Interaction energy between cluster and additions in Mg-Zn-Y-LPSO

Department of Informatics, Kwansei Gakuin Univ., S. R. Nishitani, R. Kubo, M. Kiyohara, Y. Sakamoto, Y. Yamamoto

Introduction

The long period stacking ordered (LPSO) structure of Mg-Zn-Y alloy was first found in 2000 by Kawamura et al.[[1]. and is now a hot candidate for the light structure materials for aircrafts.The high angle annular dark field scanning transmission electron microscopy(HAADF-STEM) observation revealed the characteristics of the LPSO structure[2]; the periodically introduced stacking faults construct the 18R or 14H structure, and the solute atoms are condensed at the stacking faults.After that, more than ten years, the formation mechanism of the this novelmicrostructure has been discussed.The players on the stage are two: the stacking faults andthe solute atoms. Two simple scenarios are immediately proposed[3]:

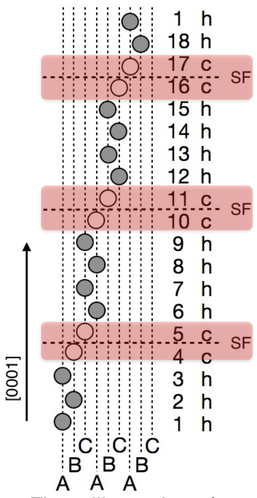


Fig.1: Illustration of atomic stacking of 18R-Mg alloy.

【A：stacking fault initiated scenario】

1. stacking faults are first introduced periodically in hcp-Mg,
2. the solute atoms are trapped around each stacking fault layer,

【B：solute ordering initiated scenario】

1. an initial stacking fault traps solute atoms,
2. other solute atoms show a middle range ordering from the initial stacking fault,
3. the condensed solute atoms initiate the stacking faults.

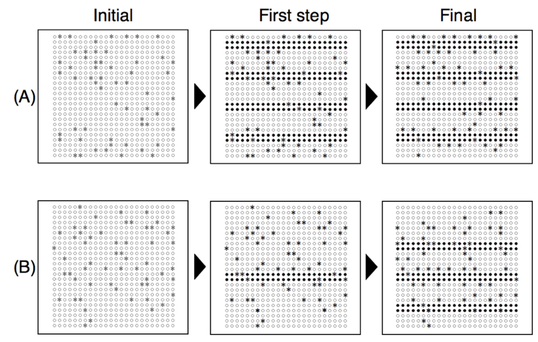


Fig.2: Two possible scenarios for the LPSO formation,
(A)：stacking fault initiated scenario.
(B)：solute ordering initiated scenario.

In the previous paper[3], we have reported the negative data for the solute ordering initiated scenario.on the other hand, Zn and Y solute atoms are strong tendency to locate in the same layer in hcp-Mg, and the solute pair accelerates the stacking fault introduction so drastically..The aim of this research is the investigation of interaction between $L1_2$ cluster[4] which constructed solute atoms and solute atoms by the energy assesments using the first principles calculations.

[1] Y Kawamura, K Hayashi, A Inoue, T Masumoto, Mater. Trans., 42 (2001) 1172.
[2] E. Abe, A. Ono, T. Itoi, M. Yamasaki, Y. Kawamura: Philosophical Magazine Letters, 91, (2011) 690.
[3] Y. Yamamoto,Y. Akamoto,Y. Masaki and S. R. Nishitani , Mater. Trans. 54, (2013), 656.
[4] H. Yokobayashi, K. Kishida, H. Inui, M. Yamasaki and, Y. Kawamura: Acta Mater., 59, (2011), 7287.

Stability of cluster

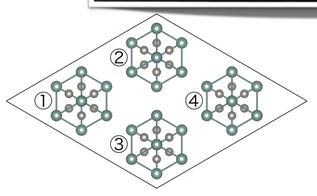


Fig3:Possible site for $L1_2$ cluster in the slug model which constructed 2x2 unit sells of hcp base plane.

Table.1:calculation results of each model.

	$Mg_{58}Zn_6Y_8$	$Mg_{202}Zn_6Y_8$
E_{Total}[eV]	-153.441	-375.406
$E_{Cluster}$[eV]	-4.043	-4.046

Table.2:one to four clusters' locations.

number of cluster	1	2	3	4
location of cluster	①	①, ②	①, ②, ③	①, ②, ③, ④

Table.3:total energy and cluster energy when introducing a few of cluster in same layer.

number of cluster	1	2	3	4
E_{Total}[eV]	-484.567	-527.695	-570.764	-613.773
$E_{Cluster}$[eV]	-4.059	-4.080	-4.067	-4.046

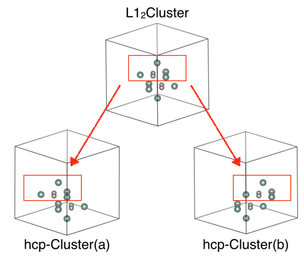


Fig.4: the cluster structure in the Mg alloy of the hcp structure. The figure above is $L1_2$ cluster. Cluster in hcp structure by moving as below the atoms in the red frame hcp-Cluster(a),(b).

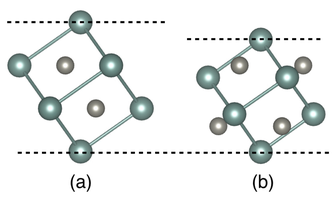


Fig5:Side views of calculated $L1_2$ cluster configurations before and after relaxations.

Cluster and solute atoms

Each Zn or Y solute atom is located on the 1st through 6th layers separated from the $L1_2$ cluster, which are 8 to 13 layers in Fig.6(a). A few sites on each layer are necessary to investigate. The possible configurations are shown in Fig.6(b), which are parsing from the top. Because of the hcp stacking, odd and even layers are different configurations. Four possiblesites are marked as 0 through 3, which are also used in the following two calculated results..

○A-layer
・four sites
・1,3,5th layer

○C-layer
・three sites
・2,4,6th layer

⇒21 models constructed by addition of Zn or Y.

Fig.7 and Fig.8 show the energy dependence on the located layer of the solute Zn or Y atom.

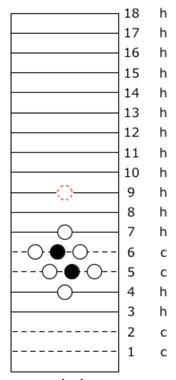
Total energy

○Additional Zn atom
⇒Energy drops about 0.02eV

The additional Zn atom doesn't show any notable tendency neither attractive nor separating from the $L1_2$ cluster.

○Additional Y atom
⇒About 0.2eV

The additional Y atom should be swept out from the stacking fault layers where the clusters are precipitated.



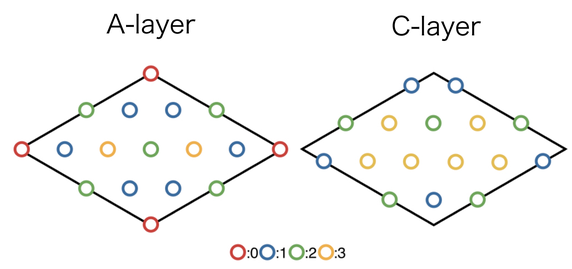


Fig.6:Schematic drawings of the slab model for investigating the interaction between cluster and solute atom; (a) side view and (b) top views of odd(left panel)and even(right panel) layers. Possible sites for the solute atom are marked as 0 through 3.

Fig.7:Energy dependence on the located layer of the Zn solute atom.

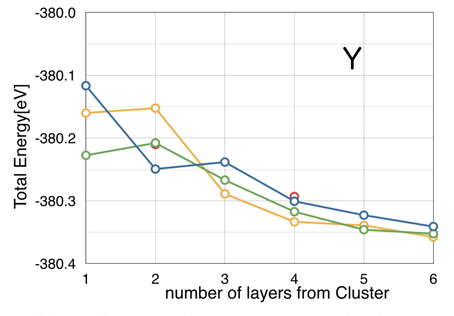


Fig.8: Energy dependence on the located layer of the Y solute atom.

Effect of atom on stacking fault formation

The other critical change is observed in the solute atom effect on the stacking fault energies. The model of the calculation is schematically drawn in Fig. 9. Two blocks below and above the stacking fault layer were displaced each other along [1 -1 0 0] direction. The energy changes during the sliding with and without Zn and Y atom pair are compared. The atom positions and the outer size are relaxed only along the z-direction.
Fig. 10 shows the energy changes of the two blocks displacing along [$1\bar{1}00$]. Note that the energies at d=1.0 mean the real stacking fault energy, and at around d=0.5 energies take maxima, which mean the activation energies of the stacking fault formation. Not only the stacking fault energy, but also the activation energy of the stacking fault formation with Zn-Y solute pair added model show the one third of those without Zn-Y solute pair.

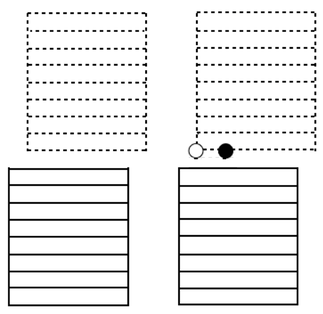


Fig.9:Schematically drawn illustrations for staking fault energy change, where the block drawn by dotted lines indicates the upper half of the slab and is displaced along [$1\bar{1}00$] direction against the lower half of the slab.

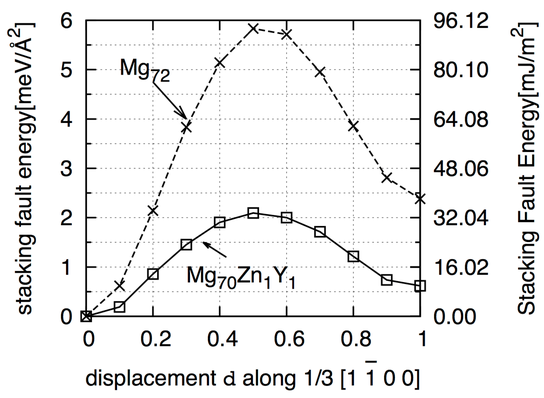


Fig.10: Energy changes on the displacement d along [$1\bar{1}00$], where solid and dotted lines represent the models with and without Y-Zn solute pair respectively.

Modified scenario

1. Zn and Y condensed layer induces the stacking fault easily,
2. the stacking fault traps Zn and Y,
3. $L1_2$ cluster are formed there,
4. further Zn and Y are swept out or step away from the stacking fault,
5. Repeat 1-4 process.

Interaction between $L1_2$ cluster and Zn-Y pair

For considering the Zn-Y simulataneouly introduction, there are a few tens of patterns. For the first step, give a name to independent site as a,b,c..., and then consider those combination.

Table 5 shows an example of the calculated results, where Zn and Y are introduced in the sites of blue and yellow circles at the C-layer. Its combination number become thiry, but we obtained only five different values. This reduction is of course due to the equivalent symmetry.
Fig.12 shows the interaction energy change depending on the distance between the cluster and Zn-Y pair before and after the relaxation.
Before the relaxation, the energy dependence is not monotonous, where the first layer shows the most stable and the second layer jumps up then further layers show gradual drops. After the relaxation, the energy drops monotonously as increasing the distance.
The final results indicate that the additional Zn-Y solute atom pair should be swept out from the stacking fault layers where the clusters are precipitated.

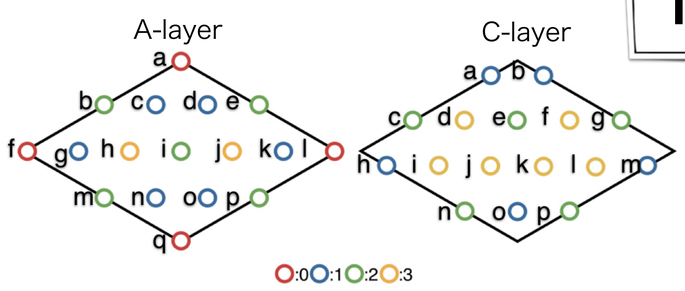
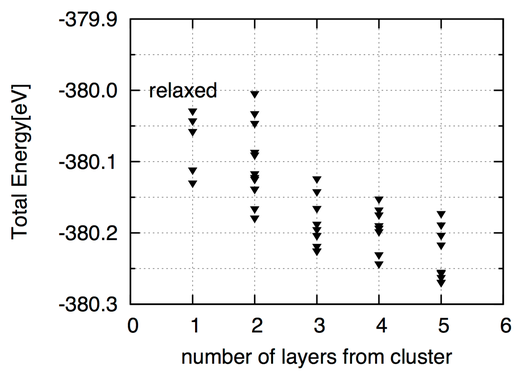


Fig.11: Schematically drawn illustrations which is distributing the number.

Table 5: Calculated results where Zn and Y are introduced in the sites of blue and yellow circles at the C-layer.

	a d	a f	a i	a j	a k	a l
[eV]	-377.417239	-377.355389	-377.317585	-377.349958	-377.317587	-377.428611
	b d	b f	b i	b j	b k	b l
[eV]	-377.355391	-377.428612	-377.428609	-377.317587	-377.355389	-377.317586
	h d	h f	h i	h j	h k	h l
[eV]	-377.355391	-377.428612	-377.428609	-377.307125	-377.355389	-377.317586
	m d	m f	m i	m j	m k	m l
[eV]	-377.428614	-377.355389	-377.317585	-377.355389	-377.317587	-377.428611
	o d	o f	o i	o j	o k	o l
[eV]	-377.317590	-377.317588	-377.406247	-377.428614	-377.428617	-377.355388



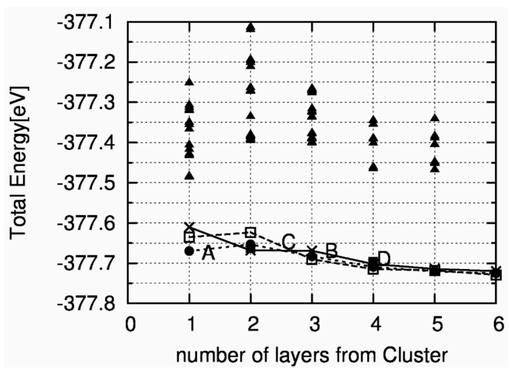


Fig.14: Interaction energy drop due to the longer distance between cluster and Zn-Y pair.