Atomic structure, stability and electronic properties of S(Al$_2$CuMg)/Al interface: A first-principles study

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ABSTRACT

Interfacial models of Al$_2$CuMg/Al were investigated by first-principles calculations based on density functional theory. Two types of Al$_2$CuMg(001)/Al(021) interface structures were investigated in consideration of two different terminations for Al$_2$CuMg(001) surface (Al-terminated and CuMg-terminated). The interaction of interfaces was analyzed by the optimized atomic structures. The ideal work of adhesion (W$_{ad}$) of the Al$_2$CuMg (001)/Al(021) interfaces was also calculated. The results show that the interface model with CuMg-terminated is more stable than that of Al-terminated. It is also demonstrated from the values of interfacial energy (γ_{int}) that the CuMg-terminated interface is more thermodynamically stable. The calculated electronic properties, including charge density distribution and density of states, reveal that there is a significant hybridization among the interfacial Cu 3d, Mg 3p and Al 3p states. It is the main reason why CuMg-terminated interface is more stable.

1. Introduction

S phase (Al$_2$CuMg) in Al series alloy has been considered as one of the most important strengthening precipitates, which has been attracted attention and investigated extensively in recent years [1,2]. There are extensive experimental and theoretical investigations on its crystal structure [3], morphology [4], growth kinetics [5] and strengthening mechanisms [6]. Interestingly, it is observed from experiments that Al$_2$CuMg phase are formed in two ways: discontinuous precipitation and continuous precipitation.

Discontinuous precipitation occurs usually on grain boundaries. In cast Al−Zn−Mg−Cu alloy, it is observed that the Al$_2$CuMg phase are directly formed during solidification process and grew along the grain boundaries at the medium temperature range (from 350 °C to 450 °C) [7,8]. In order to dissolve the coarse Al$_2$CuMg phase, which is greatly influenced on the strength and stress corrosion resistance of alloy, homogenization treatment is needed. During homogenization treatment, the phase transformation of the solid solution Mg(Zn,Cu,Al)$_2$→Al$_2$CuMg is observed at high temperature [9]. Liu et al. [10] proposed that this phase transition was very difficult when Zn content was higher than 8% (mass fraction). Unfortunately, the crystallographic orientation relationships between Al$_2$CuMg phase and Al matrix are few observed in this system.

However, the continuous precipitation sequence in Al−Cu−Mg alloys is widely reported to be: supersaturated solid solution (SSS)→GP I zone→GP II zone→materstable S'→stable S [11]. The Al$_2$CuMg phase has a laths-shaped morphology as along ⟨100⟩$_{Al}$ with {012}$_{Al}$ habit [12]. According to early investigation [13], three kinds of crystallographic orientation relationships between Al$_2$CuMg phase and Al matrix are proposed as follow: [100]$_S$//[100]$_{Al}$, [001]$_S$//[021]$_{Al}$, and [010]$_S$//[01$\bar{2}$]$_{Al}$. Later, Radmilovic et al. [14] observed two types of Al$_2$CuMg/Al interfaces by using quantitative high resolution electron microscopy: (001)$_S$//(021)$_{Al}$ and (043)$_S$//(021)$_{Al}$.

It is well known that the interfaces between precipitate phase and matrix play an important role in the room temperature toughness and the high temperature strength of alloys [15]. Therefore, it is worthwhile to explore the atomic structure and chemical bonding of the Al$_2$CuMg/Al interfaces in order to understand exactly the strength mechanism of Al alloys. However, it is still difficult to gain systematic information of Al$_2$CuMg/Al interface from the experiments.

Recently, the first-principles method has been successfully performed to evaluate the interface properties between Al matrix and ceramic or precipitate [16–18]. It is of great significance to reveal interface behavior (i. e. interface stability, adhesion strength, atomic bonding) of Al matrix and ceramic or precipitate. To date, there are few experimental and theoretical methods are available to quantitatively

investigate Al_2CuMg/Al interface behavior from atomic level point of view.

In the present work, the $Al_2CuMg(001)/Al(021)$ interface was chosen as our research objective. We mainly concentrate on the atomic structure, stability and electronic properties of the Al_2CuMg/Al interface by using the first-principles method for a better understanding of the mechanisms responsible of Al_2CuMg phase in Al matrix.

2. Calculation method

In this paper, we investigated the Al_2CuMg/Al interface by using the first-principles total energy program CASTEP (Cambridge Serial Total Energy Package) within the framework of density functional theory [19]. The plane-wave ultra-soft pseudopotential method was used to describe the interactions between ionic core and valence electrons [20]. Electron exchange and correlation were treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerh (PBE) functional [21]. In the present calculations, the plane wave cutoff energy was chosen to be 400 eV. Integrations in the Brillouin–zone were performed using special *k* points generated with Monkhorst–Pack mesh [22]. The Pulay scheme of density mixing was applied for the evaluation of energy and stress [23]. The Brodyden–-Fletcher–Goldfarb–Shanno (BFGS) minimization scheme was employed for geometry optimization to complete the relaxation of atoms in supercells [24]. The calculation of total energy and electronic structure were followed by cell optimization with self consistent field (SCF) tolerance of 5.0×10^{-7} eV/atom. The maximum ionic displacement was set at 5×10^{-4} Å and maximum stress within 0.02 GPa. A convergence criterion of 0.01 eV/Å was used for the maximum ionic Hellmann-Feynman force. For calculation of the electronic density of states (DOS), we used the linear the tetrahedron Blöchl method with corrections [25].

3. Results and discussion

3.1. Bulk properties

In order to assess the accuracy of our computational method, a series of calculations on the bulk properties of Al and Al_2CuMg are performed. Table 1 lists the calculated values for each material, together with the available data from experiments and other calculations. The calculated lattice constant for bulk face centered cubic (fcc) Al is a = 4.047 Å, which agrees well with the experimental value (4.050 Å) [26] and other theoretical value [27]. Meanwhile, the plane spacing of Al(021) is 0.905 Å, which is agreed with those determined by the experiments [14]. The deviations from first-principles calculation are in the reasonable range of computational errors.

As shown in Fig. 1 (a) and (b), Al_2CuMg phase crystallizes in the

Table 1
Comparison of lattice parameters and bulk modulus between calculations and experiments for bulk Al and A_2CuMg.

Bulk	Method	Lattice parameters (Å)			Bulk modulus (GPa)
		a	*b*	*c*	
Al	Present	4.047	–	–	78.43
	Experiments	4.050[a]	–	–	79.00[b]
	Calculations	4.050[c]	–	–	77.32[d]
A_2CuMg	Present	4.028	9.338	7.131	72.57
	Experiments	4.012[e]	9.265[e]	7.124[e]	–
	Calculations	4.050[f]	9.279[f]	7.206[f]	75.210[f]

[a] Ref. [26].
[b] Ref. [31].
[c] Ref. [27].
[d] Ref. [32].
[e] Ref. [28].
[f] Ref. [29].

orthorhombic BRe_3-type structure with space group *Cmcm* (No. 63). For orthorhombic Al_2CuMg phase, the calculated lattice constants are a = 4.028 Å, b = 9.338 Å and c = 7.131 Å, which are also in good agreement with the experimental and other theoretical values [28,29]. In addition, our calculated formation energy for Al_2CuMg (−16.5 kJ/mol) is slightly higher than other calculated value (−19.5 kJ/mol) [30]. These results show that the adopted parameters in our calculations can ensure enough precision to conduct the subsequent calculations.

Fig. 2 shows the total and partial density of state (DOS) of Al_2CuMg phase, where the Fermi level is set as the origin of the energy scale. It can be seen that the region from −10 eV to Fermi level is mainly composed of the hybridization of Al 3p and the delocalized Cu 3d states with some Mg 2p states, constituting the bonding states below the Fermi level. The finite DOS value at the Fermi level implies metallic nature, suggesting strong covalent character. Antibonding levels above the Fermi level are mainly the hybridization of Al 3p and Mg 2p. Our calculated results are also consistent with other calculated results [29].

3.2. Surface properties

The Al(021) surface was modeled by a slab of 3–11 atomic layers separated by a vacuum region of 15 Å. The 2×2 supercells with $12 \times 6 \times 2$ Monkhorst–Pack k-points in the Brillouin zone were used to calculate the Al(021) surface in this work. The unit cell of Al_2CuMg is stacked with atomic layers along the *c* direction in the following order: ABAABA (A and B denote Al-terminated and CuMg-terminated layers, respectively). Therefore, there are two kinds of surfaces for Al_2CuMg (001): Al-terminated (Surface I) as well as CuMg-terminated (Surface II), as shown in Fig. 1 (c) and (d). Both surfaces were modeled by a slab of 3–12 atomic layers separated by a vacuum region of 15 Å, which was found to be sufficient to prevent interactions between periodic images. In this case, the Brillouin zone was sampled using a $12 \times 6 \times 8$ grid.

Generally, it is important to make sure the two slabs are thick enough to show the bulk-like character interiors. Therefore, the convergence tests on the Al(021) and $Al_2CuMg(001)$ surfaces with respect to slab thickness were performed. Here, we used surface energy to estimate the convergence of surface thickness, which is one of the basic qualities to describe stabilities of surface. It is converges to a fixed value when attaining a critical thickness [33]. Surface energy is calculated according to the formula as below

$$E_{surf} = \frac{E_{slab} - \left(\frac{N_{slab}}{N_{bulk}}\right)E_{bulk}}{2A} \tag{1}$$

where E_{slab} and E_{bulk} are total energies of the surface slab and the bulk unit cell, respectively. N_{slab} and N_{bulk} are numbers of atoms in the surface slab and the bulk unit cell, respectively. A is the surface area of supercell. The factor 2 accounts for the double surface of the supercell. The equation (1) is generally applied to calculate the surface energy of stoichiometric surface model.

We have conducted surface energies of Al(021) slabs thickness ranging from 3 to 11 layers, as shown in Fig. 3. It is found that the surface energies are converged to about 1.0 J/m² (dashed line in Fig. 3) for the thickness of Al(021) being equal or larger than 9 atomic layers. It means that the slab with more than 9 atomic layers exhibits bulk-like interiors. Therefore, all of the following calculations are based on the slab with 9 layers for Al(021) surface.

The surface energies of two types $Al_2CuMg(001)$ surfaces were also calculated by Equation (1). The number of atomic layers (n) was set as 3, 6, 9 and 12, respectively. The results are listed in Table 2. It is found that the surface energies of the Surface I with more than six layers can converge to 1.40 J/m². The surface energies of Surface II nearly remain unchanged with the increasing of slab thickness and converge to about 1.23 J/m² when n ≥ 6. Therefore, the $Al_2CuMg(001)$ surfaces with 6 atomic layers were adopted in the following calculations to insure the