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# Intercalation of Al into *M*C (*M* = Ti, V, Cr)

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## Abstract

The energetics of point defects and twins in $MC_x$ ($x<1$, $M$ = Ti, V, Cr, space group $Fm\bar{3}m$) was studied using density functional theory. Our goal is to contribute towards understanding the underlying atomic mechanisms enabling the Al intercalation into $MC_x$. As the valence electron concentration is increased by substituting Ti in $TiC_x$ with V and further with Cr, the energy of formation for C vacancies is decreased. This may be understood based on the electronic structure. Upon increasing the valence electron concentration, the bonding becomes less ionic and more covalent. In covalent crystals, directional bonding may be rearranged and local relaxation is observed upon vacancy creation, while this gives rise to repulsive Coulomb forces in ionic crystals, and hence the energy of formation is expected to decrease as the valence electron concentration of $M$ is increased. The difference between the energy of formation for an Al substitution at a C site and a C vacancy, the migration energy for Al, the point defect ordering energy, and the twin boundary energy may be overcome, for instance, during vapor phase condensation. These results may be of general relevance for the formation of MAX phases (space group $P6_3/mmc$) at low temperatures.

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*Keywords:* Carbides; Defects; Density functional theory

## 1. Introduction

Transition metal carbides exhibit many striking properties. They are known to be refractory solids,[1] possess large stiffness[2–4] and relatively low chemical reactivity,[1] as well as they are good thermal conductors.[5] However, the intrinsic brittleness is limiting their application potential.[6] The design of transition metal carbide/metal composites is one possibility to address the brittleness challenge.[7] In conch shells[8] and lobster cuticles,[9] biomineral composites of hard and soft phases may result in ductility and the arrest of cracks. The discovery of the so-called $M_{n+1}AX_n$ phases (space group $P6_3/mmc$), where layers of transition metal carbides or nitrides ($M_{n+1}X_n$) are interleaved with A-layers (mostly IIIA and IVA elements, such as Al or Si),[10–12] also provides a way to address the brittleness challenge discussed above. Owing to this particular nanolaminated atomic arrangement, these ternary derivatives of transition metal carbides or nitrides exhibit a combination of metallic and ceramic properties, ranging from machinability, large stiffness, good conductivity of heat and electricity, and good thermal shock resistance, to good corrosion resistance.[10]

A seemingly natural pathway to form these ternary phases is intercalation, for instance known to be successful for graphite.[13,14] In a recent study, this pathway has been utilized by Riley and Kisi[15] and they have demonstrated that $Ti_3AlC_2$ can be synthesized by the rapid intercalation of Al into $TiC_{0.67}$ (space group $Fm\bar{3}m$). The notion that $M_{n+1}AX_n$ phases can be formed by intercalating A-group elements into $M_{n+1}X_n$ has been introduced by Zhou and coworkers.[16,17] Riley and Kisi have suggested that, after the ingress of molten Al into $TiC_{0.67}$, vacancy ordering facilitates the formation of $Ti_3AlC_2$.[15] Similar pathways might be viable for the formation of $Ti_3SiC_2$ as well.[18] In a previous work,[19] we have studied the energetics of point defects at a C site in $TiC_x$ ($x<1$): C vacancies and Al substitution at a C site. We have found minute energy differences for incorporation of Al at a vacant C site.[19] Our data indicate that $Ti_3AlC_2$ is formed by Al surface ingress into $TiC_x$ and C vacancy ordering.[19] Furthermore, it is also known that both Al and Si promote twinning in $TiC_x$, which is another prerequisite to form $M_{n+1}AX_n$ phases.[20] The ability to form twins and the relevance thereof for the formation of $M_{n+1}AX_n$ phases has not been considered theoretically. Furthermore, there is no systematic study

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available in literature exploring theoretically the possibility to form other $M_{n+1}AX_n$ phases than $Ti_3AlC_2$ by intercalation.

In this work, we study the energetics of point defects and twins in $MC_x$ ($x<1$, $M$ = Ti, V, Cr, space group $Fm\bar{3}m$) using *ab initio* calculations. In particular, we evaluate C vacancies, Al substitution at a C site, ordering of C vacancies with and without Al, migration of Al in the $MC_x$ lattice, as well as twin boundary energy with and without Al. Our ambition is to contribute towards understanding the underlying atomic mechanisms enabling the Al intercalation into $MC_x$. We show that the difference between the energy of formation for an Al substitution at a C site and a C vacancy in bulk $MC_x$ and on $MC_x$(1 0 0), the migration energy, the point defect ordering energy, and the twin boundary energy may be overcome, for example, during vapor phase condensation. Based on this study, it is reasonable to assume that intercalation of Al into $MC_x$ ($M$ = V, Cr) is realizable.

## 2. Theoretical methods

Density functional theory was used herein,[21] as implemented in the Vienna *ab initio* simulation package (VASP), where the projector augmented wave potentials with the generalized-gradient approximation are employed.[22] The following settings were employed: the total energy convergence criterion of 0.01 meV, Blöchl corrections for the total energy,[23] a cut-off of 500 eV, and integration in the Brillouin zone according to Monkhorst-Pack[24] with 262144 grid points in the FFT-mesh. Spin polarization was tested for CrC and only negligible energy corrections were found. $M$C 2 × 2 × 2 supercells, built of 64 atoms, were relaxed with respect to atomic positions and cell volumes. Since there were no local structural relaxations beyond the second coordination shell, the calculations were found reliable with respect to the supercell size.[19] Vacancies and Al substitutions were always considered at C sites, except for the twinning energy studies where Al substituted $M$ elements as suggested previously,[20] which resulted in the following compositions: $MC_x$ ($x$ = 0.97 for single C vacancy, 0.91 for triple C vacancy, 0.97 and 0.91 for Al substitution, 0.94 for migration, 1.00 and 1.33 for twinning). It is also known that Al may substitute $M$ elements in these binary carbides.[25,26] However, according to Riley and Kisi[15] C vacancies are required to form $M_{n+1}AX_n$ phases by Al substitutions on C sites. Bulk moduli were obtained by fitting the energy-volume curves using the Birch-Murnaghan equation of states.[27] Two different reference points were used to evaluate the point defect data: isolated atoms[28] and chemical potentials.[28–30] Energy of formation ($E_V$ or $E_S$) for the vacancy or Al substitution at a C site, respectively, was calculated as follows:

$$E_V = \frac{E_{MC,V(C)} + nE_C - E_{MC}}{n}$$
$$E_S = \frac{E_{MC,S(Al)} + nE_C - E_{Al} - E_{MC}}{n} \qquad (1)$$

where $E_{MC,V(C)}$, $E_C$, $E_{MC}$, $E_{MC,S(Al)}$, and $E_{Al}$ are the total energy of $M$C with $n$ C vacancies, the total energy of isolated C (broken periodic boundary conditions) or its chemical potential (space group $Fd\bar{3}m$), the total energy of the defect-free $M$C, the total energy of $M$C with an Al substitution at a C site, and the total energy of isolated Al (broken periodic boundary conditions) or its chemical potential (space group $Fm\bar{3}m$), respectively. This method was used for dealing with the energetics of both bulk and surface point defects. Migration energy for Al in [1 1 0] direction was also calculated. There are several possible pathways for Al to move to a neighboring vacant site and a saddle point was identified in our previous work.[19] The migration energy was calculated by evaluating the energy difference between the displaced Al and the supercell with Al at its ideal site. In this procedure, Al was always quenched at its displaced position while all other atoms were fully relaxed. Twin boundary energy ($E_T$) was obtained as follows:

$$E_T = \frac{E_{MC,T} - E_{MC}}{2A}, \qquad (2)$$

where $E_{MC,T}$ and $A$ designate the total energy of the $M$C crystal containing two twin boundaries and area of the twin, respectively. For the twin boundary energy determination, supercells containing 16 atoms were used, as previously introduced by Yu et al.[20] The electronic structure was studied by evaluating electron density distributions[31] and effective charges.[32] The effective charge was calculated for $M$C unit cells by the Bader charge analysis applying the Henkelman code.[33,34] Core charges were added to the electron density distribution to verify the Bader regions.

## 3. Results and discussion

### 3.1. Structure and elastic properties

Table 1 contains the calculated data of the lattice parameters, the bulk moduli, the energy of formation for the point defects, the migration energy, and the twin boundary energy for $MC_x$ ($M$ = Ti, V, Cr). The following bulk configurations were considered: (i) one C vacancy, (ii) three C vacancies dispersed in the $MC_x$ lattice [(0,0,0), (1/4,3/4,0), (1/4,1/4,1/2)], (iii) three C vacancies ordered along the [1 1 0] direction [(0,0,0), (1/4,1/4,0), (1/2,1/2,0)], (iv) one Al substitution at a C site, (v) two C vacancies and one Al substitution dispersed in the $MC_x$ lattice [Al at (0,0,0), vacancies at (1/4,3/4,0), (1/4,1/4,1/2)], (vi) two C vacancies and one Al substitution ordered along the [1 1 0] direction [Al at (0,0,0), vacancies at (1/4,1/4,0), (1/2,1/2,0)], (vii) twins in pure $MC_x$, and (viii) twins in $MC_x$ with Al placed at the twin boundary. The migration energy for Al at the (0,0,0) site was calculated in the [1 1 0] direction. Finally, the following (1 0 0) surface configurations were examined: (i) one C surface vacancy and (ii) one Al substitution at a C surface site. The calculated lattice parameter for pure TiC, VC, and CrC differs by 0.2%, −0.3%, and 1.0%, respectively, from the experimental data,[35–37] which is in good agreement. Upon introducing point defects, the lattice parameter decreases for vacancies and increases for Al substitution, which is consistent with literature.[36–39] The calculated bulk modulus for pure TiC is 12.1% larger than the experimentally obtained value,[38] which is within the expected deviation for the exchange-correlation approximation used here. Minor changes in the bulk moduli are observed when C vacan-

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