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Effect of anti-site point defects on the mechanical and thermodynamic properties of $MgZn_2$, $MgCu_2$ Laves phases: A first-principle study

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ABSTRACT

A theoretical investigation on the effect of anti-site point defects on mechanical and thermodynamic properties of $MgZn_2$ and $MgCu_2$ based on the first-principles calculations has been implemented. The results show that Mg anti-site defect on Zn or Cu site plays a reinforcing role, while exhibiting a more brittle behavior. However, the defect phase of Cu anti-sites on Mg sublattice shows a ductile tendency. The temperature-dependent thermodynamic properties are also predicted along with Debye-Grüneisen model including Debye temperature, thermal expansion coefficient and vibrational heat capacity as well as vibrational entropy. Taking into account the contribution of the lattice vibration and thermal electronic excitations, the Helmholtz free energy F can be calculated, suggests that anti-site defects caused by the occupancy of Mg at the Zn or Cu site are thermodynamically unstable compared to the defect-free phases. In addition, the total amount of charge transfer, the overall and the local difference charge densities are further discussed to analyze the mechanism of mechanical properties.

1. Introduction

The Laves phase $MgZn_2$ with hexagonal structure C14 is the most important strengthening phase in the Mg-Zn alloys, but its range of application is limited due to its low ductility and brittle fracture at room temperature [1,2]. By adding copper to the magnesium alloys form $MgCu_2$ structure, which is a face-centered C14 type Laves phase can effectively improve the ductility of magnesium alloys [3]. But the stoichiometry of Laves phase often correlates with the original point defects, and the point defects can seriously affect the mechanical and functional properties of Laves phase [4].

The native point defects of ternary C14 Laves phase Mg_2Cu_3Si has been suggested that the local distortions around point defects increase from Si_{Cu} to Si_{Mg}, showing that the polyhedral symmetry and coordination number for constituent atoms will affect the structure of defects [5]. The point defect structures of C15 $ZrCo_2$ Laves phase were investigate by JH. Zhu [6], and constitutional anti-site defects were found in Co-rich off-stoichiometric sides. Ni_{Al} is the most important anti-site defect in Ni_3Al alloy, and Al-site is the most easily formed defect, Nb preferentially occupies the Al lattice in Ni_3Al, and the addition of Nb atoms can improve the stability of Ni_3Al [7,8]. For instance, the typical point defect in C14 $MgZn_2$ Laves phase has been suggested that the Mg anti-site on Zn_2 site under strong Mg-rich condition is energetic, which exhibits the lowest defect formation energy [9]. M. Andersson et al. [10] calculated the vibrational free energy and the chemical mixing entropy of the four possible point defects of C14 $MgZn_2$ at 790 K, and the result was consistent with the investigation of the above. Base on first-principles study, Jie Zheng et al. [11] found the dominating defect structure Mg_{Cu} and Cu_{Mg} antisite defect on Mg-rich and Cu-rich side of off-stoichiometry, respectively. However, the effect of point defect structure of off-stoichiometry in Laves phase C15 $MgCu_2$ and C14 $MgZn_2$ has not been reported by theoretically so far. So it is valuable to investigate the effect of point defects on the mechanical and thermodynamic properties of $MgCu_2$ and $MgZn_2$ phases.

Due to the dense arrangement of two constituent elements of the typical binary Laves phase AB_2 in space, the interstitial point defects do not exist [11]. In C14 $MgZn_2$, the Zn_1 and Zn_2 atoms located at Wyckoff position 2a and 6 h sites, respectively, so four different defect structures are possible on Zn sublattices: two vacancy defects denoted as V_{Zn1} and V_{Zn2}, and two anti-site defects are Mg_{Zn1} and Mg_{Zn2}. On Mg sublattice two types of point defects represented as V_{Mg} and Zn_{Mg}. For C15 $MgCu_2$ phase, Mg atoms located at Wyckoff position 8b, and Cu atoms at Wyckoff position 16c, so there are four possible point defects, which are Mg_{Cu} for Mg antisites on Cu sublattice, Cu_{Mg} for Cu antisites at Mg position, Mg vacancy V_{Mg} and Cu vacancy V_{Cu}. In view of the Mg anti-site on Zn_2 site Mg_{Zn2} (Mg_5Zn_7) under strong Mg-rich condition has the lowest formation energy [9], Mg_{Cu} ($Cu_{15}Mg_9$) and Cu_{Mg}

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($Cu_{17}Mg_7$) are energetic with the lowest formation energy and compound formation enthalpies in $MgCu_2$, which indicates these defects are most likely to exist in magnesium alloys [11].

Atomistic-scale computational techniques provide a powerful means for exploring, comparing the difference in the properties of materials [12]. The Debye-Grüneisen model [13] is used in this paper because it has been used to describe the behavior of the vibrating lattice and to explain the anharmonic effect [14], and quasi-harmonic Debye model [15] is widely used to predict the thermodynamic properties of materials [16–18]. Thus, in this work, based on density function theory (DFT), the first-principle calculations are performed to systematically compare the mechanical and thermodynamic properties of point defect structure Mg_5Zn_7 ($Cu_{15}Mg_9$, $Cu_{17}Mg_7$) with perfect phase $MgZn_2$ ($MgCu_2$). Finally, the electronic structure has been further deeply studied as a potential mechanism to explore the causes of changes in the mechanical properties.

2. Computational details

In this study, all the phases namely, Mg_5Zn_7, $MgZn_2$, $Cu_{15}Mg_9$, $Cu_{17}Mg_7$, and $MgCu_2$ have been calculated by using the first-principles method on the basis of the density functional theory (DFT) method as implemented in VASP (Vienna Ab-inito Simulation Package) [19] software package. The electronic exchange–correlation energy is determined by using the generalized gradient approximation of Perdew–Burke–Ernzerh (GGA–PBE) [20,21]. Pseudoatomic calculations are performed for Mg $3s^2$, Zn $3d^{10}4p^2$ and Cu $3d^{10}4p^1$. All phases are relaxed with respect to degrees of freedom including position, cell shape, and cell volume using a convergent energy cut-off of 380 eV for Mg_5Zn_7 and $MgZn_2$ with $7 \times 7 \times 4$ k-points within Gamma-centered Monkhorst-Pack scheme [22], and 400 eV for $Cu_{15}Mg_9$, $Cu_{17}Mg_7$, and $MgCu_2$ with $8 \times 8 \times 8$ k-points, which are significantly higher than the VASP defaults. The electronic iterations convergence is 1.0×10^{-5} eV using the Normal (blocked Davidson) algorithm and reciprocal space projection operators. Using first order Methfessel-Paxton smearing with a width of 0.2 eV [23]. Elastic properties calculation using a strain of 0. 5%, and the convergence criterion is 0.02 eV/Å for the atom positions will be relaxed in structures where the atoms are not fixed by symmetry.

3. Results and discussion

3.1. Mechanical properties

As we know that the elastic constants are among the most fundamental properties of materials, they can be used to measure the resistance of a crystal to an externally applied stress and also provide the information about the bonding characteristic [24]. The calculated equilibrium lattice constant of $MgCu_2$ is 7.041 Å, which is in accordance with the available data 7.051 Å of experimental measurement [25] and theoretical calculation of 7.065 Å [26], and a = 5.195 Å and c = 8.518 Å for $MgZn_2$ are comparable to experimental measurement of a = 5.223 Å and c = 8.580 Å [27]. Therefore, the computational method and the design conditions for phases selected in the paper should be suitable.

Elastic constants can be obtained by calculating the total energy as a function of strain [28]. Using the Voigt-Reuss-Hill (VRH) approximation [29–31], bulk modulus (B), Young's modulus (E), and shear modulus (G) are calculated. In addition, G/B [32,33], the general anisotropy index A^U based on Ranganathan's formula [34] and Poisson's ratio (υ) are calculated for all phases, as shown in Table 1. It can be clearly seen that the current results are in good agreement with other previous theoretical results for $MgZn_2$ and $MgCu_2$ phases.

For defect phase Mg_5Zn_7, the large size of Mg atom replaces Zn_2 atom, making a degree of the lattice distortion, this result is consistent with the investigation of Ref. [9] where the distances of Mg_{Zn2}-Zn and Mg_{Zn2}-Mg become longer, implying the nearest neighbor Zn and Mg atoms are away from the Mg anti-site atom. Lattice distortion produces solid solution strengthening [37]. And the bulk modulus B, shear modulus G, and Young's modulus E of Mg_5Zn_7 increase, implying the strength increases and is greater than $MgZn_2$ but its ductility decreases. These are consistent with the reduced results of B/G (the B/G ratio is an indicator that provides a rough estimation of the intrinsic ductility/brittleness of a material, the critical value of B/G is about 1.75, if $B/G > 1.75$, the material is expressed in ductility, otherwise the material is brittle [32,33]), A^U (elastic anisotropy could predicate the mechanical durability of materials [38]) and Poisson's ratio υ (A low value of Poisson's ratio υ implies a brittleness tendency [39]). However, the results for $MgCu_2$ and its corresponding two kinds of anti-site point defects are not the same. For $Cu_{17}Mg_7$, it shows better ductile nature than $MgCu_2$ by comparing calculated data, while $Cu_{15}Mg_9$ shows the opposite. Because mechanical parameters for anti-site defects may be related to the electronic structure, one may go beyond the simple atomic size effects in determining the mechanical properties of defective $MgCu_2$, so study of electronic structure is necessary.

Table 1
Calculated bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa) derived from the Voigt-Reuss-Hill approximation, G/B, anisotropy index A^U and Poisson's ratio υ as well as Debye temperature Θ_D (K) for all phases at 0 K.

Phase		B	G	E	B/G	A^U	υ	Θ_D
$MgZn_2$	Present	65.43	22.26	59.96	2.94	0.41	0.35	272.2
	Cal.	59.20[a]	19.00[a]	51.40[a]	3.12[a]	–	0.35[a]	250.6[a]
Mg_5Zn_7	Present	45.20	27.53	68.64	1.64	0.57	0.25	311.7
$MgCu_2$	Present	89.63	39.82	104.04	2.25	0.32	0.31	358.4
	Cal.	98.59[b]	35.73[b]	95.64[b]	–	–	0.32[b]	341.6[b]
$Cu_{15}Mg_9$	Present	103.60	46.78	122.03	2.21	0.23	0.30	396.5
$Cu_{17}Mg_7$	Present	83.19	35.87	94.09	2.32	0.86	0.31	334.1

[a] Reference [35].
[b] Reference [36].

3.2. Thermodynamic properties

Debye temperature (Θ_D) can be used to describe the strength of the covalent bond of solid matter, a high Θ_D value associates with strong covalent bond. The Θ_D can be calculated from elastic constants by using the average sound velocity (υ_m) according to the following equation [40]:

$$\Theta_D = \frac{h}{k_B}\left(\frac{6\pi^2 q}{V_0}\right)^{1/3} \quad (1)$$

where q is the number of atoms in the unit cell, V_0 its volume, and h and k_B are the Planck and Boltzmann constants, respectively. It follows that there is a stronger covalent bond in Mg_5Zn_7 and $Cu_{15}Mg_9$ than the perfect phases, but $Cu_{17}Mg_7$ is the opposite, as shown in Table 1.

Through the Debye-Grüneisen model to maintain the Grüneisen constant γ_G [13] is 2, thermal expansion coefficient (α_L) and vibrational heat capacity at constant volume C_V (both thermodynamic properties ignore the electronic contribution to heat capacity) as a function of temperature can then be calculated the following equations [41]:

$$\alpha_L(T) = \frac{1}{3}\gamma_G \frac{C_V(T)}{B \cdot V_0} \quad (2)$$

$$C_V(T) = 9qk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{x_D} \frac{x^4}{(exp(x)-1)^2}dx \quad (3)$$

where $x_D = \Theta_D/T$ [42]. The vibrational heat capacities of Mg_X anti-site defects Mg_5Zn_7 and $Cu_{15}Mg_9$ are higher than the vibrational heat capacity of its corresponding defect-free phase, as shown in Fig. 1, but the result is the opposite for $Cu_{17}Mg_7$ –Cu anti-sites on Mg sublattice. Vibrational heat capacities increase rapidly when temperature below

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