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The crystal structure of the LPSO phase of the 14*H*-type in the Mg–Al–Gd alloy system

K. Kishida [a,*], H. Yokobayashi [a], H. Inui [a], M. Yamasaki [b], Y. Kawamura [b]

[a] Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
[b] Department of Materials Science, Kumamoto University, 2-39-1, Kurokami, Kumamoto 860-8555, Japan

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ABSTRACT

The crystal structure of a long-period stacking-ordered (LPSO) phase of the 14*H*-type formed in a Mg–Al–Gd alloy as a local small part in the intergrowth structure together with that of the 18*R*-type (the majority) has been investigated by scanning transmission and transmission electron microscopy. The LPSO phase of the 14*H*-type in the Mg–Al–Gd system is found to form by stacking structural blocks, each of which consists of seven close-packed atomic planes. In each of the structural blocks, a long-range ordering occurs for the constituent Mg, Al and Gd atoms with the enrichment of Gd atoms in the four consecutive atomic planes. The in-plane long-range ordering in the four consecutive atomic planes occurs so as to form Al_6Gd_8 clusters in a periodic manner. This is exactly the same as what is observed in the LPSO phase of the 18*R*-type. The crystal structure of the 14*H*-type LPSO phase can thus be described to form simply by adding a Mg layer to the crystal structure of the 18*R*-type LPSO phase so as to form triple (three consecutive) Mg layers to sandwich the Gd-enriched quadruple layers. The ideal chemical formula of the structural block is $Mg_{35}Al_3Gd_4$ (Mg – 7.1 at.% Al – 9.5 at.%Gd). The crystal structure of the LPSO phase can thus be crystallographically described as one of the order–disorder (OD) structures, and the space group of either $P6_322$ or $R\bar{3}c$, is assigned when the simplest stacking of structural blocks is assumed.

1. Introduction

Because of the ever-increasing demands for lightweight structural materials, there is a great deal of attention to high-strength Mg alloys that can achieve high strength and high ductility simultaneously [1–3]. From this point of view, Mg alloys containing ternary Mg–TM (Transition-metal)–RE (Rare-earth) phases with long-period stacking-ordered (LPSO) structures have received a considerable amount of attention in recent years [4–9]. Although reasons why these alloys can simultaneously exhibit high strength and high ductility have been remained largely unsolved, ternary LPSO phases have been believed to play important roles in endowing them with excellent mechanical properties. When TM is Zn, LPSO phases in Mg–TM–RE ternary systems are reported to consist of structural blocks with 5–8 close-packed atomic planes, forming various polytypes with different numbers of the close-packed atomic planes in the structural blocks and with different stackings of the structural blocks [10–19]. In the absence of the in-plane long-range ordering of the constituent atoms (as usually assumed in most studies in Mg–TM–RE LPSO phases), polytypes expressed as 10*H*, 14*H*, 18*R* and 24*R* polytypes (according to the Ramsdell notation) are reported to form, among which 14H- and 18*R* polytypes are the most dominantly observed ones [10-19].

We have very recently investigated the crystal structure of a LPSO phase corresponding to the 18*R* polytype newly found to form in the Mg–Al–Gd system [17,18]. The crystal structure of the LPSO phase of the 18*R*-type in the Mg–Al–Gd system is definitely different from those of LPSO phases in other Mg–TM–RE systems in that (1) the enrichment of RE (and TM) atoms occurs in four consecutive close-packed atomic planes in each structural block instead of two (this was confirmed to also be the case, at least, for the LPSO phase in the Mg–Zn–Y system in our previous study [17,18]) and that (2) long-range atomic ordering occurs in the four consecutive atomic planes in which the enrichment of RE (and TM) atoms occurs. Because of these characteristics, the LPSO phase in the Mg–Al–Gd system cannot be described as 'LPSO' phase any longer in a strict sense and the crystal structure is described with the concept of the order–disorder (OD) structure, in which a crystal structure is described with the symmetry of a structural block (an OD layer) and the relative relation between adjacent two OD layers [18,20–28]. With the layer group of $P(\bar{3})1m$ of the trigonal-type determined for the structural block (the OD layer), the OD

* Corresponding author. Tel./fax: +81 75 753 5461.
E-mail address: kishida.kyosuke.6w@kyoto-u.ac.jp (K. Kishida).

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groupoid family for the 'LPSO' phase in the Mg–Al–Gd system is described using the so-called OD groupoid symbols proposed by Dornberger–Schiff [18,21,22,26–31], as follows.

$$\begin{matrix} P & 1 & 1 & 1 & (\overline{3}) & \frac{2}{m} & \frac{2}{m} & \frac{2}{m} \\ \left\{ 1 & 1 & 1 & \begin{pmatrix} \overline{3} \\ 3_3 \end{pmatrix} & \frac{2_{1/3}}{n_{1/3,2}} & \frac{2_{-1/3}}{n_{1/3,2}} & \frac{2}{n_{-2/3,2}} \right\} \end{matrix} . \quad (1)$$

The readers are referred to [21,22,26–31] for the meaning of the OD groupoid symbols and some detailed discussion will also be made in the present paper. The expression for the crystal structure of the 'LPSO' phase corresponding to the 18*R* polytype in the Mg–Al–Gd system is thus quite different from those of LPSO phases in other Mg–TM–RE systems. This stems from the fact that the long-range atomic ordering occurs in the four consecutive atomic planes in which the enrichment of RE (and TM) atoms occurs. For LPSO phases of other types, however, nothing is known about the number of close-packed atomic layers in which the enrichment of RE (and TM) atoms occurs (usually assumed to be two in most previous studies) and whether or not long-range atomic ordering occurs in these RE (and TM)-enriched atomic layers. In view of the fact that the LPSO phases of the 14*H* polytype are observed as frequently as those of the 18*R* polytype are, it is of particular interest to determine the crystal structure of the LPSO phase of the 14*H*-type as in the case of that of the 18*R*-type found in the Mg–Al–Gd system.

In the present study, we investigate the crystal structure of a 'LPSO' phase in the Mg–Al–Gd system formed locally as 14*H*-type in the same ingot used in our previous study to investigate the crystal structure of the 18*R*-type LPSO phase, by means of scanning transmission electron microscopy (STEM). We focus primarily on the detection of the in-plane ordering of Gd (and possibly Al) atoms in the close-packed atomic planes in which the enrichment of Gd and Al atoms are expected to occur and on the full description of the crystal structure with the concept of the OD theory. Then, we expand our analysis to the other LPSO phases composed of structural blocks with different numbers of layers, i.e. 10*H* (5-layers) and 24*R* (8-layers) in Mg–Al–Gd alloys in order to establish general ways to describe their crystal structures with the OD theory and to deduce simple polytypes based on the OD theory. Finally, we describe how to distinguish the OD-type LPSO phases with previously reported (disordered) LPSO phases by electron diffraction in transmission electron microscopy (TEM).

2. Experimental procedures

Ingots of a Mg–Al–Gd ternary alloys with a nominal composition of Mg – 3.5 at.%Al – 5.0 at.%Gd were produced by high-frequency induction-melting in an argon atmosphere. The ingots were homogenized at 550 °C for 2 h and then heat-treated at 400 °C for 10 h. Microstructures were examined by STEM with a JEM-2100F electron microscope operated both at 200 kV. Specimens for STEM observations were cut from heat-treated ingots, mechanically polished, and electropolished in a solution of perchloric acid (60%), *n*-butyl alcohol and methanol (3:30:130 by volume) with 0.2 M of LiCl under 17 V at −55 °C.

3. Results

3.1. Stacking and in-plane atomic arrangements within each structural block

In the Mg–Al–Gd alloys, the LPSO phase with the 14*H*-type stacking sequence is rarely observed, unless it appears as a small part in an intergrowth structure with a few to a several structural blocks consisting of seven close-packed planes. While the 18*R*-type LPSO phase dominates in the intergrowth structure, the 14*H*-type LPSO phase often appear in the peripheries of the interface between the Mg matrix and 18*R*-type LPSO phases together with thin plates with 10*H*- and 24*R*-type stacking, as shown in the low-magnification high-angle annular dark-field (HAADF)-STEM image of Fig. 1. Atomic-resolution HAADF-STEM images of the 14*H*-type LPSO phase taken along $[2\overline{1}\overline{1}0]$[1] and $[1\overline{1}00]$ directions from the same region are shown in Fig. 2(a) and (b), respectively. Because of the strong contrast dependence on the average atomic number *Z* in the atomic columns in the HAADF-STEM image [17,18,32–35], atomic columns enriched with heavy Gd atoms are imaged as brighter spots in Fig. 2(a) and (b). It is apparent from the images that the Gd enrichment occurs in the four consecutive close-packed planes instead of two, which has been repeatedly reported for other Mg–TM–RE LPSO phases [15,16]. The occurrence of the in-plane ordering of the Gd atoms in the four consecutive Gd-enriched planes is obvious, as will be described in detail later. If the in-plane ordering of the Gd atoms in the four consecutive Gd-enriched planes is ignored, the stacking sequence of the present 14*H*-type LPSO phase in the Mg–Al–Gd system is identical to that previously reported for the other Mg–TM–RE LPSO phases of the 14*H*-type, as indicated in Fig. 2(a) [14–16]. Two types of structural blocks, each of which consists of seven close-packed atomic planes, with ABABCAC and ACACBAB stackings are identified to stack alternatively. The stacking sequence of these two types of structural blocks are obviously related with each other in the twin relationship with the mirror plane being the central Mg layer in the stacking position A of the three consecutive Mg layers (Fig. 2(a)). These two types of the structural blocks are hereafter designated δ and δ_T blocks, respectively. If the twin relationship is taken into account, the atomic arrangements of these two types of structural blocks are identical with each other. The present LPSO phase of the 14*H*-type is thus confirmed to be formed by stacking these two types of seven close-packed layer structural blocks, which are related in the twin relation with each other.

The in-plane ordered arrangement of Gd and Al atoms in the four Gd-enriched layers with an f.c.c. type stacking sequence in the structural block is confirmed to be identical to that of 18*R*-type Mg–Al–Gd LPSO phase reported in our previous paper [18] through careful inspection of the arrangement of the brighter spots in the HAADF-STEM images. The in-plane long-range ordering in the four consecutive atomic planes can be described to occur so as to locate Al_6Gd_8 clusters with the $L1_2$ type atomic arrangement on lattice points of a $2\sqrt{3}a_{Mg} \times 2\sqrt{3}a_{Mg}$ primitive hexagonal lattice, where a_{Mg} is referred to the length of the unit vector along the *a*-axis of Mg [18]. Atomic arrangements in each of the seven atomic planes in the structural block together with the periodic arrangement of Al_6Gd_8 clusters in the quadruple layers projected along [0001] are depicted in Fig. 3 for the δ block with the stacking of the ABABCAC type. The inner two layers of the Gd-enriched quadruple layers are in B and C stacking positions with the chemical composition of $Mg_6Al_3Gd_3$, whereas the outer layers with the chemical composition of $Mg_{11}Gd$ are both in the A position. In addition, there exist three pure Mg layers in the structural block; two Mg layers in A and B positions and an Mg layer in the C

[1] Since the unit cell of the LPSO phase in the Mg–Al–Gd system cannot unambiguously be determined because of the stacking disorder of structural blocks along the direction perpendicular to the close-packed planes, Miller-Bravais indices and Weber symbols to express planes and directions for the LPSO phase, respectively, are referred to as those of the matrix phase of Mg with the h.c.p. structure unless otherwise stated.