First Principles Calculations of Solute Ordering in Mg–Zn–Y Alloys

Yosuke Yamamoto*1, Yuichi Sakamoto*1, Yoshihiro Masaki*2 and Shigeto R. Nishitani

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

The formation mechanism of the LPSO structures of Mg–Zn–Y alloys has been investigated by the energetic assessments with the first principles calculations. For the key players of the LPSO structures, the stacking faults and the solute elements of Zn and Y, two scenarios are proposed; one is the stacking fault control and the other is the solute atom pair control. Both of them were declined through the detailed investigations of the energetic assessments. The enrichment of solute atoms induced by the stacking fault is suggested.


(Received November 16, 2012; Accepted January 21, 2013; Published March 1, 2013)

Keywords: first principles calculations, stacking fault, magnesium alloy, long period stacking order

1. Introduction

Mg–Zn–Y alloys are good candidates for the next generation light structural metallic materials due to their superior specific strengths. These alloys show novel microstructures with long period stacking order (LPSO). Figure 1 shows a schematic illustration of one of the LPSO structures, 18R in Ramsdell notation, i.e., the 18 layers stacked in a rhombohedral unit. The 18R structure is based on the hcp structure, and the stacking faults are introduced periodically. In Fig. 1, the local stacking order of hcp like “ABAB…” is indicated with “h” and that of fcc like “ABC…” is indicated with “c”. Stacking faults are located in the “cc” region. The 18R structure is constructed with six sequential layer units of two c and four h layers. For the periodicity going back to the original column A, three units of them are stacked and making 18 layers. The outer shape of a unit cell composed of 18 layers is crystallographically rhombohedral (“R”). The other LPSO structures are so-called 14H and 10H, meaning 14 and 10 layers with the hexagonal outer shape, respectively.

The solute atoms of Zn and Y are experimentally observed to be enriched around the stacking faults. The good mechanical properties of Mg–Zn–Y alloys are predicted due to this query structure, however, its formation mechanism has not been clarified yet.

One proposal of the stability of the 18R structure has been shown by the first principles calculations including the finite temperature effects of the phonon vibration. In their calculation, the hcp structure (2H) of pure Mg is the most stable at lower temperatures, but the 18R structure becomes more stable than the hcp structure at higher temperatures. The energy difference between the 2H and 18R structures is 2.5 meV/atom, which is very small compared with the interaction energy of solute atoms and stacking fault as well as the thermal fluctuation.

In this paper, we will explore the formation mechanism of LPSO from the energetic assessment with the first principles calculations. The key players are the stacking faults and the solute atoms. Before stepping into the detailed calculating results, two possible outlines will be shown as the scenarios of the formation of LPSO structures. Then the conditions of the first principles calculations will be given. Each atomistic configuration of the calculating model will be described in detail in the result section.

2. Scenarios of the LPSO Formation

The LPSO structure was firstly found in the rapidly quenched alloy of Mg97Zn1Y2. After the first finding, the LPSO was obtained in the alloy annealed from a homogeneous solid solution. Furthermore, these heated alloys contain other periodicities, 14H and 10H. Thus, we assume that the initial state of the kinetic process of the LPSO formation is a solid solution.

Even in this solid solution, the solute atoms of Zn and Y should not be isolated. The atomic radii of Mg, Zn and Y are 1.5, 1.4 and 1.8 Å respectively. Zn atoms are smaller than Mg atoms, but Y atoms are larger than Mg atoms. These size differences of alloying elements lay heavy strains around

*1Graduate Student, Kwansei Gakuin University
*2Graduate Student, Kwansei Gakuin University. Present address: TechMatrix Corp., Tokyo 108-8588, Japan
solute atoms in the hcp Mg matrix. The pairing of Zn and Y, smaller and larger atoms, is expected to make large reduction of a strain, which will be discussed in the result section. Thus, the initial stage of the LPSO formation is a homogeneous solid solution of Zn and Y pairs in the hcp Mg matrix.

Then, two scenarios of the LPSO formation are speculated as shown in Fig. 2, where hcp Mg, fcc Mg and Zn–Y pairs are denoted with the white, black and gray circles, respectively. First of all, if the stacking fault energy is low, which is the case of Mg, the intrinsic type of stacking fault is easily created by two widely spread Shockley partial dislocations.

- **Stacking fault control, or scenario A:** As shown in the first step of Fig. 2(A), equally separated multiple stacking faults are introduced in the hcp Mg matrix, and then, the solute atoms between them are trapped at these stacking faults.

- **Solute pair ordering control, or scenario B:** As shown in Fig. 2(B), a stacking fault traps the solute atoms first, and then, induce the successive stacking fault formation. In this scenario, in order to make the stacking faults introduced periodically, the solute pairs should show some kind of a long range ordering.

### 3. Results and Discussion

#### 3.1 Computational conditions

The first principles calculations were performed by VASP (Vienna ab initio simulation package). We used the GGA Perdew–Wang 91 for the exchange–correlation functional and the PAW (Projector Augmented Wave) method for pseudopotentials. The energy cut-off is set at 300 eV for the consistency with the PAW potentials of Mg, Y and Zn. For all calculations, the electronic energy convergence of self consistent loop and the force convergence of atomic relaxation loop are set $10^{-4}$ eV and $10^{-2}$ eV/Å, respectively. The $k$-point meshes of Brillouin zone sampling in a primitive cell were based on the Monkhorst-Pack scheme. The actual values of $k$-meshes were $18 \times 18 \times 1$, $9 \times 9 \times 3$ and $9 \times 9 \times 1$ for the models in section 3.2, section 3.3 and section 3.4, respectively.

#### 3.2 Hexagonality dependency of Mg polytypes

In scenario A, the stacking fault control, the stacking faults with a long periodicity are firstly introduced in the hcp Mg matrix. For assuring this model, the energies of a few polytypes, which are perfect lattices with the stacking faults with long periodicities, are calculated. Each polytype shows a different stacking sequence, which is characterized by the hexagonality. This is defined as $n_h/(n_c + n_h)$, where $n_h$ and $n_c$ are the numbers of hexagonal and cubic layers respectively. Each calculation model is constructed with the $1 \times 1 \times N$ unit cells, where $N$ means the half of the number of stacking layers of Ramsdell notation. For example, the model with the hexagonality of 67% is 18R structure, and its cell is $1 \times 1 \times 9$ unit cells with two stacking faults. Figure 3 shows the correlation between hexagonality and the energy per Mg atom of each polytype. The 2H structure of an unit hexagonality is the most stable and the 3C structure of zero hexagonality is the most unstable in the ground state. The relationship between hexagonality and total energy draws an almost straight line in the graph of Fig. 3. The energy of the 18R structure (hexagonality of 67%) shows no typical deviation from the tie line between 3C and 2H structures. Because such a small deviation is easily buried in the thermal fluctuation, scenario A, the stacking fault control is declined.
3.3 Interaction energy of Zn and Y in hcp Mg

In the initial state of the formation of LPSO, rapidly cooled alloys show the homogeneous solid solution of the 2H structure. The local arrangement of Zn and Y atoms, however, is controlled by the interaction energy between these atoms. The calculation models are \(2 \times 2 \times 3\) hcp unit cells of Mg\(_{22}\)Zn\(_1\)Y\(_1\), whose atomistic configurations are shown in Fig. 4. The first column shows the models viewed from top. The solid and dashed circles indicate the A and the B sites of the hcp structure respectively. The second and further columns represent schematic drawings viewed from the side, and the headers indicate how far Zn and Y locating layers are separated. The same layer means that Zn and Y are substituted with Mg on the A and the A' sites in the same layer respectively. In the top row, Zn and Y are located at near sites, and in the bottom row they are located at far sites. The 1st layer at the third column means that Zn and Y are substituted with Mg in the adjacent layers. In this case, the near site means the A and B sites are in the same unit cell, and the far site means the A site of a unit cell and the B' site of the adjacent unit cell. The 2nd layer on the fourth column means that Zn is located on the 2nd layer separated from the Y located layer. In this case, the near site is the same site viewed from top. The notations of the last column are the same as those in the 1st layer column.

The calculated results are shown in Fig. 5. Because the number of atoms, Mg\(_{22}\)Zn\(_1\)Y\(_1\), is the same in this calculations, the results are given in the total energy. In these calculations, the outer shapes and inner atom positions are fully relaxed. The configuration where two atoms are located in the same layer shows the lowest energy. The far site of the 1st layer configuration shows very high energy, whose reason has not been clarified. Regardlessly, the other results shows a general tendency that the closer the layers are, the more energy decreases. The energy difference between the same layer model and the further separated models shows 0.2 eV, which is not large but sufficient for the gathering at the room temperature or the annealing temperature of 673 K. Thus, Zn and Y show the pairing tendency in the hcp Mg matrix. Larger clusters are also expected to be formed, but they make their traveling rate slow. We assumed that the pairs of Zn and Y atoms are moving around in the hcp or the 18R Mg matrix.

3.4 Interaction energy between two pairs of Zn–Y

Zn and Y atoms make pairs in the hcp Mg matrix. In scenario B, the solute pair ordering mechanism, each pair is expected to be located periodically. For assuring this hypothesis, the energies of two pairs of Zn and Y should be checked. However, the number of possible configurations of two pairs will increase. In order to restrict the possibility, more assumptions in the models are necessary. At the final state of the LPSO, Zn and Y should be located around the stacking fault regions. The cluster formations are observed in the more stable LPSO structure, for instance, in the Mg–Al–Gd system.\(^{13}\) In the Mg–Zn–Y system, such a clear cluster formation has not been observed as it is under discussion.\(^{14}\) Thus, we assumed that Zn and Y at a stacking fault are located on a c-site and the nearest neighbor h-site, respectively.

Under this assumption, these two pairs locating in \(2 \times 2 \times 15\) supercell constructed with the hcp unit cell including two stacking faults, are characterized by two parameters; the first is the number of the layers between two pairs, and the second is the type of their combination, as shown in Fig. 6. In the top row, two pairs of Zn and Y are placed as YZn–YZn, and in the bottom row, they are placed as YZn–ZnY. The head notation of “no layer” means that the two pairs are located without any layer in between as shown in (a) and (d). The one and two layers mean that the two pairs are located with one layer in between, and with two layers in between, respectively. The one pair is placed at a stacking fault as denoted by dashed lines in Fig. 6. We introduced two stacking faults for the unit cell periodicity. For reducing the strain energy around the inserted atoms, the atoms around the pairs are relaxed.

The calculated results are shown in Fig. 7, where the values are given in the total energy of Mg\(_{116}\)Zn\(_2\)Y\(_2\). The total
energy includes those from interactions among Mg, Zn and Y, and from two stacking faults. The energy dependence on the number of layers between pairs oscillate and show opposite phases in YZn–YZn and YZn–ZnY combinations. In the YZn–YZn combination, the pairs with zero or two layers in between show relatively low energies, and in a similar way in the YZn–ZnY combination the pairs with one or three layers in between show relatively low energies. For the YZn–YZn combination, higher energy models show a specific configuration of Zn atoms, which are located at the same columnar site in (0001) direction. This behavior also applies to the YZn–ZnY combination. We expected that the energy drop would occur in the pairs with three or four layers in between. However, the result shows that it occurred in the pairs with one layer. The reason of these behavior has not been clarified, but we emphasize here that the maximum energy drop observed between the pairs separated by four or more layers and those with one layer is 0.05 eV. Although the configurations of the two pairs of Zn and Y atoms discussed in this research do not cover all possibilities, some trial changes of the configurations do not alter energy differences so much. The simple solute ordering around the stacking fault is not observed in our calculations, which implies that scenario B of the solute ordering hardly occurs. Thus, the two simple scenarios shown before should be declined. The energy shows minimum at the pair with one layer in between as in Fig. 7. Zn–Y pairs should travel by diffusion with a vacancy. The configurations between YZn–YZn and YZn–ZnY combinations can easily transform to each other. Thus, the energy of the Zn–Y pair monotonically decreases to the level of the pair with one layer in between. This indicates that the solutes are enriched around stacking faults. The long range ordering of solutes are not expected, but the concentrated solute atoms may affect the next step of the LPSO formation.

4. Conclusions

Two proposed scenarios of the LPSO structure have been examined with the energetic assessment of the first principles calculations. Scenario A, the stacking fault control mechanism, is declined by the small energy deviation of 18R from the tie line between those of pure hcp and pure fcc in pure Mg. Scenario B, the solute ordering control mechanism, is examined by several configurations of Zn–Y pairs. The pair configurations, however, show no typical energy drop at the pairs with three or four layers in between. This means that the long range ordering of solutes is not expected. The energy drop near the Zn–Y pairs at the stacking faults has been confirmed to accelerate the enrichment of the solutes around the stacking faults. This enrichment of the solute atoms around pre-existed stacking fault should induce the other stacking faults. The other scenario such as the larger cluster formation or the stacking fault nucleation is necessary to explain the LPSO formation.
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

2) L. S. Ramsdell: Am. Mineralogist 32 (1947) 64.