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Effect of 6.25 at% Al addition on structural stability of magnesium under high pressure: A first-principles study

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ABSTRACT

The structural stability of pure Mg and Mg–6.25 at% Al under hydrostatic pressures at zero temperature was investigated by employing first-principles total energy calculations. The results show that the adding Al leads to higher enthalpy of forming for all structures of Mg with the increase in the enthalpy for the bcc structure being the highest. The structural stability order does not get affected by the application of hydrostatic pressure. However, compared with pure magnesium, the magnesium with added 6.25 at% Al shows higher hcp → bcc phase transformation pressure point, but lower hcp → fcc pressure point.

1. Introduction

Magnesium has great potential in many important industrial fields, such as aerospace, automobile, computers and mobile communication, due to its low density, highly specific stiffness, excellent castability and easy recycling capability [1–7]. However, the comparatively poor mechanical performance has greatly obstructed its application in more important fields [8–10]. Addition of aluminum element has been proved to be an effective method to improve the mechanical properties of magnesium. Up to now, many Mg–Al system alloys such as AZ91, AZ71 and AZ61 have been developed.

It is well known that microstructure plays a critical role in determining the properties of materials and can be adjusted by means of structural phase transformation. High pressure can lead to the structural transformation of materials, and many previous studies have been focused on the structural stability of magnesium under high pressure. For instance, McMahan and Moriarty [11,12] predicted the possible sequence of structures hcp → bcc → fcc in magnesium by first-principle calculations and predicted a hcp to bcc transformation under 50 ± 6 GPa at zero temperature. These transformations has been confirmed by experimental or calculation methods [13,14]. The crystal structures of magnesium have been examined after adding Zn and Y atoms, which was studied by Datta et al. [15,16]. In addition, the influence of alloying Al and Li elements on the lattice parameters and mechanical properties of Mg have been studied [17,18]. However, the effect of adding aluminum atoms on the structural stability of magnesium under high pressure has not yet been examined.

In this paper, therefore, the structural stabilities for the hcp, bcc and fcc structures of magnesium with added 6.25 at% Al (chemical component similar to a typical Mg–Al system alloy – AZ71) and pure magnesium under hydrostatic pressures are studied by first-principles total energy calculations, respectively. The present work is expected to be beneficial to the further improvement of mechanical property for more widely use of magnesium alloy – Mg–Al series alloy.

2. Computational methods

The first-principle calculation is performed with the CASTEP code based on the density-functional and pseudopotential methods. Vanderbilt-type ultrasoft pseudopotentials [19] are employed to describe the electron–ion interactions. The exchange and correlation terms are described with generalized gradient approximations (GGA) in the scheme of Perdew–Burke–Eruzerhof (PBE) [20]. The geometric optimization of unit cell is carried out with the BFGS minimization algorithm [21] provided in this code.

The hexagonal-close-packed (hcp) structure belongs to hexagonal crystal system, space group *P*63/*MMC*, with cell parameter: $a = b = 3.20940$ Å, $c = 5.21050$ Å. The unit cell of the hcp structure of magnesium has two atoms. However, the primitive cells of the bcc and fcc structures of magnesium belongs to cubic crystal system, with the lattice constant $a = 3.10379$ Å and $a = 3.19872$ Å, and

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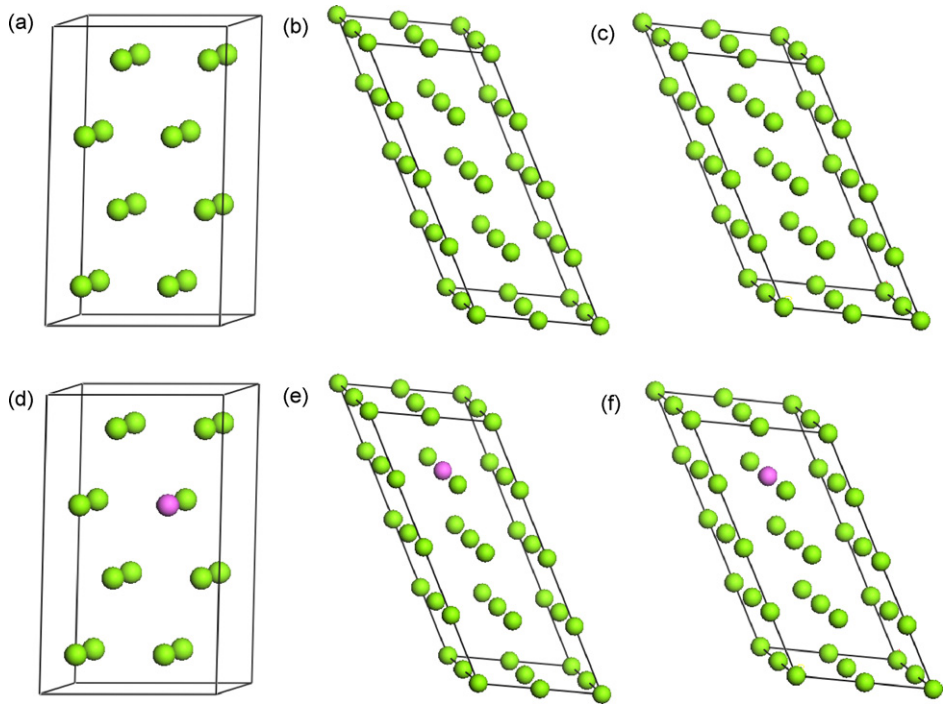

Fig. 1. Crystalline structure models of Mg and Mg–6.25 at% Al. (a) Hexagonal-close-packed of Mg. (b) Body-centered cubic of Mg. (c) Faced-centered cubic of Mg. (d) Hexagonal-close-packed of Mg–6.25 at% Al. (e) Body-centered cubic of Mg–6.25 at% Al. (f) Faced-centered cubic of Mg–6.25 at% Al.

space groups *IM*-3*M* and *FM*-3*M*, respectively. In order to study the effect of adding 6.25 at% Al atoms on the structures structural stability of pure magnesium under high pressure, calculations are performed with hcp structure of magnesium, using $2 \times 2 \times 2$ supercells, while, for the bcc and fcc structures of magnesium, using $2 \times 2 \times 4$ supercells. The hcp, bcc and fcc structures of pure Mg and Mg–6.25 at% Al are shown in Fig. 1. In order to confirm the convergence of our calculations, we investigate the total energy on the dependence on the energy cutoff from 280 eV to 600 eV. At last, we choose energy cutoff 450 eV, 400 eV and 400 eV for the hcp, bcc and fcc structure of magnesium, respectively. The *k*-point set mesh parameters are (6, 6,3), (8, 8, 4)and (10, 10, 5) respectively. Each calculation is considered to be converged when the maximum force on the atom is below 0.01 eV Å^{-1} and the maximum displacement between cycles is below 5×10^{-4} Å. The self consistent field (SCF) calculations are converged when the energy threshold is lower than 5.0×10^{-7} eV/atom.

In our work, hydrostatic pressure is applied to three structures of pure magnesium and magnesium with 6.25 at% Al added to investigate the effect of pressure on their structural stability. The geometry optimization is performed at a fixed value 200 GPa for the three structures.

3. Results and discussion

The ground state properties of the hcp, bcc and fcc structures of pure magnesium and magnesium with 6.25 at% Al added are investigated from their total energy. Meanwhile, the geometry optimization is performed for the crystal lattice constant and atomic coordinates of the three structures under hydrostatic pressures ranging from 0 GPa to 200 GPa. According to the calculation results, the calculated *P*–*V* dates are fitted to the third-order Birch–Murnaghan equation of state [22–24]. The corresponding equilibrium lattice constant a_0, bulk modulus B_0, and pressure derivative of bulk modulus B_0' for the hcp, bcc and fcc structure of magnesium with 6.25 at% Al added and pure magnesium at zero pressure are presented in Table 1.

Furthermore, we calculate the relative volume (v/v_0) at various pressures for the three structures of magnesium with 6.25 at% Al added and pure magnesium, as shown in Fig. 2. It can be seen that 6.25 at% Al addition leads to larger relative volume for three structures of magnesium and the increase in the relative volume for the bcc structure is the most, then followed by hcp and fcc structure. Therefore, we can conclude that the compressibility of three structures of magnesium with 6.25 at% Al added is poorer than magnesium's. The results are consistent with the B_0, which are fitted by the EOS. Obviously, the increase of strength for magnesium with 6.25 at% Al should be related with 6.25 at% Al addition, since aluminum can result in structural distortion of Mg crystal when dissolved in the pure Mg.

Moreover, the enthalpy for the three structures of Mg and Mg–6.25 at% Al under different pressures is shown in Fig. 2. The calculated results have shown that, under zero pressure, 6.25 at% Al addition leads to higher enthalpy for the hcp, bcc and fcc structures of magnesium. The enthalpy for the hcp, bcc and fcc structure increase 57.55314 eV/atom, 57.59124 eV/atom and 57.58781 eV/atom, respectively. Clearly, the increase in the enthalpy for the bcc structure is the most, then followed by the fcc and hcp structures. As the pressure becomes larger, the enthalpy for both pure magnesium and magnesium with added 6.25 at% Al increases. In this case, the average enthalpy increment for magnesium with 6.25 at% Al relative to that of the similar structure

Table 1
Calculated equilibrium lattice constants a_0, cell volume (V) and bulk modulus B_0 and B_0'.

Structure	a_0 (Å)	V (Å^3)	B_0 (GPa)	B_0' (GPa)
Mg–6.25 at% Al-hcp	6.471998	359.937027	37.95572	3.83900
Pure Mg-hcp	–	–	36.03834[a]	3.83117[a]
Mg–6.25 at% Al-bcc	7.109092	359.287916	37.35587	3.85234
Pure Mg-bcc	–	–	35.05696[a]	3.84977[a]
Mg–6.25 at% Al-fcc	9.305891	725.750354	36.70761	3.83202
Pure Mg-fcc	–	–	35.52171[a]	3.81513[a]

[a] Ref.[25].

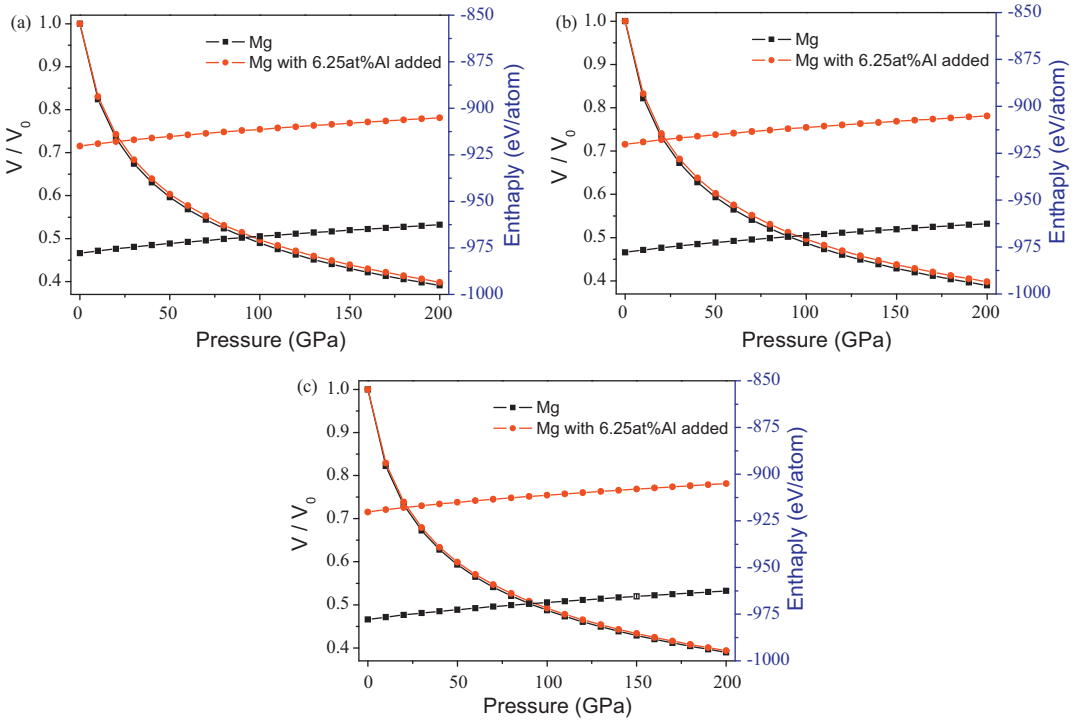

Fig. 2. The relative volume and enthalpy of three structures of magnesium and magnesium with 6.25 at% Al added as a function of pressure. (a) Close-packed hexagonal structure of Mg and Mg–6.25 at% Al. (b) Body-centered cubic structure of Mg and Mg–6.25 at% Al. (c) Face-centered cubic structure of Mg and Mg–6.25 at% Al.

of magnesium becomes 57.5125 eV/atom, 57.5229 eV/atom and 57.5055 eV/atom, respectively. The increase sequence of enthalpy is as follows: bcc > hcp > fcc, which is different from the case at zero pressure.

Furthermore, in order to investigate the effect of aluminum atoms on structural stability of magnesium under different pressure, based on the results shown in Fig. 2, the enthalpy differences (ΔH) for bcc and fcc structures relative to hcp are calculated and plotted in Fig. 3. As shown in Fig. 3, at zero temperature and under zero pressure, the hcp structure for pure magnesium and magnesium with added 6.25 at% Al should be the most stable structures due to its lowest enthalpy. However, the case becomes different with the pressure increasing. For magnesium, when the pressure becomes higher than about 65 GPa, the enthalpy for the bcc structure is lower than that for the hcp structure, implying that the transformation from hcp structure to bcc structure may occur. Similarly, the lower enthalpy for the fcc structure of magnesium

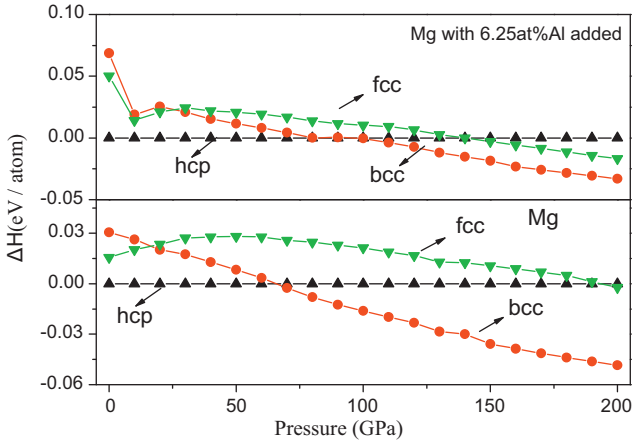

Fig. 3. Enthalpy different (ΔH) for bcc and fcc phase relative to hcp structure vs. pressure plot for magnesium and magnesium with 6.25 at% Al added.

at 190 GPa should also be considered a more stable structure in comparison to the hcp structure of magnesium. As for magnesium with 6.25 at% Al added, the phase transformation pressure for the hcp structure to bcc structure or to fcc structure is about 80 GPa and 140 GPa, respectively. Obviously, there exists similar phase transformation sequence for pure magnesium and magnesium having added 6.25 at% Al with the pressure increasing, indicating no evident effect of 6.25 at% Al addition on the structural stability sequence of magnesium. However, the 6.25 at% Al addition shows obvious impact on the phase transformation pressure point under which phase transformation of magnesium occurs. Compared with pure magnesium, the magnesium with added 6.25 at% Al shows higher hcp → bcc phase transformation pressure point, but lower hcp → fcc pressure point. This may be associated with the enthalpy increment for magnesium with 6.25 at% Al under high pressures. Just as mentioned above, the enthalpy for magnesium with added 6.25 at% Al becomes higher with the pressure increasing. The average enthalpy increment, however, is dependent upon the structure of magnesium. The increase in enthalpy for the bcc structure (57.5229 eV/atom) is more than that for the hcp structure (57.5125 eV/atom), implying that, compared with the case of pure magnesium, the phase transformation from the hcp to the bcc structure for magnesium with 6.25 at% Al will become more difficult, therefore, higher phase transformation pressure will be needed. Similarly, due to the more enthalpy increment for the hcp structure (57.5125 eV/atom) than that for the fcc structure (57.5055 eV/atom), it can be deduced that the phase transformation from the hcp to fcc structure of magnesium with 6.25 at% Al will become more easy. Therefore, this phase transformation for magnesium with 6.25 at% Al added will happen under a lower pressure than that for pure magnesium.

4. Conclusions

In order to study the effect of aluminum atoms on structural stability of magnesium, in this paper, the structural stability for

the hcp, bcc and fcc structures of pure magnesium and magnesium with added 6.25 at% Al under hydrostatic pressures at zero temperature are systematically investigated by first-principles total energy calculations based on the density-functional theory, respectively. The results have shown that, 6.25 at% Al addition leads to higher enthalpy for the hcp, bcc and fcc structures of magnesium, and, the increase in the enthalpy for the bcc structure is the most. As the pressure increases, the enthalpy for both pure magnesium and magnesium with added 6.25 at% Al increases. However, the sequence of increase in enthalpy for magnesium with added 6.25 at% Al becomes as follows: bcc > hcp > fcc, which is quite different from the case at zero pressure. In addition, there exists similar phase transformation sequence for pure magnesium and magnesium having added 6.25 at% Al with the pressure increasing, indicating no evident effect of 6.25 at% Al addition on the structural stability sequence of magnesium. However, the 6.25 at% Al addition shows obvious impact on the phase transformation pressure point under which phase transformation of magnesium occurs. Compared with pure magnesium, the magnesium with added 6.25 at% Al shows higher hcp → bcc phase transformation pressure point, but lower hcp → fcc pressure point. In addition, the equation of state of magnesium and magnesium with 6.25 at% Al added is calculated, indicating that the three structures of magnesium become harder with aluminum adding.

Acknowledgements

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