First Principles Calculations of Solute Sweeping and Stacking Faults in Mg-Zn-Y Alloy

Yuichi Sakamoto, Chihori Shirayama, Yosuke Yamamoto, Rika Kubo, Motoyuki Kiyohara and Shigeto R. Nishitani

Department of Informatics, Kwansei Gakuin University, Sanda 669-1337, Japan

The formation mechanism of the long-period stacking-ordered (LPSO) structure of a Mg-Zn-Y alloy was investigated through energy assessments using first-principles calculations. The solute atoms are swept out from stacking fault regions because of their repulsive interaction with precipitated L12 clusters. The swept-out solute atoms are condensed a few layers away from the stacking-fault regions and accelerate the introduction of other stacking faults. A new scenario in the formation of the LPSO structure is proposed. [doi:10.2320/matertrans.MH201410]

(Received December 25, 2014; Accepted March 16, 2015; Published May 8, 2015)

Keywords: LPSO (long period stacking order structure), precipitation, L12 cluster, relaxation, activation energy, gamma surface

1. Introduction

The long period stacking ordered (LPSO) structure of a Mg-Zn-Y alloy was first reported in 2000 by Kawamura et al. and is now a promising candidate for light structural materials for aircraft. High-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) observation has revealed the characteristics of the LPSO structure; periodic stacking-faults constitute the 18R or 14H structure, and solute atoms are condensed at the stacking-faults. More than ten years later, the formation mechanism of this novel microstructure has been discussed. Two factors play a role in the formation mechanism: stacking faults and solute atoms. Two simple scenarios have immediately been proposed.

Stacking-fault-initiated scenario
- Stacking faults are first periodically introduced in hcp-Mg.
- Subsequently, solute atoms are trapped around each stacking-fault layer.

Solute-ordering-initiated scenario
- An initial stacking fault traps solute atoms.
- Other solute atoms show middle-range ordering from the initial stacking fault.
- The condensed solute atoms then initiate stacking-faults.

For the system to develop the above scenarios, each step should show a reasonable energy difference between the initial and final states and/or activation energy. For the stacking-fault-initiated scenario, long-period stacking should be stable in pure Mg or Mg alloys, and the solute atoms should be stable in the stacking-faults. For the solute-ordering-initiated scenario, the solute atoms should show middle-range ordering in 2H-Mg, and the condensed solute atoms should accelerate the stacking-fault introduction.

In a previous paper, we reported negative data for the solute-ordering-initiated scenario. For investigating the solute ordering, we checked the interaction energies of many configurations between solute atoms, between solute pairs, and between stacking-faults and solute atoms. All the interaction energies are very small and attractive in nature, and no middle-range ordering was observed. Meanwhile, the stability of the 18R structure at elevated temperatures has been reported by Ikubo et al. These results suggest that the stacking-fault-initiated scenario may be the mechanism for the LPSO formation. However, at a heat-treatment temperature of approximately 600 K, the energy difference between the 18R and 2H structures is 0.004 eV/atom (0.1 kJ/mol), which is small compared to the thermal fluctuation of 0.05 eV. Therefore, a sufficiently large energy difference is necessary for the stacking-fault-initiated scenario.

Transmission electron microscopy observation has revealed the existence of clusters of L12 structure with Al6Gd8 on the stacking fault region of the LPSO structure in the Mg-Al-Gd system. Subsequently, such L12 clusters have been detected in the Mg-Zn-Y system as well. Scanning tunneling microscopy (STM) has also revealed the existence of the clusters. The L12 clusters play a key role in the formation of the LPSO structure.

This study aimed to investigate the scenarios including the L12 cluster through energy assessments using first-principles calculations. We obtained two critical energy changes to reveal the formation mechanism. The first is the interaction energy change between the solute atoms and the L12 cluster. The second is the effect of atoms on the energy change during the stacking-fault introduction. The calculation conditions are given in the next section. The detailed description of the slab models used are given in the results and discussion section. From the obtained results, we propose a slightly modified scenario of the LPSO formation in the conclusion section.

2. Computational Method

The first-principles calculations were performed using the Vienna ab initio simulation program (VASP). We used GGA Perdew-Wang 91 for the exchange-correlation functional and the projector augmented wave (PAW) method for pseudopotentials. The energy cut-off was set at 300 eV for consistency with the PAW potentials of Mg, Y, and Zn. The electronic energy convergence of the self-consistent loop is $10^{-4}$ eV, and the force convergence of the atomic relaxation loop is $10^{-2}$ eV/Å. The k-point meshes of Brillouin zone sampling in a primitive cell were based on the Monkhorst-
The primitive cell of the stacking-fault model was constructed of $2 \times 2 \times 9$ hcp unit cells containing a total of 72 atoms, and the $k$-point was $9 \times 9 \times 1$. Detailed computational models are described in the next section, together with the related results.

3. Results and Discussions

3.1 Interaction between L1$_2$ cluster and solute atoms

The side and top views of the models for investigating the interaction energy between an L1$_2$ cluster and a solute atom are shown in Fig. 1. The slab model is constructed in $2 \times 2$ unit cells of hcp basal plane. Two stacking-faults are introduced between layers 1 and 2 as well as 5 and 6, marked with ‘c’ and dotted lines. The other layers have an hcp structure and are marked with ‘h’. Two stacking-faults were set to have opposite stacking directions to satisfy the periodic boundary condition. The L1$_2$ cluster is located at one of these stacking faults. Eighteen layers are stacked to separate the stacking fault from the additional solute atom. The atom positions and outer sizes are fully relaxed with the outer hexagonal shape preserved. Usually, the energy is measured from some standard, such as the segregation limit, but the plotted data in the results that follow are the total energy as it is in the output of VASP. The slab model to which Zn or Y is added is composed of Mg$_{202-1}$Zn$_{6+1}$Y$_8$ or Mg$_{202-1}$Zn$_{6}$Y$_{8+1}$, respectively. Although the additional replacement of Zn or Y with Mg induces a large shift in the total energy, the energy change in each figure would be focused.

The starting model of the L1$_2$ cluster is constructed using the reported one with 202 Mg, 6 Zn, and 8 Y atoms. Side views of the calculated L1$_2$ cluster configurations are shown in Fig. 2, where (a) and (b) are views before and after relaxations, respectively. Mg atoms surrounding the L1$_2$ cluster are eliminated for simplicity. The horizontal dotted lines show the heights of L1$_2$ clusters, in which a significant shrinkage of 10% is observed. Other significant movements of Zn atoms are also observed, which are consistent with the previous report. The shrinkage of the L1$_2$ cluster layers should indicate the strong bonding of the L1$_2$ cluster, which would induce the weakening of the back bond. The easy cleavage observed with STM indicates the weakness of the bonding of the inter-layers next to the L1$_2$ cluster.

Each Zn or Y solute atom is located on the 1st through 6th layers away from the L1$_2$ cluster, which are the 8th to 13th layers in Fig. 1(a), respectively. A few sites on each layer should be investigated. The possible configurations are shown in Fig. 1(b), which shows parsing from the top. Because of the hcp stacking, odd and even layers have different configurations. Four possible sites are marked as A through D, which are also used in the following two calculated results.

Figure 3 shows the dependence of the energy on the layer at which the solute Zn atom is located. The energies of the first layer show slightly lower values than those of the others, but the energy drops are as small as 0.01 eV. The additional Zn atom shows neither an attractive nor a repulsive tendency that is notable, away from the L1$_2$ cluster.

On the other hand, the additional Y atom significantly changes the energy. Figure 4 shows the dependence of energy on the layer at which the Y atom is located. All possible sites show the monotonous tendency of repulsion from the L1$_2$ cluster, and their values are approximately 0.2 eV. This is a very strong tendency compared to the other behavior of the solute. The additional Y atom should be swept out from the stacking-fault layers where the clusters are precipitated.
The difference in the sweeping-out behavior of the solutes between Zn and Y should be related to their atomic radii. The atomic radii of Mg, Zn and Y are 1.5, 1.4, and 1.8 Å, respectively. The strong tendency of Y to sweep out should be related to the remarkable shrinkage of stacking layers observed around the L1₂ cluster. The shrinkage of the stacking fault layers could be a strong driving force for the removal of the large element Y.

3.2 Effect of solute atom on stacking fault formation

Another critical change is observed in the effect of the solute atom on the stacking-fault energies. The calculation model is schematically shown in Fig. 5. Two blocks below and above the stacking-fault layer were displaced with respect to each other along the [1100] direction. The energy changes during the sliding with and without the Zn and Y atom pair are compared. The atom positions and outer size are relaxed only along the z-direction.

Figure 6 shows the energy changes of the two blocks displaced along [1100]. Note that the energies at \( d = 1.0 \) indicate the real stacking fault energy, and around \( d = 0.5 \) energies have maxima, which indicate the activation energies of the stacking-fault formation. The activation energy as well as stacking-fault energy of the stacking-fault formation in the model to which the Zn-Y solute pair is added are one third of those in the model without the Zn-Y solute pair. The activation energy of the stacking-fault introduction is approximately 30 mJ/m², which is so small that stacking faults are easily introduced by small stresses. Therefore, the solute pair drastically accelerates the stacking-fault introduction.

4. Conclusions

One of two proposed scenarios of LPSO formation, the solute-initiated scenario, has been investigated through the energy assessment using first-principles calculations. The energy difference of the Y location is 0.2 eV, as shown in Fig. 4, which is notably large compared to the thermal fluctuation of 0.05 eV around the heat treatment temperatures. The strong tendency of the swept-out Y from the L1₂ cluster and the acceleration of the stacking-fault introduction by the Y and Zn pair are suggested to cause the frequent occurrence of stacking faults, which is also accelerated by the stability of the 18R structure in finite temperatures as reported by Iikubo et al. or a thermal stress. On the basis of the obtained results, we propose a new scenario for the LPSO formation mechanism:

1. A layer at which Zn and Y are condensed easily induces a stacking fault.
2. The stacking fault traps Zn and Y.
3. L1₂ clusters are formed at the stacking fault.
4. Additional Zn and Y atoms are swept out or displaced away from the stacking fault.
5. Steps 1–4 are repeated.

A previous paper showed that Zn and Y solute atoms have a strong tendency to be located in the same layer in hcp-Mg, because of the strain relaxation of their large and small atomic radii comparing to Mg, respectively. The pairings of Y with Zn may decrease the tendency of Y to be swept out. Possible configurations of the Zn and Y pair located in the same layer are so large in number that their energy calculations require significant computational effort. However, such calculations are in progress. For the proposed scenario, the periodicity of the stacking faults constituting the 18R or 14H structure requires the vertical movement of the stacking faults, which was observed using TEM by Kiguchi et al. and would be clarified through a theoretical treatment.
Acknowledgements

This work was partly supported by MEXT KAKENHI Grant Number 23109006 (Grant-in-Aid for Scientific Research on Innovative Areas, “Synchronized Long-Period Stacking Ordered Structure — The Evolution of the Material Science for Innovative Development of the Next-generation Lightweight Structure Materials —”).

REFERENCES