First-Principles Study of Carbon Vacancy in Ta₄AlC₃

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We have investigated the carbon mono-vacancy in Ta₄AlC₃ by first-principles calculations. We identify the 2a sites as the probable carbon vacancy sites in Ta₄AlC₃ based on the energetics of vacancy formation. It was found that introducing carbon vacancies decreased the phase stability of Ta₄AlC₃. There are no significant changes in volume by introducing carbon vacancy. However, the bulk modulus decreased when introducing carbon vacancy. The differences in density of states of Ta₄AlC₃ with and without carbon vacancies are analyzed. Some vacancy peaks near the Fermi level were observed. Additionally, the density of states at the Fermi level increases by introducing carbon vacancies, which may be of benefit to the electron transport in Ta₄AlC₃. [doi:10.2320/matertrans.MAW200803]

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1. Introduction

MAX phases (M_{n+1}AX_n, where $n = 1, 2$ or 3 , M is an early transition metal, A is an A-group element, and X is either C or N) are a family of layered ternary compounds, which have attracted considerable attention due to their unique combination of metallic and ceramic properties.¹⁻³⁾ According to the value of n , MAX phases are classified into three groups, i.e. 211, 312 and 413 phases. For a long time, Ti₄AlN₃ is believed to be the only member of 413 phases.⁴⁾ As a result, research on 413 phases is not as intensive as research on 211 and 312 phases. However, recently, important progresses on 413 phases were reported in Ta-Al-C system, in which Ta₄AlC₃ bulk materials were synthesized either in the form of polycrystals⁵⁻⁹⁾ or single-crystals.¹⁰⁾ The structural, mechanical and physical properties of Ta₄AlC₃ have been studied.⁵⁻¹¹⁾ It was found that Ta₄AlC₃ exhibits a combination of improved mechanical properties, good damage tolerance and excellent thermal shock resistance, which makes it a promising technological material.

It is known that many MAX phases usually exist in substoichiometric form with a substantial amount of carbon or nitrogen vacancies. For example, the nitrogen vacancies in Ti₄AlN₃ have been found and studied experimentally and theoretically.^{12,13)} These nitrogen vacancies have remarkable influence on structural, mechanical and physical properties. At present, the defect formation in Ta₄AlC₃ has not been investigated. In this paper, we studied the carbon mono-vacancy in Ta₄AlC₃ by first-principles calculations.

2. Details of Calculation

We have used density functional theory implemented into the WIEN2K code for the calculations in the present work.¹⁴⁾ The generalized gradient approximation (GGA) exchange correlation functional of Perdew, Burke, and Ernzerhof was used. Detailed computational procedures can be found in our previous works, in which we studied the electronic structure

Fig. 1 The model of the carbon mono-vacancy at (a) 2a; and (b) 4f site for Ta₄AlC₃.

and phase stability of Ta₄AlC₃.¹¹⁾ It is known that Ta₄AlC₃ crystallizes in the $P6_3/mmc$ space group and has 16 atoms in one unit cell. The thermodynamic ground state equilibrium structure of Ta₄AlC₃ has been determined to be the Ti₄AlN₃-like crystal structure, which is denoted as α polymorph.^{11,15)} In the present study, all the calculations are based on the α polymorph of Ta₄AlC₃. There are two different sites for carbon mono-vacancy in Ta₄AlC₃, namely 2a and 4f in the Wyckoff notation. As shown in Fig. 1, the carbon mono-vacancy structure was represented by a $2 \times 2 \times 1$ supercell containing 63 atoms after removing one C atom, corresponding to a sub-stoichiometry of Ta₄AlC_{2.875}. In our calculations, all the structural parameters for Ta₄AlC₃ with and without carbon vacancies were fully relaxed. As a first step, the lattice parameters for vacancy-free Ta₄AlC₃ were optimized. This was performed by applying hydrostatic pressure by changing the volumes while keeping the c/a ratio constant. And then, with the optimized volume, the c/a ratio was varied to find the values corresponding to the crystal energy minimum. Thirdly, the equilibrium positions of the internal Ta and C atoms were evaluated by calculating the Hellman-Feynman forces,¹⁶⁾ and the final forces on each atoms were less than 1 mRy/a.u. Finally, for Ta₄AlC₃ with carbon mono-vacancy,

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Table 1 The calculated formation energy (E_{form}) of carbon vacancy, total energy (E_{tot}), volumes (V), bulk modulus (B) and density of states at the Fermi level ($N(E_F)$) for Ta₄AlC₃ with and without carbon mono-vacancy.

	E_{form} (eV)	E_{tot} (Ry/unit cell)	V (Å ³ /unit cell)	B (GPa)	$N(E_F)$ (states/eV.unit cell)
Ta ₄ AlC ₃	...	-251446.621116	206	266	4.18
Ta ₄ AlC _{2.875} (2a)	2.22	-251446.604596	205.6	261	6.71
Ta ₄ AlC _{2.875} (4f)	2.40	-251446.591381	205.3	243	4.77

the atomic arrangements around the carbon vacancy were also optimized by using calculated Hellmann-Feynman forces exerted on atoms in the vicinity of carbon vacancy.

3. Results and Discussion

As mentioned above, there are two different sites for carbon mono-vacancy in Ta₄AlC₃. To determine what defects are likely to form, the formation energy E_f for a carbon vacancy was determined by:¹³⁾

$$E_f = E_t(v) + \mu_C - E_t \quad (1)$$

where $E_t(v)$ is the total energy of Ta₄AlC₃ with a carbon vacancy at 2a and 4f site respectively. μ_C and E_t designate the total energy of an isolated C atom, and the total energy of vacancy-free Ta₄AlC₃, respectively. As listed in Table 1, the vacancy formation energy is calculated as 2.22 eV for a carbon mono-vacancy at 2a site, lower than 2.40 eV for a carbon mono-vacancy at 4f site. It is obvious that C vacancies at 2a sites are energetically more favorable than at 4f sites.

To determine the relative phase stabilities of Ta₄AlC₃ with and without carbon mono-vacancy, their total energies were also calculated and compared. The total energy of Ta₄AlC₃ without carbon vacancies is compared with the total energy of Ta₄AlC₃ with carbon vacancies plus the total energy of the extra carbon in the graphite structure, the most stable form of carbon, i.e.,

$$E_{\text{tot}} = E_t(v) + xE(\text{C}_{\text{graphite}}) \quad (2)$$

The calculated ground state energies for Ta₄AlC₃ with and without carbon mono-vacancy are also listed in Table 1. It is seen that the total energy of Ta₄AlC₃ with carbon vacancies at 2a sites is lower than at 4f sites, which means that the former is energetically more stable. This conclusion is consistent with the analysis of the vacancy formation energy. However, the total energies of Ta₄AlC₃ with carbon vacancies are higher than the vacancy-free Ta₄AlC₃, which means that carbon vacancies are slightly difficult to form in this compound. Thus, high quality samples of Ta₄AlC₃ with stoichiometric composition will be easier to be prepared experimentally in comparison with other MAX phases. This result is supported by a recent experimental work on the crystal structure of Ta₄AlC₃, where the occupancy factors were refined and no significant deviations from the stoichiometric composition were found.¹⁰⁾

The equilibrium volume and the bulk modulus of Ta₄AlC₃ with and without carbon vacancy were calculated by fitting the Murnaghan equation of states to the energy-volume data. All calculated equilibrium volumes for Ta₄AlC₃ with and without carbon vacancies are within 1.8% from the experimental value. As listed in Table 1, introducing carbon

Fig. 2 The total density of states for Ta₄AlC₃ with and without carbon mono-vacancy.

mono-vacancy leads to a slight decrease in volume. The bulk modulus calculated for vacancy-free Ta₄AlC₃ is 266 GPa, in good agreement with the experimental value of 261 GPa.⁶⁾ While the bulk modulus decreases to 261, and 243 GPa for Ta₄AlC₃ with 2a and 4f carbon vacancies respectively. It is obvious that the introduction of carbon vacancies at 4f sites causes a larger decrease in bulk modulus.

The density of states (DOS) was calculated to see how the electronic states change in the presence of carbon vacancies. Figure 2 shows the DOS of Ta₄AlC₃ with carbon mono-vacancies at 2a and 4f sites respectively. For comparison, the DOS without carbon vacancies is also plotted. It can be seen that the total DOS of Ta₄AlC₃ with and without carbon vacancies exhibit some similar features. The states from about -14 eV to -11 eV are derived from the C 2s and Ta 5d states. The states just below the Fermi level are dominated by strong covalent bonding states of the Ta 5d orbital and the p-derived orbitals of Al and C. The states in the vicinity of the Fermi level are mainly occupied by Ta 5d states, which contribute to the electronic conductivity. The detailed description of DOS can be found in our previous work.¹¹⁾ Figure 3 shows the partial DOS of two nonequivalent Ta atoms nearest to the carbon vacancy. For comparison, the partial DOS of two nonequivalent Ta atoms in Ta₄AlC₃ without carbon vacancies is also shown in the figure. As can be seen, when carbon vacancies are included, some new peaks are seen to emerge just below the Fermi level. These vacancy peaks are of mainly Ta 5d character. These peaks

Fig. 3 The partial density of states showing the Ta-Ta 5d hybridizations in Ta_4AlC_3 with and without carbon mono-vacancy.

are the so-called vacancy peaks that are associated with Ta-Ta bonds through the vacancy sites. Similar vacancy states were also found in the typical MAX phase, Ti_3SiC_2 previously.¹⁷⁾ Generally, the electronic conductivity has close correlation to the DOS at the Fermi level ($N(E_F)$). As can be seen from Table 1, the value of $N(E_F)$ increases from 4.18 states/eV.unit cell for Ta_4AlC_3 without carbon vacancies to 6.71, and 4.77 states/eV.unit cell for Ta_4AlC_3 with 2a and 4f carbon vacancies respectively. This result indicates that introducing carbon vacancies leads to the metallization of Ta_4AlC_3 and can improve the electronic conductivity of Ta_4AlC_3 .

4. Conclusions

We have performed first-principles calculations to study the carbon mono-vacancy in Ta_4AlC_3 . The 2a sites are identified as the probable carbon vacancy sites in Ta_4AlC_3 based on the energetics of vacancy formation. It was found

that introducing carbon vacancies decreased the phase stability of Ta_4AlC_3 . There was no significant change in volume between Ta_4AlC_3 with and without carbon vacancy. The introduction of carbon vacancies decreased the bulk modulus of Ta_4AlC_3 . It was observed that some vacancy states exist near the Fermi level. These vacancy states are associated with Ta-Ta bonds through the vacancy sites. Additionally, introducing carbon vacancies can improve the electronic conductivity of Ta_4AlC_3 .

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