



The native point defects in C14 Mg₂Ca Laves phase: A first-principles study



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ABSTRACT

The native point defects in C14 Mg₂Ca Laves phase are studied from the first-principles density functional theory calculations within GGA approximation. The defect formation energies indicate that anti-site defects are energetically favored over vacancies. Under Mg-rich and even general Ca-rich condition, defect Mg_{Ca} of Mg anti-site on Ca sublattice is favorable owing to the lowest formation energy. The Ca_{Mg2} defect of Ca anti-site on Mg₂ sublattice is also likely dominant only under extreme Ca-rich environment. The present results could explain reasonably the asymmetric off-stoichiometry of Mg₂Ca. The effective point defect concentrations of Mg₂Ca as a function of composition and temperature at experimental range are also calculated from a canonical statistical model, and the derived results show a linear relationship between the logarithm of defect concentration and T^{-1} . Geometrical factor is further studied, and it is found that atomic size possesses an obvious influence on the structure of point defect in Mg₂Ca. The electronic feature is further studied to reveal underlying mechanism for formation of point defects.

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1. Introduction

In recent years, Mg-based alloys as structure materials are increasingly applied to the automotive and aircraft industry due to low densities, good stiffness and high specific strength [1–3]. However, applications of Mg-based alloy in modern industry are still limited significantly because of the restrained properties at high temperature, especially the inferior creep, corrosion, ignition resistance, and the limited tensile strength [4–6]. Therefore, much effort has been devoted to improving the mechanical properties of Mg-based alloys.

Addition of alloying elements is found to be one of the most effective ways to improve mechanical properties of Mg-based alloys. Ca is an inexpensive and lightweight alternative to rare-earth elements for improving the ignition-proof properties of Mg-based alloys, and could be utilized for precipitation hardening through formation of the Mg₂Ca phase [7,8]. Due to the good oxidation and combustion resistance, Mg–Ca alloy has attracted great attention.

Especially, C14 Laves phase Mg₂Ca alloy as an excellent strengthening phase has been the research focus in Mg–Ca alloy. So far, numerous theoretical and experimental investigations of mechanical, electronic and thermodynamic properties of Mg₂Ca Laves phase have been performed [9–12]. On the other hand, Mg-based Laves phase as one class of typical intermetallic is extremely attractive both scientifically and technologically because of high-melting, high strength, good creep and oxidation resistance, and other excellent mechanical properties, so Mg-based Laves phase is very crucial in many practical applications, and exhibits the bright prospect in future [13–16].

Many Laves phases are off-stoichiometric and exhibit some range of homogeneity on either the A-rich or B-rich side of stoichiometry [17], the off-stoichiometry is closely related to the constitutional point defects. It is important to understand the constitutional defect structure in the compounds, because the point defect may strongly affect the physical, mechanical and functional properties, and has a decisive impact on their performance in application [18,19]. For example, the existence of vacancies in the Laves phase could assist the synchroshear deformation and enhance the toughness of Laves phases [16]. Also, off-stoichiometry in Laves phase is found to affect the hydride

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stability of ZrMn₂ [20] and hydrogen storage capability of TiMn₂ alloy [21]. Although literatures have reported that in C14 Laves phase NbFe₂ [22] the anti-site defects were dominant on both sides of the stoichiometric composition, the point defect structures in hexagonal C14 Laves phase associated with the deviation from stoichiometry are far from the complete understanding.

Suzuki et al. [23] showed that Mg₂Ca Laves phase contains 68.2 at.% Mg at 773 K based on the phase analysis by electron-probe microanalysis (EPMA) and X-ray diffraction, demonstrating Mg-rich off-stoichiometry in Mg₂Ca Laves phase. Up to now, no theoretical work has been conducted to carefully study off-stoichiometry and point defects in the Mg₂Ca Laves phase. Especially, point defect structure is closely connected to the structural and mechanical properties of Laves phase. Hence, the study of point defects in Mg₂Ca Laves phase is necessary and important.

The main aim of this work is to investigate point defect structures in Mg₂Ca Laves phase. The formation energy of point defect in Mg₂Ca is obtained from first-principles calculations, and the concentration of point defect as a function of composition and temperature is also derived. Furthermore, we also discuss the effect of atomic size and the electronic structure on formation and structure of native point defects in Mg₂Ca.

2. Computational method

The first-principles calculations were performed by using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [24]. The Perdew-Wang (PW91) version of the generalized gradient approximation (GGA) [25] was used to describe the exchange-correlation energy functional and the projector augmented wave (PAW) potentials [26] have been used in this present work. The cutoff energy of plane wave was set at 300 eV for all the calculation. The present study adopted a $2 \times 2 \times 1$ supercell, and the Brillouin zone integration was sampled by the Gamma-centered Monkhorst-Pack scheme [27] of a $5 \times 5 \times 7$ k-points for optimizing geometry and calculating the energy, and $7 \times 7 \times 9$ k-points for calculation of the density of states. In order to obtain a precise crystal structure, shape and internal atoms coordinate were optimized by full relaxation, until Hellman-Feynman forces on each atom was less than 0.01 eV/Å, the maximum stress on the atom was 0.02 GPa. The total energy calculations were performed using the linear tetrahedron method with the Blöchl correction, and the calculated total energy was converged to less than 10^{-5} eV/atom.

3. Results and discussion

3.1. Structural parameters of perfect Mg₂Ca

The C14 Laves phase Mg₂Ca crystallizes in hexagonal structure with space group $P6_3/mmc$ (No.194) and highest symmetry D_{6h}^4 . The unit cell contains 12 atoms, 8 Mg atoms on Wyckoff position 2a (Mg1) and 6h (Mg2), and 4 Ca on 4f site. In this work, the unit cell of Mg₂Ca Laves phase is at first optimized, the obtained lattice parameters of $a = 6.2358$ Å and $c = 10.1038$ Å are in good agreement with the experimental [28] and other calculated values [29,30]. Good agreement shows reasonability of chosen parameters and reliability of the present calculation results.

3.2. Formation energy of point defect

The formation energy of a point defect is calculated according to the ab initio thermodynamic approach by the following equation [18,31–33]:

$$E_f = E_{total}(defect) - E_{total}(perfect) - \sum_i \Delta n_i \mu_i \quad (1)$$

where $E_{total}(defect)$ and $E_{total}(perfect)$ are respectively the total energy of the defected and perfect supercell, n_i indicates the number of atoms i that is added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell when the defect is created, and μ_i is the corresponding chemical potential of atom, which represents the energy of the reservoir with which atoms are being exchanged. Because the point defect formation energy depends on the chemical potential of atom, it is very important to define reasonable bound on the chemical potential and investigate the defect formation energy within those limits.

The chemical potentials are constrained by equilibrium condition and by the requirement of no appearance of secondary unwanted phases. In the state of equilibrium, the chemical potentials for Mg and Ca atoms in solid phase Mg₂Ca should be equal to ones in reservoirs. Thus, to maintain a stable Mg₂Ca compound at equilibrium condition, the chemical potentials should satisfy the following equation:

$$2\Delta\mu_{Mg} + \Delta\mu_{Ca} = \Delta H_f(Mg_2Ca) \quad (2)$$

$\Delta\mu_{Mg}$ and $\Delta\mu_{Ca}$ are the relative chemical potentials for Mg and Ca (using the energy of an atom in elemental solid as reference), denoted as: $\Delta\mu_{Mg} = \mu_{Mg} - \mu_{Mg}^0$ and $\Delta\mu_{Ca} = \mu_{Ca} - \mu_{Ca}^0$. Here μ_{Mg}^0 and μ_{Ca}^0 are the chemical potential of pure metal Mg and Ca, respectively. The $\Delta H_f(Mg_2Ca)$ in Eq. (2) is the formation enthalpy of one formula unit for Mg₂Ca in solid phase, and the calculated formation enthalpy of Mg₂Ca is about -0.3933 eV/f.u. To avoid the occurrence of precipitate of element solid Mg and Ca, the chemical potential of every atom need to be less than the chemical potential of element solid [34], which gives $\Delta\mu_{Mg} \leq 0$ and $\Delta\mu_{Ca} \leq 0$.

Meanwhile, atoms Mg and Ca in reservoirs may also form secondary unwanted phases. Because four intermetallic phases including Mg₃Ca, Mg₂Ca, MgCa and MgCa₃, are contained in Mg–Ca system [35], Mg₂Ca would equilibrate with Mg₃Ca under the Mg-rich condition, and under the Ca-rich condition Mg₂Ca is equilibrated with MgCa. For avoiding the occurrence of these compounds, the chemical potentials must also be bounded by

$$\begin{aligned} 3\Delta\mu_{Mg} + \Delta\mu_{Ca} &\leq \Delta H_f(Mg_3Ca) \\ \Delta\mu_{Mg} + \Delta\mu_{Ca} &\leq \Delta H_f(MgCa) \end{aligned} \quad (3)$$

With the formation enthalpies computed from first principles, valid ranges of chemical potentials for Mg and Ca can be determined by the above equations, so the defect formation energies of various point defects are further derived.

Since Laves phases have topological close-packed structure and space-filling is relatively dense, there are no interstitial sites with a size comparable to that of the component atoms, so interstitial defects can be excluded. Therefore, the possible defects in binary Laves phases include only constitutional vacancy and anti-site substitution. According to the structural feature of Mg₂Ca Laves phase, six types of point defects are considered here: Mg vacancies and Ca anti-site defects formed on the Mg lattice sites which are denoted respectively as V_{Mg1} , V_{Mg2} and Ca_{Mg1} , Ca_{Mg2} , and the V_{Ca} and Mg_{Ca} formed on the Ca lattice sites.

The calculated formation energies of above six types of point defects are shown in Fig. 1. It is found that the defect formation energy of Mg_{Ca} is much lower than V_{Ca} over the whole range under Mg-rich condition. Under the Ca-rich condition, the defect formation energies of Ca_{Mg1} and Ca_{Mg2} are also lower than V_{Mg1} and V_{Mg2} . It is noted that under Mg-rich even general Ca-rich condition, the calculated defect formation energy exhibits that the Mg_{Ca} is most

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