Computational Materials Science 153 (2018) 297–302

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Long-range interactions in Mg-Al-rare earth alloys with 10H-type long-period stacking ordered structure

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ARTICLE INFO

Keywords:
Magnesium alloys
LPSO structure
Order-disorder structure
Mg-Al-Y alloy
Long-range interaction
First-principles calculation
Density functional theory

ABSTRACT

We calculate long-range interactions between Al-Y clusters along the stacking direction in Mg-Al-Y alloys with long-period stacking ordered (LPSO) structure by using first-principles calculation based on density functional theory (DFT). We find that the highly ordered LPSO structure, recently observed in $Mg_{75}Al_{10}Y_{15}$ alloy with 10H-type stacking sequence, is the most stable in thirteen polytypic structures. Relative energy differences in the thirteen polytypic structures suggest that significant long-range interactions between the separated stacking faults bring the highly ordered LPSO structure although short-range interactions are dominant for the stability of the alloy. In addition, we calculate and compare the long-range interactions for sixteen Mg-Metal (M)-Rare Earth (RE) alloys which have been experimentally observed to form the LPSO phase, and reveal that the long-range interactions in the alloys with M = Al are one digit larger than those with M = Zn. These results suggest that the long-range interactions between Al-RE clusters play an important role to form the highly ordered LPSO structure in Mg-Al-RE alloys.

1. Introduction

Mg-based alloys have attracted much attention as light-weight structural materials of the next generation for wide-range applications such as components of aircrafts and vehicles. Especially, Mg-M-RE ternary alloys (M and RE represent Metal and Rare Earth elements, respectively) have been actively studied for the past decade since the long-period stacking ordered (LPSO) phase with a high tensile strength exceeding extra super duralumin was first found in the $Mg_{97}Zn_1Y_2$ alloy by Kawamura et al. [1].

The LPSO phase has been observed in several M-RE combinations listed in Table 1 [2–10], and found to have an anomalous LPSO structure, where the periodic stacking fault appears along the stacking direction in hcp-Mg matrix and impurity elements are enriched around the stacking faults [11]. There are various cases for the period of stacking faults, and various stacking sequences such as 10H, 18R and 14H, corresponding to five, six, and seven-layer period, respectively [12]. In addition, it have been found that the impurity elements distribute in the four layers around each of the stacking fault and constitute $L1_2$-type M_6RE_8 clusters by the precise experiments of high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM) and first-principles calculation [13]. In general, this $L1_2$-type clusters are not arranged regularly in the stacking direction, but sometimes it can be described as a order-disorder (OD) structure preserving positional relations between two adjacent cluster layers [7]. The OD structures have been found for 18R and 14H-type Mg-Al-Gd alloys and 10H, 18R and 14H-type Mg-Zn-Y alloys, so far [7,14,15].

Very recently, highly ordered LPSO structure in which the $L1_2$-type clusters arrange not with the OD-manner but with a complete regularity in the stacking direction has been found in $Mg_{75}Al_{10}Y_{15}$ alloys by Takeda et al. [9]. As shown in Fig. 1, this LPSO structure has the 10H-type stacking sequence and is characterized by the complete order of the $L1_2$-type clusters both in the in-plane and along the stacking direction; the unit-cell of this alloy is composed of 20 layers with four-cycle cluster positions and includes 240 atoms (244 atoms if an interstitial atom exists at the center of $L1_2$-type cluster), but the symmetry belongs to the space group P1 (no symmetry operator except for identity). In addition, the volume fraction of the highly ordered LPSO phase is about 70% of the whole product when it is annealed at 823 K for 24 h, which is relatively short time compared with other alloys, and the volume fraction increases with the heat treatment. These facts suggest that (1) interactions in the Mg-Al-Y alloys with 10H-type LPSO structure are more long-range than those in the alloys that have been studied so far, and that (2) this structure is the thermodynamically stable structure discovered for the first time for LPSO structures. Then, the Mg-Al-Y alloy is the interesting subject not only as a new light-weight material

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https://doi.org/10.1016/j.commatsci.2018.06.048
Received 3 February 2018; Received in revised form 29 June 2018; Accepted 30 June 2018

Table 1
The combinations of M and RE elements with which the LPSO phases in Mg ternary alloys are experimentally observed [2–10].

M\RE	Y	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm
Al	○	○	○	○		○	○	○	
Zn	○			○	○	○	○	○	○
Co	○								
Ni	○								
Cu	○								

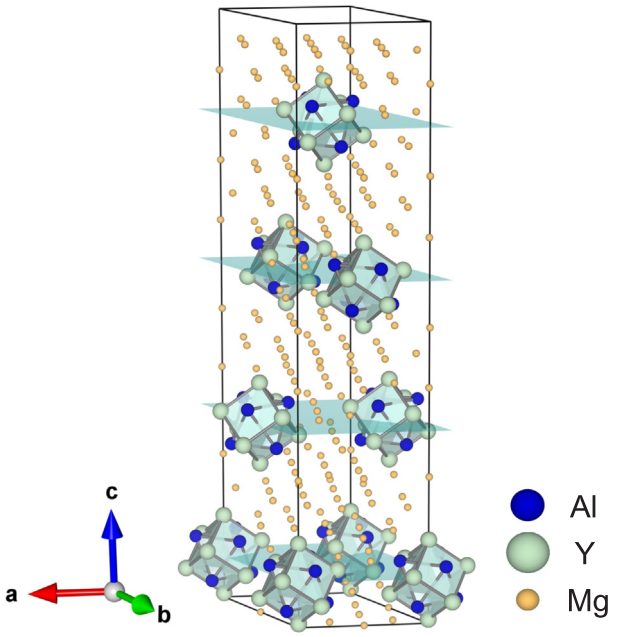

Fig. 1. The unit cell of the highly ordered LPSO structure observed in $Mg_{75}Al_{10}Y_{15}$ alloy [9,26]. In this structure, Mg matrix has the 10H-type stacking sequence including a stacking fault appearing on five-layer period and $L1_2$-type impurity clusters are regularly arranged in both in-plane and stacking direction. The gray, black and small spheres (in the case of color print, blue, light green and orange spheres) indicate Al, Y and Mg atoms, respectively. Four horizontal rhombuses show the stacking faults in Mg layers, which pass through the central positions of each cluster. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

but also a model case for understanding basic properties of the LPSO phase. That is, researching the Mg-Al-Y alloy may clarify the following mechanisms: (1) Formation of the stacking fault and its relation to impurity enrichment or clustering. (2) Generation of long periodicity along the stacking direction from the viewpoint of the interactions between impurity and clusters.

In this study, we investigate the cluster interactions in Mg-Al-Y alloy, especially for the stacking direction. In the Mg-Al-Y alloy as mentioned above, highly ordered LPSO structure (10H-type), where the clusters are arranged regularly, is obtained with relatively short-time heat treatment, annealed at 823 K for 24 h, in contrast with 773 K for 72 h for Mg-Zn-Y alloy (10H-type) and 800 K for 64 h for Mg-Al-Gd alloy (18R-type) [9,15,16]. This suggests that the significant long-range interactions between the Al-Y clusters exist in Mg-Al-Y alloy with 10H-type stacking sequence and that the Mg-Al-Y alloy will become a unique model case for researching the long-range arrangements of the clusters in LPSO structures.

The concept of cluster interactions has already been proposed in the previous literatures mainly in 18R stacking sequence of ternary alloys such as Mg-Zn-Y and Mg-Al-Gd [10,17–19]. In these alloys, the alignments of clusters are very often observed in the OD manner, so that the discussions about the cluster interaction have been mainly focused on the interactions within the stacking fault region (in-plane) except for Ref. [19], in which effects of phonon on the inter-planer ordering are investigated by the one-dimensional chain model with a mass-change. On the other hand, we deal with the 10H-type Mg-Al-Y alloys, which have the regularity in the alignment of the cluster not only in-plane but along the stacking direction with the short-time treatment. Therefore, we concentrate our discussion on the interaction between the clusters (cluster layers) along the stacking direction, especially the interaction beyond the first nearest cluster layer, assuming that the $L1_2$-type clusters regularly align in the stacking fault region.

In the present paper, we construct thirteen polytypic structural models of the LPSO structure with composition of $Mg_{188}M_{24}RE_{32}$ including the highly ordered LPSO structure discovered by Takeda et al. [9], and evaluate the relative stabilities of these structures by using first-principles calculation based on density functional theory (DFT).

First, we calculate the relative energies of thirteen polytypic structure of Mg-Al-Y alloy and reveal that (1) the observed structure is the most stable among the thirteens, and that (2) the long-range interactions between the separated layers substantially exist, that is, the highly ordered structures are formed by the long-range interactions.

Second, we calculate and compare the long-range interactions between the cluster layers in Mg-M-RE alloys for sixteen M-RE combinations listed in Table 1 [2–10], and reveal that the long-range interactions in the alloys with M = Al are one digit larger than those with M = Zn. These results suggest that the long-range interactions along the stacking direction play an important role to form highly ordered LPSO structure in Mg-Al-Y alloys. Furthermore, we find the long-range interaction energies in the Mg-Al-RE with RE = lanthanoids become large with increasing the atomic number of RE elements. We believe that these results provide a fundamental knowledge to elucidate the formation mechanism of the anomalous LPSO structure with impurity clustering and its interactions, and to develop thermodynamically stable LPSO structures applicable to industrial materials.

2. Methodology

2.1. Structural models

For simulating the interactions in LPSO phase related to the highly ordered structure shown in Fig. 1, we construct some of structural models on the following assumptions.

1. Mg matrix has the 10H-type stacking sequence including a stacking fault appearing on five-layer period, i.e., *AB*/*CACAC*/*BAB*-type stacking sequence, where slash marks indicate the position of the stacking faults [12]. Hereinafter we call the set of five layers with a stacking fault, *AB*/*CAC* or *AC*/*BAB*, *Structural Packet (SP)*.
2. Impurity elements M and RE are distributed in the four layers around each of the stacking fault, *AB*/*CA* or *AC*/*BA* [13], and constitute the $L1_2$-type M_6RE_8 clusters which align regularly and densely, that is, the closest packed in SPs; one M_6RE_8 cluster is located on a rhombus of the $2\sqrt{3} \times 2\sqrt{3}$ Mg matrix [9]. In each cluster, a Mg atom is contained at the central site [20].
3. The positions of the clusters are 2-dimensionally shifted SP by SP. Since clusters are the closest packed by the assumption 2, the position of one cluster in a $2\sqrt{3} \times 2\sqrt{3}$ rhombus determines that of all clusters. Here, we specify the positional relation of clusters between two adjacent SPs by the relative shifts. According to the hexagonal symmetry, we can classify the relative shifts into four groups, A1-A4, with the 2-dimensional translation vectors, A1: (0, 0), A2: $\pm(L/3, -L/3)$, A3: $\pm(0, L/2)$, $\pm(0, L/2)$, $\pm(-L/2, -L/2)$ and A4: $\pm(L/6, L/3)$, $\pm(L/6, -L/6)$, $\pm(-L/3, -L/6)$, where L is the side length of a 2×2 rhombus [14]. Fig. 2 shows the relative shifts and the corresponding translation vectors of the cluster center for each of A1–A4 groups.
4. SPs are stacked four-cycle within the relative shifts in each of A1–A4