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Review

Crystal structure of the mirror symmetry 10H-type long-period stacking order phase in Mg–Y–Zn alloy

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ABSTRACT

The crystal structure of the 10H-type long-period stacking order structure in Mg–Y–Zn alloy was investigated by first-principle calculations. The calculated results show that the accurate positions and distinctive arrangement of Zn and Y atoms in the most stable 10H-type LPSO phase exhibit mirror symmetry with respect to the atomic layer C_6, which agrees well with the experimental observations. Theoretical calculations still indicate that the mirror symmetry 10H-type ABACBCBCAB phase is not distorted, the lattice distortion of other LPSO phases may originate from the asymmetry of Zn element in the chemical order and stacking order. The obtained electronic density of states (DOS) reveals the underlying mechanism for mirror symmetry of 10H-LPSO phase.

Contents

1. Introduction

As structural materials, Mg alloys have advantages such as low density, good stiffness and the highest strength-to-weight-ratio [1–3]. Especially, because of their ease of recycling the Mg alloys widely used can contribute for maintenance of a clean environment [4]. Up to now, Mg alloys are becoming more and more attractive due to its applications in the microelectronics, automobile and aerospace industries [5–8]. However, the applications of Mg alloys in various fields are still restrained by low tensile strength and inferior ductility.

It is well known that the addition of rare-earth elements and transition metals is one of the most effective methods to optimize the microstructure and improve mechanical properties [9,10]. In recent years, Mg–Y–Zn alloys have received considerable attention due to their excellent mechanical properties and unique microstructures [11–20]. In particular, various novel lamellar structure of long-period stacking order (LPSO) phases have been observed, including 6H, 10H, 14H, 18R and 24R [21–31]. The 6H and 14H structure are commonly observed in conventional casting production [22], while 18R is the main phase by rapid solidification (RS) processing [23]. According to structural feature revealed by electron diffraction experiments, CTEM and HRTEM observa-

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tions, 10H phase has mirror symmetry with ABACBCBCAB stacking sequence [21]. Naturally, the special mirror symmetry of stacking sequence would be related to the distinctive atomic configuration especially the distribution of Zn and Y in the novel structure, and further show novel mechanical properties. So the 10H-LPSO structure with the perfect mirror symmetry stacking sequence would be very interesting, and should be given considerable attention.

Unfortunately, 10H LPSO is less commonly observed, and has been less investigated experimentally, so the atomic arrangement rule of Y and Zn elements in the mirror symmetry stacking sequence is still not well understood. In order to get a deeper insight into the detailed atomic configurations and the arrangement role of the Y and Zn in the structural evolution, theoretical investigation is necessary. In this paper, we have carried out first-principles calculations for the 10H LPSO structure in Mg–Y–Zn alloys based the density functional theory within the generalized gradient approximation (GGA). In the present work, the mirror symmetry stacking sequence and chemical order of Zn and Y element in 10H LPSO phase were determined theoretically for the first time, the geometrical evolution and the lattice distortion were also investigated in detail, and the electronic structures were further discussed.

2. Computational details

The present calculations were performed using the Vienna ab initio Simulation Package [32] based on density functional theory (DFT). The well established Predew-Wang (PW91) version of the generalized gradient approximation (GGA) was used to describe the exchange-correlation functional [33], and the valence electron–core interaction was described by PAW potentials [34] with Mg ($2p^6 3s^2$), Y ($4p^6 4s^2 4d^1 5s^2$) and Zn ($3d^{10} 4s^2$) as valence states. To ensure enough convergence, the plane-wave energy cutoff was chosen to be 350 eV, and the Brillouin zone was sampled with a mesh of $5 \times 5 \times 2$ generated by Monkhorst-Pack method [35]. The structural optimization was performed via the conjugate gradient method by full relaxation of the shape and volume of unit cell as well as internal coordinates of atoms, until the forces on atoms is converged to less than 0.01 eV/Å. Then the calculations of total energy and density of states were performed using the linear tetrahedron method with Blöchl correction [36].

3. Results and discussion

3.1. Crystal structure of mirror symmetry stacking

Because LPSO phase is not only stacking ordered but also chemically ordered structure [22], the crystal structure of LPSO phase is sensitive to the Zn and Y concentrations, different contents of Zn and Y would lead to adjustment of the crystal structure. On the other hand, it was also indicated by experiments that the ratio of Y/Zn in LPSO phase was approximately between 1 and 3 [37–39]. Up to now, the chemical compositions of $Mg_{97}Zn_1Y_2$, $Mg_{94}Zn_2Y_4$, $Mg_{91}Zn_3Y_6$, $Mg_{87}Zn_3Y_{10}$, $Mg_{90}Zn_4Y_6$, $Mg_{88}Zn_4Y_8$ (at.%) have been found in the five kinds of LPSO structures, respectively [40,41]. To investigate the mirror symmetry of 10H LPSO structures in Mg–Y–Zn alloy, the various chemical compositions must be determined theoretically. For the sake of convenient description, 10H-type ABACBCBCAB LPSO structure was marked as $A_1B_2A_3C_4B_5C_6B_7C_8A_9B_{10}$ in the present study and the subscript of ten numbers are used to distinguish the different atomic layers. Here, a unit cell of $3 \times 3 \times 5$ (10 layers) was used, which contains 90 atoms. Fig. 1 shows a 3×3 unit cell in the atomic plane of the 10H-LPSO phase perpendicular to *c*-axis with yellow, gray and green circles representing atoms in the A, B and C layer, respectively.

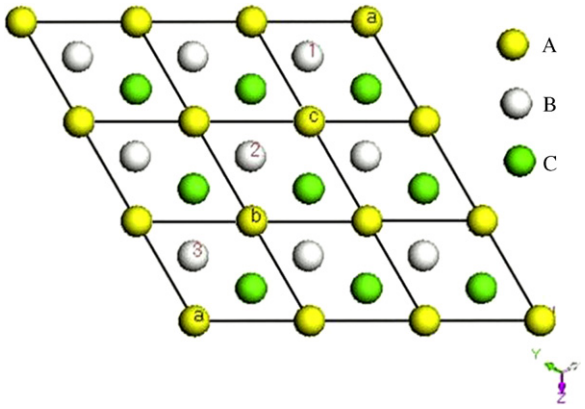

Fig. 1. The 3×3 unit cell in the basal plane of structural model for 10H-LPSO phase, in which yellow, gray and green circles represent the A, B and C layer atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The calculated results in Table 1 show that when the additive atom is only one Zn or Y atom, the total energy for the additive atom in the symmetry layers which respect to the atomic layer C_6 are equal. For example, $E_{B_2} = E_{B_{10}}$, $E_{A_3} = E_{A_9}$, and so on. Therefore, when the 10H-LPSO phase contains only one Y or Zn atom, the arrangement and distribution of Y or Zn atom in the 10H LPSO phase exhibit always mirror symmetry. Furthermore, when Y or Zn atom is located in the A_1, B_2, C_6 and B_{10} layers the total energy is relatively lower. Fig. 2 visually shows the mirror symmetry of the total energies for Zn atom in different layers of 10H-LPSO structure. Consequently, the Zn atom would be located in B_2 or B_{10} layer, and the Y atom would be located in A_1 layer due to the lowest energy.

As one Zn atom and one Y atom are added simultaneously, there are two ways of addition of the substitution atoms. One way is that Zn atom firstly occupied in B_{10} layer and kept it unchanged, and then the Y atom was added in different layers. Similarly, the other way is Y atom occupied firstly in the A_1 layer, and then the Zn atom was added. The calculation results in Tables 2–4 shows that when Zn and Y atoms are located simultaneously on A_1 layer, the total energy was the lowest. Furthermore, Y atom firstly located at position a in A_1 layer in Fig. 1, then Zn atom located at position b in the vicinity position of Y atom. It is noted that given the small difference in energy between different variants, Zn atoms may not only occupy the B_2 and B_{10} layers, but also A_1 or C_6, Y as well B_2 or C_6. However, it such an arrangement also does not change the symmetric feature. From the thermodynamic point of view, the partial enthalpy for ZnY is −151 kJ/mol, which is a far higher negative value than −27 kJ/mol for ZnMg, so Zn is more likely to form bonding with Y than Mg [42]. The calculated result is consistent with the experimental observations.

When two Zn or Y atoms are added, the calculation results in Table 5 indicate that the two of substitution atoms were not limited in the single layer, but diffused into two different atoms layers B_2 and B_{10}, being symmetrical with respect to the atomic layer C_6. Therefore, the 10H-LPSO structure of $Mg_{88}Zn_2$ and $Mg_{88}Y_2$ alloys also exhibit strict mirror symmetry with respect to the atomic layer C_6.

When a higher ratio of substitution atoms *x* at.%Zn + *y* at.%Y was added into 10H-LPSO structure, following the above procedure in which Zn and/or Y atom was added eventually one by one, the accurate positions and arrangement rule of substituted atoms were determined completely. By a large number of calculations, the accu-