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Effect of transition metal (M) and M–C slabs on equilibrium properties of Al-containing MAX carbides: An *ab initio* study

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ABSTRACT

The effect of transition metal (M) and M–C slabs (n) on crystal structure and equilibrium properties of Al-containing MAX-phase carbides $M_{n+1}AlC_n$ ($n = 1–3$) was investigated. There is a linear relation between lattice parameters and Goldschmid diameter of M atoms. For a given n, c/a ratios always fall into a narrow range. The theoretical density almost increases with increasing VEC (valence electron concentration), n and d-electron shell number. In general, the formation energy and cohesive energy increase with the increase of VEC. The bond length decreases with increasing VEC. The bond length of 3d compounds is much higher than those of 4d and 5d compounds. Among M–C bonds, the lowest bond length is present in the M–C bonds with the M atoms near to Al atoms. Overall, the M–Al bond angle decreases with increasing d-electron shell number. In addition, M–C bond angles increase with increasing the corresponding M–C bond length. Overall, the total density of states at Fermi energy increases with increasing VEC and n, but decreases from 3d, 4d to 5d for M_3AlC_2, and M_4AlC_3. In addition, a weak M1–M2 bond was found in M_4AlC_3 with VEC = 5 and 6.

1. Introduction

Recently, a class of ternary layered compounds $M_{n+1}AX_n$ phases (MAX for short, where n = 1, 2 or 3, M is early transition metal, A is an A-group element (mostly groups 13 and 14), and X is C or N) have attracted much attention because of the unique combination of both metal- and ceramic-like properties that include high fracture toughness, high Young's moduli, high thermal and electrical conductivities, easy machinability, excellent thermal shock resistance, high damage tolerance, microscale ductility [1–3]. According to the value of n, the MAX phases can be classified into three groups, viz. 211, 312, and 413 phases [1], where notably most of them belong to 211 phases (H-phases). To date, over 60 MAX compounds have been identified in experiments. In 1996, Barsoum and El-Raghy succeeded in synthesis and characterization of high-purity and dense Ti_3SiC_2 using HIP (Hot isostatic bonding) process [4], which makes the researchers give much attention on this class of materials. Due to the relatively low density, good oxidation resistance, and high high-temperature strength, some typical MAX materials like Ti_3SiC_2 [4], Ti_3AlC_2 [5,6], and Ti_2AlC [7,8] are candidates for high-temperature applications.

The oxidation resistance usually plays a crucial role in the high-temperature applications. It is well established that the oxidation resistance of some Al-containing MAX carbides like Ti_2AlC [9,10], Ti_3AlC_2 [6,11,12], and Cr_2AlC [13–15] is better than that of Ti_3SiC_2 [16,17], due to the formation of a protective and dense Al_2O_3 scale on the substrate to prevent further oxidation [18]. Therefore, it is reasonable to assume that other Al-containing MAX carbides would also exhibit the high oxidation resistance, such as Ti_2AlC, Ti_3AlC_2 and Cr_2AlC. Then, it is very necessary to perform a systematical study of the former. Moreover, the Al-containing compounds have the largest group (13 compounds) in the MAX phases identified in experiments [2,19]. In addition, some new Al-containing compounds, such as Ta_3AlC_2 [20], Ta_4AlC_3 [20], V_4AlC_3 [21], and Nb_4AlC_3 [22], were discovered recently, and exhibit some interesting properties, including polymorphism in Ta_4AlC_3 [23], high high-temperature strength in Nb_4AlC_3 [24].

Today's materials science has yielded an unprecedented frequency of new material discoveries. Much of this work, however, has historically been performed in a trial-and-error manner, and improved theoretical input in guidance of experimental work is essential. In particular, the rapid development of computer hardware and computational methods during the past two decades has provided strong means to explore the structures and properties of materials at the atomic scale. Since 1998, these theoretical investigations have been conducted heavily in the field of MAX

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phases [25–33]. All these studies have been performed using density functional theory (DFT) and have much progress in predicting the stability, lattice parameters, electronic structure, compressibility, optical and elastic properties of this class of MAX compounds. The ultimate aim of these *ab initio* calculations is to predict properties and lead experimentalists to new compounds with potentially extraordinary properties. In the past, however, most of the previous work focuses on the M_2AX compounds [27,29,30,34–38]. And only a few papers [39,40] were published on 312 MAX phases. Recently, much progress has occurred in the discovery of some new 312 and 413 compounds in experiments since 2006, such as Ta_3AlC_2 [20], Ti_3SnC_2 [32,41], Ti_4SiC_3 [42], Ti_4GeC_3 [43], Ta_4AlC_3 [20], V_4AlC_3 [21], Nb_4AlC_3 [22], and Ti_4GaC_3 [28,31,44].

However, there are no systematic reports on 413 MAX phases to date because only one 413 compound was identified in experiments before 2006 [45]. Since then, the following 413 compounds have been discovered, with some interesting properties: Ti_4SiC_3 [42], Ti_4GeC_3 [43], Ta_4AlC_3 [20], V_4AlC_3 [21], Nb_4AlC_3 [22], and Ti_4GaC_3 [28,31,44]. It is reasonable to believe that their number would continue increasing in future. Therefore, it is both timely and important to perform a theoretical analysis of these phases.

In MAX phases, transition metal M and M–C slabs have a significant effect on the crystal structure (lattice constants, bond length, and bond angle) and other equilibrium properties. For instance, the elastic moduli generally increase with increasing M–C slabs in Ti_2AlC and Ti_3AlC_2 [46] as well as Nb_2AlC and Nb_4AlC_3 [24]. A careful examination for the effect of transition metal (M) and M–C slabs (n) on lattice constant, bond length, bond angle, and other equilibrium properties would contribute to a better understanding for the properties, and design new MAX compounds with excellent performance.

The present work is to conduct a systemic study on the effect of transition metals and M–C slabs on the crystal structure and equilibrium properties of Al-containing MAX carbides $M_{n+1}AlC_n$ ($n = 1–3$) using First principle calculations, and also report those of 413 series in detail. These results would contribute to a better understanding of the crystal structure and equilibrium properties of MAX phases.

2. Calculation details

In the present work, all first principle calculations on Al-containing MAX carbides were conducted using CASTEP [47] code, a plane-wave pseudopotential total energy calculation method based on density functional theory (DFT) [48], with the employed plane-wave energy cutoff of 450 eV and the Brillouin zone sampling of $10 \times 10 \times 2$ special k-point meshes, respectively. The Vanderbilt-type ultrasoft pseudopotential [49] was used to represent the interactions of electrons with ion cores. Perdew–Wang generalized-gradient approximation (GGA-PW91) [50] was employed to treat the electronic exchange–correlation energy.

The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme [51] for the minimization of the total energy and internal forces was used to optimize the crystal structures by independently modifying the lattice parameters and internal atomic coordinates. The convergence criteria for geometrical optimization were set such that the difference in total energy was within 5×10^{-6} eV/atom, the maximum ionic Hellmann–Feynman force being within 0.01 eV/Å, the maximum ionic displacement being within 5×10^{-4} Å, and the maximum stress being within 0.02 GPa.

The cohesive energy played an important role in understanding phase equilibrium, because it can be used to estimate strength of the forces that bind atoms together in the solid state. In the present work, the cohesive energy $E_{\mathrm{coh}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n}$ was defined as the energies of all the pure constituent atoms at infinite separation minus the total energy of the compound

$$E_{\mathrm{coh}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n} = \frac{(n+1)E_{\mathrm{atom}}^{\mathrm{M}} + E_{\mathrm{atom}}^{\mathrm{Al}} + nE_{\mathrm{atom}}^{\mathrm{C}} - E_{\mathrm{total}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n}}{2(n+1)} \tag{1}$$

where $E_{\mathrm{total}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n}$ referred to the calculated total energy of $M_{n+1}AlC_n$ at equilibrium and 0 K, and $E_{\mathrm{atom}}^{\mathrm{M}}$, $E_{\mathrm{atom}}^{\mathrm{Al}}$, and $E_{\mathrm{atom}}^{\mathrm{C}}$ were the pseudo-atomic energies of the pure constituents M, Al, and C, respectively.

The formation energy was that released in the chemical reaction that a compound was synthesized from simple substances, and used for the characterization of thermodynamic phase stability. In the present work, it was also calculated as the difference between the total energy of the compound and the sum of the total energies of the involved simple substances. For this purpose, the total energies of all the sample's elements, in their most stable form, were calculated. The formation energy of $M_{n+1}AlC_n$ phases, $\Delta E_{\mathrm{f}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n}$, could be expressed as follows:

$$\Delta E_{\mathrm{f}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n} = \frac{(n+1)E_{\mathrm{total}}^{\mathrm{M}} + E_{\mathrm{total}}^{\mathrm{Al}} + nE_{\mathrm{total}}^{\mathrm{Graphite}} - E_{\mathrm{total}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n}}{2(n+1)} \tag{2}$$

where $E_{\mathrm{total}}^{\mathrm{M}_{n+1}\mathrm{AlC}_n}$, E_{total}^{M}, $E_{\mathrm{total}}^{\mathrm{Al}}$, and $E_{\mathrm{total}}^{\mathrm{Griphite}}$ referred to the calculated total energy at 0 K of $M_{n+1}AlC_n$, M, Al, and graphite at equilibrium, respectively.

3. Results and discussion

3.1. Lattice parameters and theoretical density

To get more insight into the effect of M–C slabs and transition metal M on lattice parameters, we examined the lattice parameters of M_2AlC, M_3AlC_2 and M_4AlC_3 as a function of VEC (valence electron concentration) of M atoms, as shown in Fig. 1. It can be found that the lattice parameters exhibit a periodic change with M–C slabs (n) and M atoms (VEC): (1) the lattice parameters a and c both decrease linearly with increasing VEC, where the slop is weakly affected by d-electron shell number of M atoms; (2) 3d compounds have higher lattice parameters than 4d and 5d ones, however, between which there is little difference; (3) with increasing n (the number of M–C slabs), a-lattice parameter almost keeps unchanged, but c-lattice parameter obviously increases. It is not surprised, considering the crystal structure (Fig. 1a of Ref. [52]) of MAX phases with different n. In addition, the lattice parameters reach the min values for $Cr_{n+1}AlC_n$, and max ones for $Zr_{n+1}AlC_n$ in each series.

We have also investigated the relation between lattice parameters and atomic diameters of M atoms, as shown in Fig. 1. It can be seen that the lattice parameters increase linearly with increasing atomic diameters. A linear function of $y = fx + b$ was used to fit the plots of the lattice parameters on atomic diameters. The fitting results of slop and determination coefficient (R^2) as a function of n (M–C slabs) are shown in Fig. 2. Overall, the high R^2 indicates that a good linear relation exists between the lattice parameters of $M_{n+1}AlC_n$ and atomic diameters of M. In other words, the periodic change of atomic diameter of M atoms contributes to the periodic change of lattice parameters of $M_{n+1}AlC_n$ phases as mentioned above. Moreover, R^2 decreases with increasing n, indicating the weakening of the linear relation. With increasing n, the decreasing slop of fitting plots (f) for a-lattice parameter shows the decreasing effect of atomic diameter on a-lattice parameter. However, due to the increase of M–C slabs, f for c-lattice parameter increases with increasing n. To eliminate the effect of M–C slabs, the $f/(n+1)$ was calculated to be 1.317 for M_2AlC, 1.251 for M_3AlC_2, and 1.184 for M_4AlC_3 (Fig. 2a), respectively. This trend is in line with that for a-lattice parameter. Therefore, it can be concluded that the effect of atomic diameter on lattice parameters becomes weak with increasing n.