

**Theoretical investigation of the solubility in  $(M_xM'_{2-x})\text{AlC}$  ( $M$  and  $M' = \text{Ti, V, Cr}$ )**

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We have performed theoretical studies of the solubility within  $(M_xM'_{2-x})\text{AlC}$ , where  $M$  and  $M' = \text{Ti, V, and Cr}$  by means of *ab initio* total energy calculations. The theoretical values of equilibrium volume and the optimized  $c/a$  ratios are in good agreement with those of experiments (within  $\sim \pm 4\%$  and  $\sim \pm 1.3\%$ , respectively). Furthermore we show that if  $x$  is increased from 0 to 2 the bulk modulus can be increased by as much as 36%. Based on the total density of states analysis as well as the energy of formation, we suggest that the investigated systems show solubility except for the  $(\text{Cr,Ti})_2\text{AlC}$  system. This conclusion is consistent with the published work where solubility within the system  $(\text{V},M)_2\text{AlC}$ , ( $M = \text{Ti and Cr}$ ) as well as a miscibility gap in the system  $(\text{Cr,Ti})_2\text{AlC}$  were experimentally observed [Schuster *et al.*, *J. Solid State Chem.* **32**, 213 (1980)].

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**I. INTRODUCTION**

In the 1960s, Nowotny reported the discovery of more than 100 carbides and nitrides.<sup>1</sup> Among them there are more than 30 so-called H- or Hägg phases with the common formula of  $M_2AX$ , where  $M$  is an early transition metal,  $A$  is a group IIIA or IVA element, and  $X$  is either C and/or N.<sup>1,2</sup> These  $M_2AX$  phases attract increasing interest owing to the combination of properties usually associated with metals and ceramics.<sup>2,3</sup> In general, they are good thermal and electrical conductors.<sup>3,4</sup> They exhibit a high modulus, and demonstrate high strength at high temperatures.<sup>3,5</sup> But they are relatively soft and exhibit a good machinability with conventional high-speed tools without lubrication,<sup>3</sup> and they demonstrate good thermal shock and oxidation resistance,<sup>3,6-8</sup> to name a few qualities. The unique properties of  $M_2AX$  phases make them technologically interesting materials.

A solid solution is one of the efficient ways to tune materials properties; however, most of the works on  $M_2AX$  in the literature focused on a single phase. The information on the mutual solubility among  $M_2AX$  phases is very limited, and no theoretical work on this issue is available. Within the  $M_2\text{AlC}$  system electronic structure calculations have been reported for  $\text{Ti}_2\text{AlC}$ ,<sup>9-11</sup>  $\text{V}_2\text{AlC}$ ,<sup>11</sup> and  $\text{Cr}_2\text{AlC}$ .<sup>11</sup> As far as we know, Pietzka and Schuster<sup>12</sup> reported the existence of  $\text{Ti}_2\text{AlC}_{0.8-x}\text{N}_x$  at 1490 °C, where  $x=0-0.8$ ; Schuster *et al.*<sup>13</sup> investigated the mutual solutions between  $\text{Ti}_2\text{AlC}$ ,  $\text{V}_2\text{AlC}$ , and  $\text{Cr}_2\text{AlC}$  by annealing series of powder mixtures in proportions 25, 50, and 75 mole % at 1000 °C for 170 h in evacuated sealed quartz tubes. Their experimental results showed that  $\text{V}_2\text{AlC}$  formed a complete series of mutual solutions with  $\text{Cr}_2\text{AlC}$  and  $\text{Ti}_2\text{AlC}$ , while the mutual solution series of  $\text{Ti}_2\text{AlC}-\text{Cr}_2\text{AlC}$  exhibited a miscibility gap which the authors attributed to the relatively high solubility of

$\text{Cr}_3\text{C}_2$  in  $\text{TiC}_{1-x}$  competing with the H-phase stability and the larger size difference of the metal atoms. Other solid solutions, such as  $(\text{Ti,V})_2\text{SC}$  (Ref. 14) and  $(\text{Nb,Zr})_2\text{AlC}$ ,<sup>15</sup> were also reported to exist, but no systematic theoretical study has been made so far.

In this paper we have investigated in detail the mutual substitutions of the transition metals in  $M_2\text{AlC}$  phases for the neighboring elements, Ti, V, and Cr by means of *ab initio* total energy calculations. The aim of the present work is to theoretically investigate the solubility between  $M_2\text{AlC}$  with the transition metals in  $3d$ , and contribute to a better basic understanding of this fascinating class of materials. The rest of the paper is organized as follows: in Sec. II, we present the calculation methods and structure constructions. Results and discussions are given in Sec. II, and the conclusions are drawn in Sec. IV.

**II. CALCULATION METHODS AND STRUCTURE CONSTRUCTIONS**

Our calculations are based on the density functional theory, using the so called VASP (Refs. 16 and 17) program package in conjunction with Generalized-gradient approximations projector augmented wave potentials.<sup>18,19</sup> We used the following parameters in our calculations: The relaxation convergence for ions was  $1 \times 10^{-4}$  eV and the electronic relaxation convergence was  $1 \times 10^{-5}$  eV. There was also a conjugate gradient optimization of the wave functions, a reciprocal-space integration with a Monkhorst-Pack scheme,<sup>20</sup> an energy cutoff of 500 eV, a  $k$ -point grid of  $9 \times 9 \times 9$ , and a tetrahedron method with Blöchl corrections used for the energy.<sup>19</sup>

To study the solution structures, we first optimized the structures of  $\text{Ti}_2\text{AlC}$ ,  $\text{V}_2\text{AlC}$ , and  $\text{Cr}_2\text{AlC}$  to get the equilib-

TABLE I. Cell parameters, the bulk moduli calculated from equation of states, as well as the optimized free internal parameter,  $z(M)$ . Herein  $a$  and  $c$  are the lattice constants. ( $\text{\AA}$ ),  $V_0$  ( $\text{\AA}^3$ ),  $B$  (GPa), and  $B'$  are the equilibrium volume, the bulk modulus, and its pressure derivative, respectively.

Phases	$a$	$c$	$c/a$	$V_0$	$B$	$B'$	$z(M)$
Ti <sub>2</sub> AlC	3.062	13.673	4.465	111.04	166	4.13	0.084
Ref. 13	3.052	13.64	4.469	110.03			
Ti <sub>1.5</sub> V <sub>0.5</sub> AlC	3.022	13.547	4.483	107.11	178	4.65	0.089
Ref. 13	3.011	13.510	4.487	106.07			
TiVAlC	2.979	13.471	4.522	103.53	185	4.22	0.085
Ref. 13	2.975	13.393	4.502	102.65			
Ti <sub>0.5</sub> V <sub>1.5</sub> AlC	2.949	13.298	4.509	100.17	194	4.23	0.084
Ref. 13	2.927	13.277	4.536	98.13			
V <sub>2</sub> AlC	2.925	13.105	4.480	97.11	203	4.24	0.083
Ref. 13	2.909	13.127	4.512	96.20			
V <sub>1.5</sub> Cr <sub>0.5</sub> AlC	2.908	12.954	4.455	94.86	209	4.24	0.083
Ref. 13	2.903	13.054	4.496	95.27			
VCrAlC	2.888	12.847	4.448	92.80	215	4.22	0.084
Ref. 13	2.893	12.970	4.483	94.00			
V <sub>0.5</sub> Cr <sub>1.5</sub> AlC	2.866	12.777	4.458	90.90	221	4.24	0.085
Ref. 13	2.873	12.928	4.500	92.41			
Cr <sub>2</sub> AlC	2.848	12.722	4.467	89.37	226	4.25	0.084
Ref. 13	2.854	12.82	4.492	90.43			
Cr <sub>1.5</sub> Ti <sub>0.5</sub> AlC	2.900	12.930	4.458	94.19	209	4.21	0.078
Ref. 13	2.901	13.105	4.517	95.51			
CrTiAlC	2.951	13.184	4.468	99.40	192	4.27	0.085
Ref. 13	—	—	—	—			
Cr <sub>0.5</sub> Ti <sub>1.5</sub> AlC	3.010	13.407	4.454	105.15	181	4.11	0.086
Ref. 13	3.041	13.593	4.470	108.86			

rium volume,  $c/a$  ratio and hence the lattice constants as given in Sun *et al.*<sup>11</sup> The atomic positions used in the present work are identical to the ones in Ref. 9, while the position for Al in Refs. 10 and 11 are not supported by experimental diffraction data.<sup>21–23</sup> We then constructed the supercells to get 25, 50, and 75 at. % of  $M_2$ AlC in  $M'_2$ AlC, where  $M$  and  $M'$  are Ti, V, Cr, but  $M \neq M'$ . Cell sizes of eight, 16, and 32

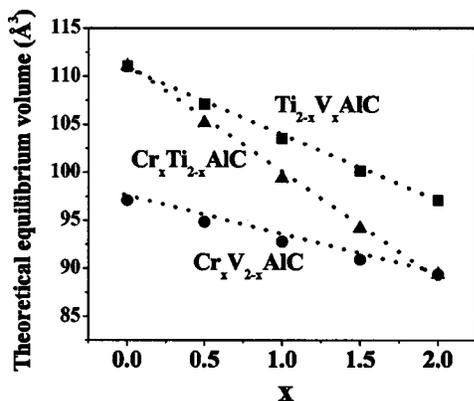


FIG. 1. The calculated values of equilibrium volume as a function of the solution contents for  $(M_xM'_{2-x})$ AlC, with  $M$  and  $M'$  = Ti, V, and Cr.

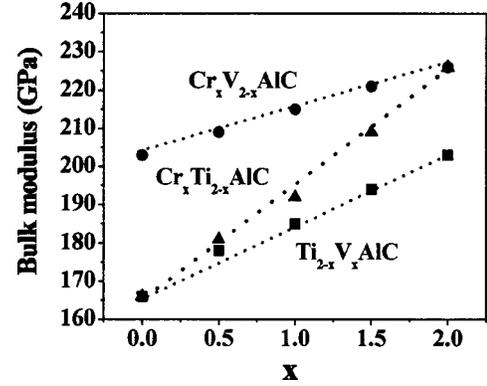


FIG. 2. The theoretical bulk moduli of  $(M_xM'_{2-x})$ AlC as function of solution content  $x$ .

atoms were used to test the size effect on the total energy. The cohesive energy difference between the eight- and 16-atom cells was around 0.007 eV/atom, while that between the 16- and 32-atom cells was around  $\sim 10^{-4}$  eV/atom. We therefore used the 16-atom supercell (2xc) for the present calculations. The supercells were fully relaxed and then followed by the total energy calculations at various cell volumes with the  $P6_3/mmc$  symmetry. The calculated data were then fitted to the third-order Birch-Murnaghan's equations of states (B-M EOS) (Ref. 24) to extract the equilibrium volume ( $V_0$ ), the bulk modulus ( $B$ ), and its pressure derivative ( $B'$ ). We have also optimized the  $c/a$  ratios and the free internal parameters,  $z(M)$ . Finally, the static total-energy calculations have been made for the constituents in their respectively equilibrium structures to evaluate the cohesive ( $E_{\text{coh}}$ ) energy and hence the energy of formation.

### III. RESULTS AND DISCUSSIONS

#### A. Equilibrium volume and bulk modulus calculated from equation of states

The calculated values of the equilibrium volume, lattice parameters, the experimental data, as well as the  $z(M)$  parameter are given in Table I.

Our estimated equilibrium volume and the lattice parameters ( $c/a$  ratio) agree well with the experimental data; the

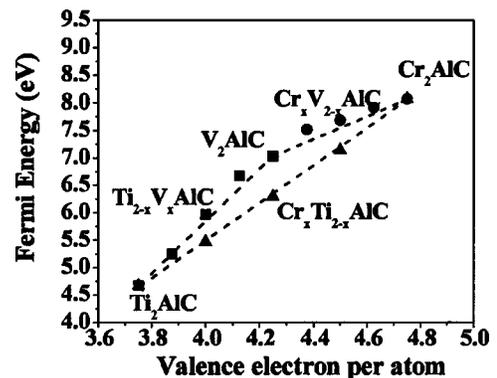


FIG. 3. The calculated Fermi energy of  $(M_xM'_{2-x})$ AlC as function of valence electrons per atom; here  $x$  is from 0 to 2.

deviations are within  $\pm 4\%$  and  $\pm 1.3\%$ , respectively. Figure 1 shows the calculated values of equilibrium volume as a function of substitution contents of the second transition metal for  $(M_xM'_{2-x})\text{AlC}$ . It is seen that the volume varies close to linearly with varying the substitution content of the second transition metal.

The bulk modulus of the  $(M_xM'_{2-x})\text{AlC}$  as a function of  $x$  is shown in Fig. 2. Note that the bulk modulus of  $(M_xM'_{2-x})\text{AlC}$  varies approximately linearly with a varying substitution content between the two end  $M_2\text{AlC}$  phases. As  $x$  is varied from 0 to 2 the bulk modulus of the solution can be varied by 36% from 166 to 226 GPa, which may be interpreted by a bond filling model as indicated in Fig. 3, showing the Fermi energy ( $E_F$ ) of the solution compounds as a function of valence electrons per atom. We see that, taking  $\text{Cr}_x\text{V}_{2-x}\text{AlC}$  as an example and starting from  $\text{V}_2\text{AlC}$ ,

the gradual substitution of V by Cr introduces extra valence electrons per atom, and correspondingly  $E_F$  moves to a higher energy level, which means that the increased extra valence electrons fill in the  $p$ - $d$  hybridized bonding states. Consequently, the filling of bonding orbital increases the bond strength and thereby bulk moduli. The same is true for both  $\text{Cr}_x\text{Ti}_{2-x}\text{AlC}$  and  $\text{V}_x\text{Ti}_{2-x}\text{AlC}$  solid solutions. Based on the results we suggest that theoretically it is possible to tune the  $(M_xM'_{2-x})\text{AlC}$  phases to get desirable mechanical properties.

### B. Formation of energy and density of states

To study the relative phase stabilities, we have calculated the energy of formation for  $(M_xM'_{2-x})\text{AlC}$ . The energy of formation per atom is defined as

$$E_{\text{form}} = \frac{E_{\text{total}}[(M_xM'_{2-x})\text{AlC}] - 4xE_{\text{coh}}(M) - 4(2-x)E_{\text{coh}}(M') - 4E_{\text{coh}}(\text{Al}) - 4E_{\text{coh}}(\text{C}_{\text{graphite}})}{16},$$

where  $4x$ ,  $4(2-x)$  and  $4$  are the number of  $M$ ,  $M'$ , Al, and C atoms used in the supercell, with the total energy of the metals calculated in the bcc structure (hcp structure for Ti),  $E_{\text{coh}}$  is the cohesive energy per atom. The energy of formation for  $(M_xM'_{2-x})\text{AlC}$  at 0 K as a function of substitution content is shown in Fig. 4, where the dotted lines show the sum of the energies of formation of the two end  $M_2\text{AlC}$  phases at various contents. The energies of formation of the solid substitutions,  $\text{V}_x\text{Ti}_{2-x}\text{AlC}$ , are below the dotted line, suggesting that the solution compounds are more stable than the correspondingly physical mixtures of the two  $M_2\text{AlC}$  phases. In other words,  $\text{V}_x\text{Ti}_{2-x}\text{AlC}$  might exist as one solution compound other than a physical mixture of  $0.5x$   $\text{V}_2\text{AlC}$  and  $[(1-0.5x)]$   $\text{Ti}_2\text{AlC}$  (with  $0 < x < 2$ ). Therefore, a complete series of mutual solutions of  $\text{Ti}_2\text{AlC}$  with  $\text{V}_2\text{AlC}$  might be expected. The same is true for  $\text{Cr}_x\text{V}_{2-x}\text{AlC}$ . The energies of formation for  $\text{Cr}_x\text{Ti}_{2-x}\text{AlC}$  are on the dotted line,

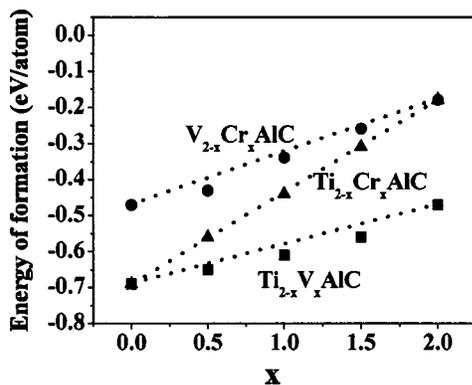


FIG. 4. The calculated formation energy as a function of the solution contents for  $(M_xM'_{2-x})\text{AlC}$ , with  $M$  and  $M' = \text{Ti}, \text{V}$ , and  $\text{Cr}$ .

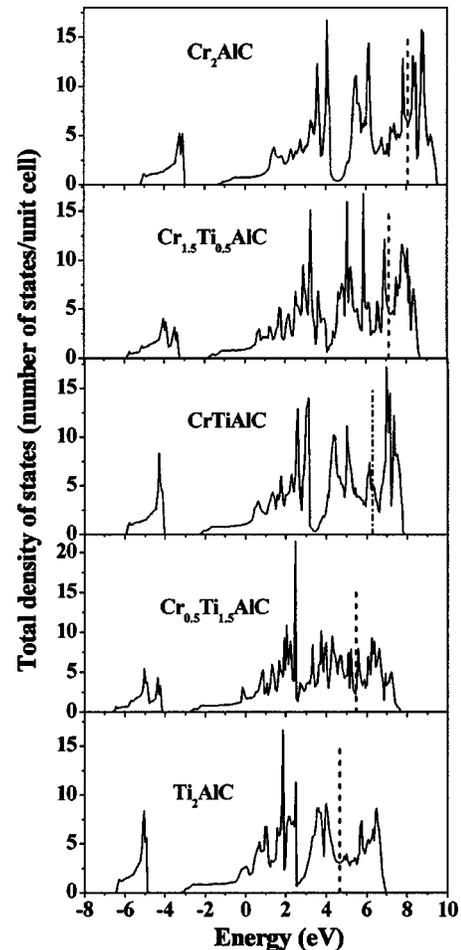


FIG. 5. The total density of states of  $\text{Cr}_x\text{Ti}_{2-x}\text{AlC}$ ; the dotted line shows the position of  $E_F$ .

indicating that these solid solutions could be metastable. The metastability of  $\text{Cr}_x\text{Ti}_{2-x}\text{AlC}$  might be explained by the larger atomic size and valence electrons difference between Cr and Ti.

To further understand the  $\text{Cr}_x\text{Ti}_{2-x}\text{AlC}$  system, in Fig. 5 we show the total density of states. Note that from  $\text{Ti}_2\text{AlC}$  at the bottom,  $E_F$  moves to higher energy level with increasing Cr content. The  $E_F$  of both  $\text{Cr}_{0.5}\text{Ti}_{1.5}\text{AlC}$  and  $\text{Cr}_{1.5}\text{Ti}_{0.5}\text{AlC}$  falls at one pseudogap between the bonding and antibonding/nonbonding states, while that of  $\text{CrTiAlC}$  lies at one peak position. As a rule of thumb, the compound might be stable if its  $E_F$  falls on the pseudogap which separates bonding states from the antibonding/nonbonding states, while it might be unstable or metastable if its  $E_F$  lies at the peak position.<sup>25</sup> From this point of view, both  $\text{Cr}_{0.5}\text{Ti}_{1.5}\text{AlC}$  and  $\text{Cr}_{1.5}\text{Ti}_{0.5}\text{AlC}$  could be observed, while  $\text{CrTiAlC}$  would not exist. This is consistent with the experimental results of Schuster *et al.*<sup>15</sup>

#### IV. CONCLUSIONS

In summary we have studied the solid substitutions of  $(M_xM'_{2-x})\text{AlC}$ , where  $M$  and  $M' = \text{Ti}, \text{V},$  and  $\text{Cr}$ , by means

of *ab initio* total energy calculations. Our calculated values of the equilibrium volume and  $c/a$  ratios agree well with the experimental results (within  $\sim \pm 4\%$  and  $\sim \pm 1.3\%$ , respectively). The bulk moduli of  $(M_xM'_{2-x})\text{AlC}$  can be varied by 36% from 166 to 226 GPa as the chemical composition  $x$  is varied from 0 to 2, which can be explained by the filling of the  $p-d$  hybridized bonding states. The results of our energy of formation calculation and total density of states analysis are consistent with the experimentally observed complete solubility in the system  $(\text{V},\text{M})_2\text{AlC}$ , with  $M = \text{Ti}$  and  $\text{Cr}$ , and the miscibility gap in the system of  $(\text{Cr},\text{Ti})_2\text{AlC}$ . Based on the present calculations, we suggest that it is possible to tune the elastic properties of the here studied  $M_2AX$  phase.

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