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Elastic properties of magnesium with virtual long-period stacking-ordered structure: First-principles study ☆

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ABSTRACT

The effect of virtual long-period stacking-ordered (v-LPSO) structures (6H, 10H, 14H, 18R and 24R) on the second order elastic constants and third order elastic constants of pure Mg are systematically investigated using first principles methods combined with finite strain theory. The predicted lattice constants and formation energies are in a good agreement with the available data. The pressure effect on anisotropy, Pugh ratio, Vickers hardness and Debye temperature are also presented. The anisotropy and Pugh ratio of 2H and v-LPSO Mg are not sensitive to pressure, except for 10H. The anisotropy of 10H increases with pressure, but Pugh ratio decreases. v-LPSO structures can only slightly improve the ductility of Mg. It is also found that 2H and 18R have nearly the same Pugh ratio and Vickers hardness.

1. Introduction

Magnesium alloys have become increasingly attractive in the fields of microelectronics, aerospace and automotive industries during the past two decades due to light weight and high specific stiffness. However, inherent limitations of strength and formability are obstacles to wider spread application of magnesium. Recently, ternary Mg–Zn–Y alloys have attracted considerable attention due to their excellent mechanical properties [1–7]. These rapidly solidified powder metallurgy Mg–Zn–Y alloys had high tensile yield strength (480–600 MPa), good elongation (5–16%) and good ductility [1]. The remarkable properties make Mg–Zn–Y alloys the promising candidate lightweight structural materials for ambient- and elevated-temperatures application. The further microstructure research indicated that a novel long period stacking ordered (LPSO) structure combined with fine precipitates plays a crucial role in improving the mechanical properties. Five typical LPSO structures (6H, 10H, 14H, 18R and 24R) in Mg–Zn–Y alloys have been revealed by various experiments [5–11]. Therefore, it is of vital importance to investigate the thermodynamic stability, mechanical properties, and inter-transformation mechanism of LPSO structures [8–11]. In order to elucidate these effects of LPSO structure, virtual LPSO (v-LPSO) models are constructed firstly by Fan et al. for pure Mg (denoted by 2H Mg due to the hexagonal structure and two atoms in unit cell) in accordance with experimental observations [12,13]. Iikubo et al. examined the transformation behavior in terms of temperature and lattice expansion by means of a first-principles calculation [5]. The results show that the substituted large atoms and temperature effect cooperatively generate LPSO structures. The deformation electron density of v-LPSO Mg are investigated by Wang et al. [14]. The electronic structure of v-LPSO are similar to that of deformation stacking fault. They articulate that transformation between LPSO structures is related to the reduction of dislocation density during heat treatment. Tane et al. calculated the elastic modulus of 18R v-LPSO structure Mg [6]. The results reveal that the elastic properties of 18R is almost the same as those of 2H Mg, which implies that the long periodicity of 18R type stacking structure hardly affects the elastic properties.

The purpose of the present study is to systematically examine the effects of v-LPSO (6H, 10H, 14H, 18R and 24R) structure on elastic properties of Mg using first-principles combined with finite strain theory. To benchmark the reliability of the presented method, we firstly calculate the lattice constants and formation energy of v-LPSO Mg. Later, the second order elastic constants (SOECs) and third order elastic constants (TOECs) are calculated for v-LPSO Mg. Based on the SOECs and TOECs, the Anisotropy, Pugh ratio, Vickers Hardness and Debye temperature under different are also presented.

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2. Computational method

2.1. Calculations of first-principles

First-principles calculations are performed using the VASP code based on the density of functional theory with the generalized gradient approximation (GGA) [15–17]. All calculations on 2H, 6H, 10H, 14H, 18R and 24R are carried out by using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation function, as implemented in VASP code [18,19]. The self-consistent converge is set to a value of 10^{-6} eV per atom on the total energy. Wave functions are expanded by the plane waves up to a cutoff energy of 500 eV for 2H Mg, the rest of LPSO structures is set at 400 eV. The convergence of the total energy with respect to both k-point sampling and plane-wave cutoff energy is carefully examined. In addition, for 2H–Mg, Brillouin-zone integrations are optimized by using the special k-point sampling of Monkhorst-Pack scheme with a $21 \times 21 \times 21$ grid k-point Monkhorst-Pack mesh for the lattice and elastic constants calculations. Further more, the k-point Monkhorst-Pack are set at $21 \times 21 \times 5$, $21 \times 21 \times 5$, $21 \times 21 \times 3$, $21 \times 21 \times 1$ and $21 \times 21 \times 1$ for 6H, 10H, 14H, 18R and 24R, respectively [20].

2.2. Finite-strain theory of elastic deformation

In this paper, finite-strain elastic theory combined with first-principles is used to calculate the elastic constants. Thurston and Wallace [21–24] have discussed this theory in details. α_i, stand for the initial coordinate of elements, after homogeneous deformation happened, its coordinate turn into $\chi_i = \chi_i(\alpha_j)$, deformation gradient of material strain is as follows

$$F_{ij} = \frac{\partial \chi_i}{\partial \alpha_j} \tag{1}$$

According to deformation gradient, Lagrangian strain tensor will be defined

$$\eta_{ij} = \frac{1}{2}\sum_k \left(F_{ki}F_{kj} - \delta_{ij}\right) \tag{2}$$

and η links a notation by

$$\eta = \begin{pmatrix} e_1 & \frac{1}{2}e_6 & \frac{1}{2}e_5 \\ \frac{1}{2}e_6 & e_2 & \frac{1}{2}e_4 \\ \frac{1}{2}e_5 & \frac{1}{2}e_4 & e_3 \end{pmatrix} \tag{3}$$

Lagrangian strain have symmetry, and it does not contain the information about the rigid rotation of material. Under the condition of constant entropy of elastic strain, the elastic constants can be defined as the Taylor series expansion of unit internal energy [21–23].

$$\rho_0 U\left(\eta_{ij}, S\right) = \rho_0 U(0,S) + \frac{1}{2}\sum_{ijkl} C^s_{ijkl}\eta_{ij}\eta_{kl} + \frac{1}{6}\sum_{ijklmn} C^s_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + \cdots \tag{4}$$

where ρ_0 is the initial mass density of material, and the initial state is assumed to be without pressure. Due to the rigid rotation, internal energy is unchanged. In terms of symmetry strain, the Taylor series expansion is appropriate, the expansion coefficient is the isentropic SOECs and TOECs

$$C^s_{ijkl} = \rho_0 \left.\frac{\partial^2 U}{\partial \eta_{ij}\partial \eta_{kl}}\right|_{\eta=0} \quad \text{(SOECs)} \tag{5}$$

$$C^s_{ijklmn} = \rho_0 \left.\frac{\partial^2 U}{\partial \eta_{ij}\partial \eta_{kl}\partial \eta_{mn}}\right|_{\eta=0} \quad \text{(TOECs)} \tag{6}$$

Similarly, under constant temperature, expansion the Helmholtz free energy of unit mass, can get isothermal elastic constants

$$\rho_0 F\left(\eta_{ij}, T\right) = \rho_0 F(0,T) + \frac{1}{2}\sum_{ijkl} C^T_{ijkl}\eta_{ij}\eta_{kl} + \frac{1}{6}\sum_{ijklmn} C^T_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn} + \cdots \tag{7}$$

In the first-principle calculation, the isothermal elastic constants will be calculated. In computing, the temperature set at 0 k, so we can get

$$F\left(\eta_{ij}, T = 0K\right) = U\left(\eta_{ij}, T = 0K\right) \tag{8}$$

In the finite-strain theory of elastic deformation, the elastic constants can completely describe the elastic response of solid. For the elastic constants of hexagonal cubic primitive, special strain tensors have to be introduced. And the none-zero partial of each strain tensor are presented by the same constant ξ. From Eq. (4), the relation between elastic energy and strain constant is as follows [24]

$$\rho_0[U(\xi), U(0)] = \frac{1}{2}A_2\xi^2 + \frac{1}{6}A_3\xi^3 + O(\xi^4) \tag{9}$$

where $U(0)$ is the initial energy, A_2 and A_3 are closely connected with the SOECs and TOECs (see [24]). As we know, the lattice symmetry is associated with the number of independent elastic constants, and the higher symmetry, the less the number of independent elastic constants. For HCP structures, there are six independent SOECs and ten independent TOECs. To obtain these SOECs and TOECs, use the relation between fitting coefficient A_2, A_3 and elastic constants, establish a series of equations, through the establishment of system of linear equations to solve. In order to get effective system of linear equations, at least to choose the number of strain tensor same as the number of independent elastic constants. In this work, ten necessary strain tensors η_{ij} will be used see [24].

3. Results and discussion

3.1. Lattice constants and formation energy

Before the calculation of elastic constants, the lattice constant have to be optimized. The structures of 2H and v-LPSO Mg are shown in Fig. 1. Both 2H and v-LPSO structure Mg have the hexagonal structures [5]. There are 6 atoms, 10 atoms, 14 atoms, 18 atoms and 24 atoms for each unit cell of 6H, 10H, 14H, 18R and 24R, respectively. The lattice constants obtained by first-principles calculations are listed in Table 1. As shown in Table 1, the lattice constants are well in agreement with previous results

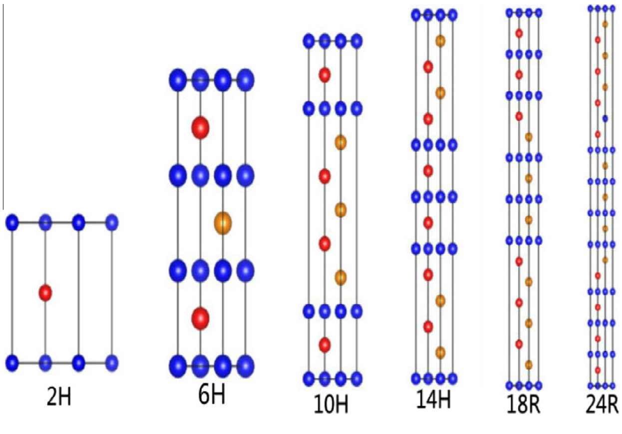

Fig. 1. Crystal structure of 2H and v-LPSO structure Mg.