Thermodynamic stability of Mg-Y-Zn ternary alloys through first-principles

Ryohei Tanaka, Koretaka Yuge
Department of materials science and engineering, Kyoto university, Kyoto, Japan
(Dated: March 4, 2015)

In order to clarify thermodynamic stability of Mg based long-period stacking ordered (LPSO) structure, we systematically study energetic preference for alloys on multiple stacking with different composition for random mixing of constituent elements, Mg, Y, and Zn based on special quasirandom structure (SQS). Bulk modulus for SQS models of 75, 87.5, and 93.75 at.% Mg are about 35 GPa and do not show significant dependence of Mg concentration, which therefore means that the effects of phonon do not play essential role on LPSO phase stability. Through calculation of formation free energy of SQS, Mg-Y-Zn alloy exhibits phase separation into Mg- and Y-Zn rich phase and SQS on fcc stacking is stabilized by introducing stacking faults.

1. INTRODUCTION

For its remarkable high tensile strength and ductility [1], Mg-based long-period stacking ordered (LPSO) structure are considered as light-weight structural alloy for next generation. From experimental and theoretical point of view, many studies are carried out to clarify its formation process, its properties, and to apply it to structural materials. In theoretical calculation, process of formation and some properties of Mg-based LPSO alloy are clarified, for example, the tendency of phase separation based on Cluster validation method [2], formation and in-plane ordering of clusters consisted of Y, Zn substitutional atoms [3], and change of thermodynamic stability when substitutional atoms are changed in Mg alloy [4]. However, Theoretical study of the effect of stacking difference and phonon on thermodynamic stability is not sufficient to understand and most calculations confine the structural model. Calculation that doesn’t confine experimentally reported structures and has high degree of freedom in atomic scale is therefore be required. Fig. 1 is a schematic illustration of stacking sequence of 18R LPSO structure. Stacking sequence is for hexagonal closed packed (hcp), which are denoted by A,B and C. "S.F." means stacking fault.

2. METHODOLOGY

To address energetics of multicomponent system comprehensively, we need to calculate tremendous number of structures of the system and computational cost therefore becomes large. In this study, we employ special quasirandom structure, SQS, to assess thermodynamic stability of LPSO phase competing random phase. SQS is used as a means to evaluate thermodynamic stability and properties, which is perfect random structure that are specified by most relevant radial correlation function. In the concept of SQS, we can find the structure, which has an average physical quantity of the system.

Let us consider the system with $N$ lattice points for component $R$. $\sigma_i$ is a variable which specifies the occupation of lattice point $i$ and $\vec{\sigma} = (\sigma_1, \sigma_2, \cdots, \sigma_N)$ can specify any atomic arrangement and we can represent structures following equation, which is called correlation function $\Phi^M_{\alpha}$,

$$\Phi^M_{\alpha} = \langle \rho_{d1}(\sigma_i) \rangle \langle \rho_{d2}(\sigma_j) \rangle \cdots \langle \rho_{dn}(\sigma_k) \rangle. \quad (1)$$
where \( \rho(\sigma_i) \) is complete orthonormal basis function at lattice point \( i \) and it is obtained by applying Gram-Schmidt technique to the linearly independent polynomial set \( \{1, \sigma_i, \sigma_i^2, \cdots, \sigma_i^{R-1}\} \). \( \alpha \) denotes a cluster included in the structure, \( d_n \) is the index of basis function \( \rho(\sigma_i) \) and \( M \) is the set of index. \( \langle \cdot \rangle \) represents average value.

In the case of ternary alloy system, the occupation of lattice point by each element, Mg, Y, and Zn, is defined by spin-like variables \( \sigma = +1, -1, 0 \) respectively, leading to the basis function of eq. (2) [6]:

\[
\rho_0 = 1, \rho_1 = \sqrt{\frac{3}{2}} \sigma, \rho_2 = -\sqrt{\frac{2}{3}} (1 - \frac{3}{2} \sigma^2).
\]

Correlation function is denoted by using eq. (1) and basis function in ternary system is represented by eq. (3),

\[
\langle \rho_0 \rangle = 1, \langle \rho_1 \rangle = \sqrt{\frac{3}{2}} \langle \sigma \rangle, \langle \rho_2 \rangle = -\sqrt{\frac{2}{3}} (1 - \frac{3}{2} \langle \sigma^2 \rangle). \tag{3}
\]

In this study, \( \langle \sigma \rangle = x_{Mg} - x_Y \) and \( \langle \sigma^2 \rangle = x_{Mg} + x_Y \), therefore we get each basis function of SQS, eq. (4), for ternary alloy system

\[
\Phi_{\alpha} = 2^{-\frac{n}{2}} \cdot 3^{-\frac{m}{2}} (x_{Mg} - x_Y)^{n-m} (1 - 3x_{Zn})^m. \tag{4}
\]

where \( n \) and \( m \) denote cluster size and the number of \( \rho_2 \) respectively.

To evaluate thermodynamic stability of Mg-Y-Zn system, we calculate formation free energy, \( F_{form} \), and bulk modulus, \( B = \frac{1}{V} \frac{\partial^2 E}{\partial V^2} \), for structures, which have multiple stacking with different composition for random mixing. \( F_{form} \) is denoted by eq. (5) and we define \( U \) by eq. (6),

\[
F_{form} = U - TS \tag{5}
\]

\[
U = E(Mg_x Y_y Zn_z) - xE(Mg) - yE(Y) - zE(Zn). \tag{6}
\]

where \( E(\gamma) \) is total energy of \( \gamma \), and we evaluate configurational entropy, \( S \), based on Bragg-Williams approximation.

In order to evaluate bulk modulus, we calculate total energies of structures, whose volume is isotropically expand at a rate of \( \pm 1\%, \pm 2\%, \pm 3\% \). We employ first-principles calculations using a DFT code, the Vienna Ab-initio Simulation Package (VASP) [7] [8], to obtain the total energies for structures of Mg-Y-Zn alloys. We calculated correlation function of SQS by optimizing its correlation function to become as close as to ideal value. The simulation was performed so that correlation functions come closer to ideal SQS correlation function 6 pair clusters finded by eq. (4). The calculation of total energy is carried out for the structures in Fig. 2 in this study. The detail of structure information is shown in Appendix. All-electron Kohn-Sham equations are solved by employing the projector augmented-wave (PAW) method [9] [10]. We select generalized-gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [11] form to the exchange-correlation functional. The plane-wave cutoff energy is set at 350 eV throughout the present calculations. Brillouin zone sampling is performed on the basis of the Monkhorst Pack scheme [12] with \( 4 \times 4 \times 4 \) k-point mesh and smearing parameter is 0.15 eV [13].

![Figure 2](https://via.placeholder.com/150)

**FIG. 2.** Composition of structural model. Further information are denoted in Appendix.

### 3. RESULTS AND DISCUSSION

We performed numerical simulation and selected SQS. Fig. 3 is simulated and ideal values of the correlation functions for each SQS. We calculated bulk modulus and formation free energy of these selected structures and evaluated thermodynamic stability.
To evaluate the effect of lattice vibration on phase stability of Mg-Y-Zn system, we calculated bulk modulus, which is shown in Fig. 4. Outlined marker represents linear averaged bulk modulus, $B_{\text{ave}}$, at a rate proportional to the composition. Bulk modulus for SQS models of 75, 87.5, and 93.75 at.% Mg are about 35 GPa. The values of bulk modulus are smaller than $B_{\text{ave}}$ through all compositions.

Bulk modulus does not show significant dependence of Mg concentration, which therefore means that the effects of phonon do not play essential role on LPSO phase stability. In this study, effects of optical mode for multicomponent system is not in consideration, so further study including optical mode is needed to clarify the effect of phonon for stability of Mg-Y-Zn alloys. Hereinafter, we consider only the configurational effect on stability.

Fig. 5 is formation free energy of pure Mg, A, B, D and E structures. At $T = 0K$, $F_{\text{form}}$ reached a maximum value at 87.5 at.% Mg and shifted to negative at all through composition at $T = 500K$. Through calculation of formation free energy of SQSs, Mg-Y-Zn alloy exhibits phase separation into Mg- and Y-Zn rich phase and this result is consistent with previous research by Iikubo et al. [2] and this suggests the validity of this simulation based on SQS.

To investigate the effect of stacking fault on the thermodynamic stability, we calculate free energies of hcp and fcc under ideal composition of 18R LPSO structure and structure introduced stacking faults in hcp stacking, which we call "mixed" structure. Fig. 6 is the formation energies of structures on different stacking (C1, C2, C3 in Fig. 2). Shown in Fig. 6, formation energy of disordered phase that is introduced stacking fault is lower than the arithmetic mean of energies of hcp stacking and fcc stacking. Accordingly, solid solution of Mg-Y-Zn alloy is shown to be thermodynamically stable with introducing stacking faults and it suggests that closely related with periodically introduced defects in LPSO structure.
4. CONCLUSION

In this study, we calculate preference of energetics of Mg-Y-Zn ternary alloy system based on SQS. Through calculation of formation free energy of SQSs, Mg-Y-Zn alloy exhibits phase separation into Mg- and Y-Zn rich phase and show thermodynamically stable with introducing stacking faults in fcc stacking. Bulk modulus for SQS models of 75, 87.5, and 93.75 at.% Mg are about 35 GPa and do not show significant dependence of Mg concentration, which therefore means that the effect of phonon does not play essential role on LPSO phase stability.

ACKNOWLEDGEMENT

This work is supported by a Grant-in-Aid for Scientific Research on Innovative Areas (26109710) from the Ministry of Education, Science, Sports and Culture of Japan.

[1] Y.Kawamura, K.Hayashi, A.Inoue and T.Matsumoto, Mater.Trans. 42, 1172 (2001).
[2] S.Iikubo, S.Hamamoto and H.Ohtani, Mater. Trans. 54, 636 (2013).
[3] H.Kimizuka, N.Fronzi and S.Ogata, Scripta Mater. 69, 594 (2013).
[4] J.Saal and C.Wolverton, Acta Mater. 68, 325 (2014).
[5] A.Zunger, Phys. Rev. Lett. 65, 353 (1990).
[6] K.Yuge, A.Seko, Y.Koyama, F.Oba, and I.Tanaka, Phys. Rev. B 77, 094121 (2008).
[7] G.Kresse and J.Hafner, Phys. Rev. B 47, R558 (1993).
[8] G.Kresse and J.Furthmuller, Phys. Rev. B 54, 11169 (1996).
[9] G.Kresse and D.Joubert, Phys. Rev. B 59, 1758 (1999).
[10] P.E.Blochl, Phys. Rev. B 50, 17953 (1994).
[11] J.P.Perdew, K.Burke, and M. Ernzerhof, Phys. Rev. Lett 77, 3865 (1996).
[12] H.J.Monkhorst and J.D.Pack, Phys. Rev. B 13, 5188 (1976).
[13] M.Methfessel and A.T.Paxton, Phys. Rev. B 40, 3616 (1989).

Appendix

Structure information

In this study, we calculated free energy and bulk modulus of structures shown in following data.

| Structure index (Mg,Y,Zn) (at.%) | number of atoms | stacking |
|----------------------------------|----------------|----------|
| A (93.75,3.125,3.125)            | 96             | hcp      |
| B1 (87.5,6.25,6.25)              | 96             | hcp      |
| B2 (87.5,6.25,6.25)              | 96             | fcc      |
| C1 (85.417,8.333,6.25)           | 96             | fcc      |
| C2 (85.417,8.333,6.25)           | 96             | fcc      |
| C3 (85.417,8.333,6.25)           | 240            | mixed    |
| D (75,12.5,12.5)                 | 96             | hcp      |
| E (50,25,25)                     | 96             | hcp      |
| F (85.417,8.333,6.25)            | 96             | including L12 cluster |

FIG. 6. The effect of stacking difference on stability

FIG. 7. Model of stacking sequence.