-fold symmetry of the OD layer. The classification results in the derivation of three OD groupoid families described commonly with the following OD groupoid symbols.

$$\begin{array}{llllllll} P & 1 & 1 & 1 & (\bar{3}) & \frac{2}{m} & \frac{2}{m} & \frac{2}{m} \\ & \{1 & 1 & 1 & \begin{pmatrix} \bar{3} \\ 3_3 \end{pmatrix} & \frac{2_s}{n_{r,2}} & \frac{2_{s'}}{n_{r',2}} & \frac{2_{s''}}{n_{r'',2}}\} \end{array} \tag{1}$$

where the first and second lines represent the λ-POs and σ-POs, respectively, based on the notation proposed by Dornberger-Schiff [20,21]. In Eq. (1), the parameters (r, r', r'', s, s', s'') are the translation components for the glide and screw operations, which depend on the preferential stacking positions; namely (1/3, −1/3, 0, 1/3, 1/3, −2/3), (0, −1/6, 1/6, 1/3, −1/6, −1/6) and (1/6, −1/2, 1/3, 5/6, −1/6, −2/3) for the C_1, C_2 and C_3 positions, respectively.

When the structural block composed of an odd number of closed-packed atomic layers (five or seven for 10*H*- or 14*H*-types), it is reasonable to consider the stacking relationship between two adjacent structural blocks containing the central four consecutive atomic layers with the ABCA and ACBA stackings. These structural blocks are hereafter assigned as δ- and δ_T-blocks, respectively [15]. The Mg–TM–RE LPSO/OD phases of this type are hereafter designated as those of the *H* (hexagonal)-type stackings. Since the stacking sequences of the close-packed atomic planes in the δ- and δ_T-structural blocks are in twin relationship, each stacking relationship between the two structural blocks is described with a combination of a translation and the subsequent 60°-rotation (equivalent to 180°- and 300°-rotations) about the axis passing perpendicularly the lattice point of the in-plane unit cell. The translation operations are characterized by twelve A positions with respect to the A positions corresponding to the lattice points of the in-plane unit cell of the δ-structural block as illustrated in Fig. 1(b). The twelve A positions are categorized into four types (A_1–A_4 in Fig. 1(b)) [15]. When either the A_2, A_3 or A_4 positions are preferentially selected, the crystal structure can be