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Energetics, electronic structure, and structure stability of the calcium alloying $Mg_{17}Al_{12}$ phase from first principles calculations

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The energetics and electronic structure of the Ca alloying $Mg_{17}Al_{12}$ phase have been calculated using a first principles pseudopotential plane-wave method based on the density functional theory. According to the calculation results, the negative heat of formation and the cohesive energy of $(Mg_{17-x}Ca_x)Al_{12}$ ($x = 0, 1, 4, 12$) gradually increase when the Mg atoms at the I, II, III positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca, which indicates that the alloying ability of $(Mg_{17-x}Ca_x)Al_{12}$ with the replacement of Ca for Mg(III) atoms is the strongest among the three substitutions and $(Mg_5Ca_{12})Al_{12}$ formed in this manner has the highest structural stability. After comparing the densities of states (DOS) for $(Mg_{17-x}Ca_x)Al_{12}$ ($x = 0, 1, 4, 12$), it is found that the increase in the structural stability of $Mg_{17}Al_{12}$ alloyed by Ca attributes to an increase in the bonding electron numbers at energy levels below the Fermi level, which mainly originates from the contribution of the valence electron numbers of Al (p) and Ca (s) orbitals.

Key words: *$Mg_{17}Al_{12}$ phase; pseudopotential plane-wave method; cohesive energy; electronic structure*

1. Introduction

Magnesium alloys have emerged as prospective candidates for numerous applications, especially in the automotive, aerospace, and electronic industries. Their good properties, such as low density, high specific strength, and damping capacity, make them promising replacements for many other structural materials, for instance steel, cast iron, and even aluminium. Widely used magnesium alloys belong to the Mg–Al-based series, exhibiting excellent castability, good room-temperature mechanical properties, and low cost. The use of these alloys, however, has been limited due to their poor heat resistance, especially poor creep property. It has been reported that the as-cast microstructure of Mg–Al-based alloys is composed of two phases:

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α-Mg and β-$Mg_{17}Al_{12}$ [1]; β-$Mg_{17}Al_{12}$ is an essential phase playing an important role in strengthening the crystal boundary and controlling high-tempeature crystal running, whereas the softening of the phase at elevated temperatures is detrimental to the creep property of the alloys. Due to low cost, calcium has been used since the 1980s to improve the poor heat resistance properties of Mg–Al-based alloys. Ca alloying magnesium alloys are a relatively new development [2, 3].

Recent investigations [4, 5] have shown that the addition of calcium to Mg–Al -based alloys has the effect of increasing the melting point and enhancing the thermal stability of the $Mg_{17}Al_{12}$ phase at elevated temperatures, by forming the structure of $(Mg,Ca)_{17}Al_{12}$ solid solution and the valence electron structure (VES) of the $Mg_{17}Al_{12}$ phase with Ca replacing Mg atoms at III positions. According to calculations by Min et al. [6] based on the empirical electron theory (EET), when the dissolved calcium atoms are substituted for Mg(III) atoms in $Mg_{17}Al_{12}$, the distribution of the valence electrons on the main bonds becomes more uniform, leading to an increase in the melting point and thermal stability of $Mg_{17}Al_{12}$. The alloying ability and structural stability of the Ca alloying $Mg_{17}Al_{12}$ phase, however, have not been well studied yet from the alloy energy point of view. Based on previous work, a first principles plane-wave pseudo-potential method based on density functional theory is used in this paper to investigate the energetics and electronic structure of the Ca alloying $Mg_{17}Al_{12}$ phase. Moreover, the structural stability and electronic mechanism of these phases are also analysed and discussed, and some new results will be presented.

2. Crystalline structures

The $Mg_{17}Al_{12}$ phase has an A_{12}-type structure as shown in Fig. 1a. Its unit cell has the highest symmetry T_d^3, space group $I\bar{4}3m$, and 58 atoms with lattice parameters of a =10.5797Å. The atomic coordinates in the unit cell are:

- 2Mg(I): (0,0,0), (1/2,1/2,1/2);
- 8Mg(II): (x, x, x), $(-x, -x, x)$ $x = 0.32$;
- 24 Mg(III): (x, x, z), $(-x, -x, z)$, $(-x, x, z)$, $(x, -x, z)$, $x = 0.36$, $z = 0.04$;
- 24Al (x, x, z), $(-x, -x, z)$, $(-x, x, -z)$, $(x, -x, -z)$ $x = 0.09$ $z = 0.28$.

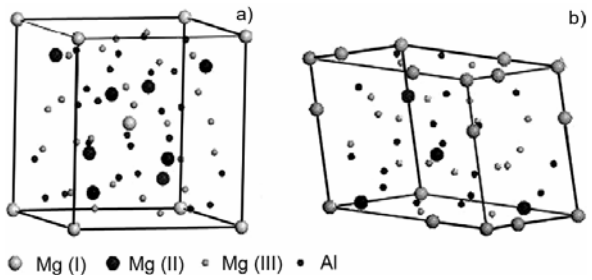

Fig. 1. The modes of the cell (a) and primitive cell (b) of the $Mg_{17}Al_{12}$ phase

The primitive cell of $Mg_{17}Al_{12}$ is used in the calculations is shown in Fig. 1b. The cell consists of 29 atoms, including 12 Al atoms, and 17 Mg atoms (1 Mg(I) atom, 4 Mg(II) atoms, and 12 Mg(III) atoms). In order to reduce computational cost, we have considered in this work structures with all Mg atoms at the I or II or III positions of the $Mg_{17}Al_{12}$ phase substituted with Ca. Hence, the corresponding structures of $Mg_{17}Al_{12}$ with calcium additions are $(Mg_{16}Ca)Al_{12}$, $(Mg_{13}Ca_4)Al_{12}$, and $(Mg_5Ca_{12})Al_{12}$.

3. Method of computation

The Cambridge Serial Total Energy Package (CASTEP) [7,8], a first principles plane-wave pseudopotential method based on the density functional theory [9] was used in this work. CASTEP uses a plane-wave basis set for the expansion of the single-particle Kohn–Sham wave functions, and psudopotentials to describe the computationally expensive electron–iron interaction, in which the exchange-correlation energy by the generalized gradient approximation (GGA) of Perdew is adopted for all elements in our models by adopting the Perdew–Burke–Ernzerhof parameters [10, 11]. Ultrasoft psudopotentials [12] represented in reciprocal space are used.

The atomic orbitals used in the present calculations are: Mg $2p^6 3s^2$, Al $3s^2 3p^1$, Ca $3s^2 3p^6 4s^2$. The cut-off energy of atomic wave functions (PWs), E_{cut}, was set at 330 eV. Sampling the irreducible wedge of the Brillouin zone was performed with a regular Monkhorst–Pack grid of special $6\times6\times6$ *k*-points [13].

A finite basis set correction and the Pulay scheme of density mixing [14] were applied for the evaluation of energy and stress. All atomic positions in our model have been relaxed according to the total energy and force by using the Broyden–Flecher–Goldfarb–Shanno (BFGS) scheme [15], based on cell optimisation criterion: a RMS force of 5.0×10^{-6} eV/Å, stress of 0.01 GPa, and displacement of 5.0×10^{-4} Å. The calculation of the total energy and electronic structure was followed by the cell optimisation with a self-consistent-field (SCF) tolerance of 5.0×10^{-7} eV.

4. Results and discussion

4.1. Crystal structure

The atomic coordinates and lattice constants of the primitive cells of $Mg_{17}Al_{12}$, $(Mg_{16}Ca)Al_{12}$, $(Mg_{13}Ca_4)Al_{12}$, and $(Mg_5Ca_{12})Al_{12}$ are estimated from the minimized total energy, and the results are given in Tables 1 and 2. It is found that there are almost no changes in the space group structure of the $Mg_{17}Al_{12}$ phase, and in the atomic coordinates of the unit cell with and without the addition of Ca. Moreover, the present lattice constant a of $Mg_{17}Al_{12}$ is 9.057 Å, which is close to the experimental value of a = 9.145 Å (the value is obtained by converting the experimental lattice constant 10.56 Å [6] of the unit cell of $A_{12}Mg_{17}Al_{12}$), and the error of the lattice constant calculated here relative to the experimental result is about 0.962%. When the Mg atoms at the I, II, III positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca, the lattice constants of the corresponding phases gradually increase, whereas the cell volume of the Ca alloying $Mg_{17}Al_{12}$ phase is in good agreement with the experimental result [6], for example the lattice constant 10.608Å of the $Mg_{16.5}Ca_{0.5}Al_{12}$ unit cell is larger than that of $Mg_{17}Al_{12}$. Hence, the computational parameters selected in this paper are suitable.

Table 1. The atomic coordinates of the $Mg_{17}Al_{12}$ phase, with and without the addition of Ca

Model		Mg(I)			Mg(II)			Mg(III)			Al		
		x	y	z	x	y	z	x	y	z	x	y	z
Calc.	$Mg_{17}Al_{12}$	0.5	0.5	0.5	0.328	0.328	0.328	0.356	0.356	0.040	0.090	0.090	0.274
	$(Mg_{16}Ca)Al_{12}$	0.5	0.5	0.5	0.322	0.322	0.322	0.357	0.357	0.038	0.091	0.091	0.277
	$(Mg_{13}Ca_4)Al_{12}$	0.5	0.5	0.5	0.317	0.317	0.317	0.355	0.355	0.029	0.090	0.090	0.274
	$(Mg_5Ca_{12})Al_{12}$	0.5	0.5	0.5	0.357	0.357	0.357	0.356	0.356	0.076	0.086	0.086	0.243
Exp. [6]	$Mg_{17}Al_{12}$	0.5	0.5	0.5	0.320	0.320	0.320	0.360	0.360	0.040	0.090	0.090	0.280

Table 2. Equilibrium lattice constant (a), formation heat (ΔH), and cohesive energy (E_{coh}) of the $Mg_{17}Al_{12}$ phase with and without the addition of Ca

Phase	a (Å)	E_{tot} (eV)	ΔH (eV·atom^{-1})	E_{coh} (eV·atom^{-1})
$Mg_{17}Al_{12}$	9.057	−17311.6439	−0.034	−2.465
$(Mg_{16}Ca)Al_{12}$	9.094	−17338.3387	−0.059	−2.508
$(Mg_{13}Ca_4)Al_{12}$	9.260	−17417.4775	−0.1023	−2.604
$(Mg_5Ca_{12})Al_{12}$	9.887	−17625.3379	−0.1085	−2.751

4.2. Heat of formation

The heat of formation (ΔH) of the $(Mg_{17-x}Ca_x)Al_{12}$ (x = 0, 1, 4, 12) primitive cell per atom was calculated using the following expression [16, 17]:

$$\Delta H = \frac{1}{29}\left[E_{\mathrm{tot}} - (17-x)E_{\mathrm{solid}}^{\mathrm{Mg}} - xE_{\mathrm{solid}}^{\mathrm{Ca}} - 12E_{\mathrm{solid}}^{\mathrm{Al}}\right] \qquad (1)$$

where E_{tot} refers to the total energy of the primitive cell at the equilibrium lattice constant, $E_{\mathrm{solid}}^{\mathrm{Mg}}$, $E_{\mathrm{solid}}^{\mathrm{Ca}}$ and $E_{\mathrm{solid}}^{\mathrm{Al}}$ are the single atomic energies of *hcp*-Mg, *fcc*-Ca and *fcc*-Al in the solid states, respectively, x refers to the numbers of the alloying Ca atoms. In this paper, we calculate the single atomic energy by the following method: at first, the energy of a pure metal crystal in the solid state was calculated, then the energy was divided by the number of atoms involved in the crystal, and this result is the energy of a single atom in the pure metal. The calculated energies of Mg, Al, and Ca atoms for our considered systems were –977.87 eV, –57.24 eV and –1003.83 eV, respectively. The calculated heats of formation for $Mg_{17}Al_{12}$, $(Mg_{16}Ca)Al_{12}$, $(Mg_{13}Ca_4)Al_{12}$ and $(Mg_5Ca_{12})Al_{12}$ are also listed in Table 2. It was found that the heat of formation of the Ca alloying $Mg_{17}Al_{12}$ phases is always negative, which means that the structure of these phases can exist and be stable [18]. Since the negative heat of formation of Ca alloying $Mg_{17}Al_{12}$ phases gradually increases when the Mg atoms at the I, II, III positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca, it can be concluded that the alloying ability of the $(Mg_{17-x}Ca_x)Al_{12}$ phase is the strongest when substituting Mg(III) atoms with Ca.

4.3. Cohesive energy

The cohesive energy (E_{coh}) of the $(Mg_{17-x}Ca_x)Al_{12}$ (x = 0, 1, 4, 12) primitive cell per atom was calculated using the following expression [17]:

$$E_{\mathrm{coh}} = \frac{1}{29}\left[E_{\mathrm{tot}} - (17-x)E_{\mathrm{atom}}^{\mathrm{Mg}} - xE_{\mathrm{atom}}^{\mathrm{Ca}} - 12E_{\mathrm{atom}}^{\mathrm{Al}}\right] \tag{2}$$

where $E_{\mathrm{atom}}^{\mathrm{Mg}}$, $E_{\mathrm{atom}}^{\mathrm{Ca}}$ and $E_{\mathrm{atom}}^{\mathrm{Al}}$ are the total energies of isolated Mg, Ca, and Al atoms. The energy of a free_atom is defined as the energy of the supercell with a free atom in the centre, while the lattice parameter of the supercell with the $P1$ space group is set to a = 10 Å. The calculated energies of Mg, Al, and Ca free atoms are –976.39 eV, –53.46 eV, –1001.84 eV, respectively. The cohesive energy of a single atom of the primitive cell is calculated from Eq. (2) and the results are listed in Table 2 and shown in Fig. 2.

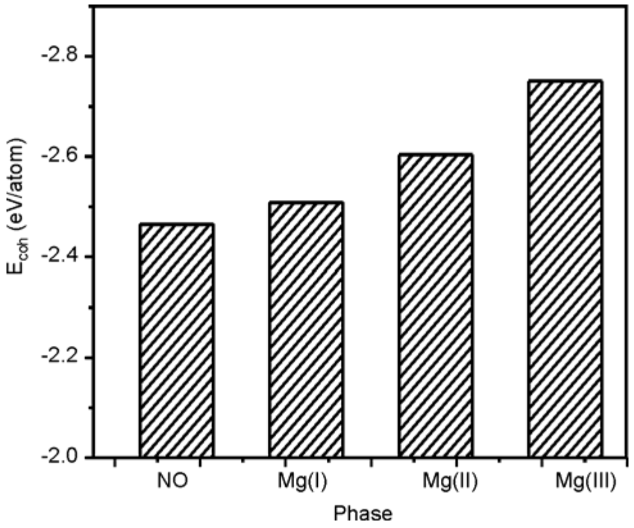

Fig. 2. Cohesive energy (E_{coh}) of the $Mg_{17}Al_{12}$ phase with and without addition of Ca. NO, Mg (I), Mg(II), and Mg(III) denote $Mg_{17}Al_{12}$, $(Mg_{16}Ca)Al_{12}$, $(Mg_{13}Ca_4)Al_{12}$, and $(Mg_5Ca_{12})Al_{12}$, respectively

It is found that the cohesive energy of the Ca alloying $Mg_{17}Al_{12}$ phase gradually increases when the Mg atoms at the I, II, III positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca. This is due to the fact that the cohesive intensity and structural stability of the crystal are correlated with its cohesive energy [19] being defined as either the energy needed to form the crystal from free atoms or the work needed to decompose the crystal into isolated atoms. Moreover, Li et al. [20] have studied the correlation between the melting temperature and cohesive energy based on the Laves phases with the same space group structure. They found that the melting temperature of the Laves phases is roughly proportional to their cohesive energy, which means that the larger the cohesive energy, the more stable is the corresponding crystal structure. In the present work, since there are almost no changes in the structure of the $Mg_{17}Al_{12}$ phase and the atomic coordinates in the unit cell with and without the addition of Ca, it can be concluded that the structural stability of the $(Mg_{17-x}Cax)Al_{12}$ phase is the highest when Mg(III) atoms are replaced with Ca. Hence, the experimental result [6] on increasing the melting point and thermal stability of $Mg_{17}Al_{12}$ with the addition of Ca are well explained from the alloy energy point of view.

4.4. Density of states

An analysis of the total and partial density of states (DOS) of the Ca alloying $Mg_{17}Al_{12}$ phase is performed to understand the electronic structure mechanism of improving structural stability, and the total and partial DOSs of $Mg_{17}Al_{12}$, $(Mg_{16}Ca)Al_{12}$, $(Mg_{13}Ca_4)Al_{12}$, and $(Mg_5Ca_{12})Al_{12}$ primitive cells are plotted in Figs. 3 and 4. Before Ca alloying, it is found that the main bonding peaks between 0 eV and –10.0 eV originate from the contribution of the valence electron numbers of Mg (s), Al (s), and Al (p) orbitals (see Fig. 3a). When Mg atoms at the I positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca, the contribution of valence electrons of $(Mg_{16}Ca)Al_{12}$ (Fig. 3b) in the energy range between 0 eV and –10.0 eV is the same as that of $Mg_{17}Al_{12}$ but there is a new bonding peak between –20 eV and –25 eV, dominated by the valence electron numbers of Al (p) orbitals. When the Mg atoms at the II and III positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca atoms, the contribution of valence electrons of $(Mg_{13}Ca_4)Al_{12}$ (Fig. 3c) and $(Mg_5Ca_{12})Al_{12}$ (Fig. 3d) in the energy range between 0 eV and –10.0 eV is almost the same as that of $Mg_{17}Al_{12}$ but there is a contribution from Ca atoms to the peaks. The peak between –20 eV and –25 eV also originates from the valence electron numbers of Al (p) orbitals, but the altitude of the peak is significantly increased compared to that of $(Mg_{16}Ca)Al_{12}$.

A further analysis of the total DOS (Fig. 4) of $Mg_{17}Al_{12}$, $(Mg_{16}Ca)Al_{12}$, $(Mg_{13}Ca_4)Al_{12}$, and $(Mg_5Ca_{12})Al_{12}$ was done. It was found that the main bonding peaks of $Mg_{17}Al_{12}$ are located from 0 eV to –10.0 eV, the peaks of $(Mg_{16}Ca)Al_{12}$ are similar to those of $Mg_{17}Al_{12}$, and the heights of the peaks are not significantly changed, but there is a new bonding peak between –20 eV and –25 eV. The height of the new peak is 10.97 electronic states/eV, which indicates that the bonding electron numbers of $Mg_{17}Al_{12}$ with the addition of Ca increase in the low energy range far below the Fermi level.

Hence, the structure of $Mg_{17}Al_{12}$ with Mg(I) atoms replaced with Ca is more stable than that of $Mg_{17}Al_{12}$ [21, 22].

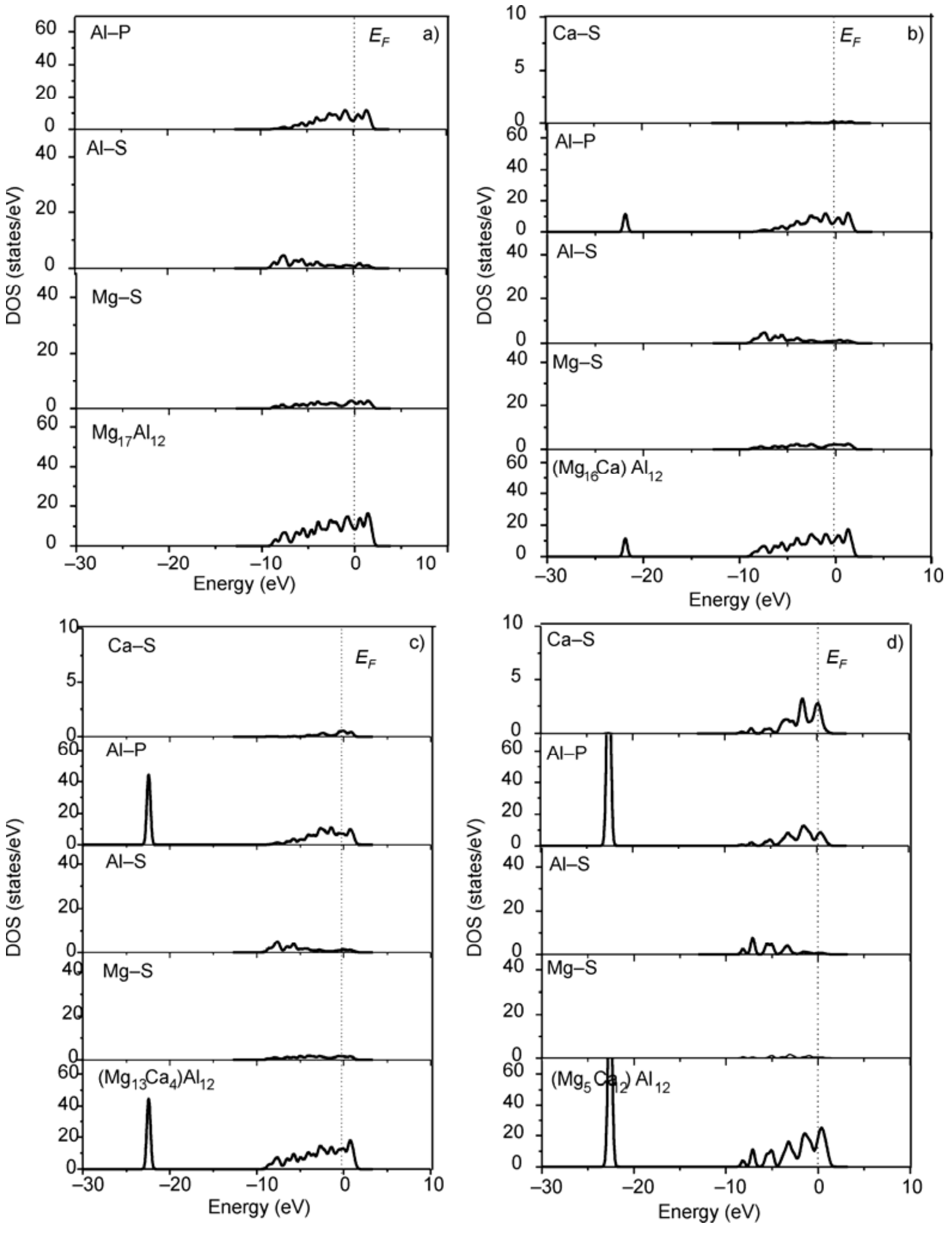

Fig. 3. Partial DOS of Ca alloying $Mg_{17}Al_{12}$ phases:
a) $Mg_{17}Al_{12}$, b) $(Mg_{16}Ca)Al_{12}$, c) $(Mg_{13}Ca_4)Al_{12}$, d) $(Mg_5Ca_{12})Al_{12}$

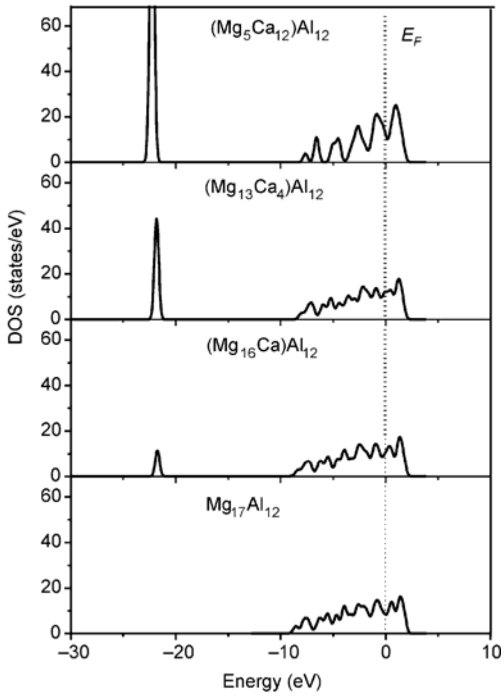

Fig. 4. Total DOS of Ca alloying $Mg_{17}Al_{12}$ phase

When the Mg atoms at the II and III positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca, the main bonding peaks of $(Mg_{13}Ca_4)Al_{12}$ and $(Mg_5Ca_{12})Al_{12}$ are also located from 0 eV to –10.0 eV, but the heights of these peaks are significantly larger. Especially between –20 eV and –25 eV, there is a new, higher bonding peak, and the height of the new peak is 43.45 electronic states/ eV and 125.45 electronic states/eV for $(Mg_{13}Ca_4)Al_{12}$ and $(Mg_5Ca_{12})Al_{12}$, respectively. Based on the above analysis, as far as $(Mg_5Ca_{12})Al_{12}$ is concerned, it is found that the number of bonding electrons from 0 eV to –10.0 eV and from –20 eV to –25 eV exceeds that in $Mg_{17}Al_{12}$, $(Mg_{16}Ca)Al_{12}$ or $(Mg_{13}Ca_4)Al_{12}$. The higher the number of bonding electrons, the stronger are electrostatic interactions. Furthermore, the presence of electrons in the energy range far below the Fermi level will lead to a more stable structure. Hence, the $Mg_{17}Al_{12}$ phase with Mg (III) atoms replaced by Ca has the highest structural stability among the three studied substitutions.

5. Conclusions

The energetics and electronic structures of Ca alloying $Mg_{17}Al_{12}$ phase were investigated using a first principles plane-wave pseudopotential method based on the density functional theory. The results show that the negative formation heat and cohesive energy of $(Mg_{17-x}Ca_x)Al_{12}$ (x = 0, 1, 4, 12) phases gradually increase when the Mg atoms at the I, II, III positions of the $Mg_{17}Al_{12}$ phase are substituted with Ca, indicating that the alloying ability of the $(Mg_{17-x}Ca_x)Al_{12}$ phase for replacing Mg(III) atoms with Ca is the strongest, and the $(Mg_5Ca_{12})Al_{12}$ phase formed in this manner has the highest structural stability. Upon comparing the densities of states of $(Mg_{17-x}Ca_x)Al_{12}$ ($x = 0, 1, 4, 12$) phases, it is found that the increase in the structural stability of the $Mg_{17}Al_{12}$ phase alloyed by Ca contributes to the increase in the bonding electron numbers in the lower energy level below the Fermi level, which originates mainly from the contribution of the valence electron numbers of Al (p) and Ca (s) orbitals.

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