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Phase stability of Ti₂AlC upon oxygen incorporation: A first-principles investigation

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The phase stability of Ti₂AlC upon oxygen incorporation has been studied by means of first-principles calculations. Recent experimental observations of this so-called MAX phase (M=early transition metal, A =A-group element, and X=C or N) show that the characteristic nanolaminated structure is retained upon oxygen incorporation, with strong indications of O substituting for C. Therefore, a solid solution of C and O on the carbon sublattice has been simulated by the so-called special quasirandom structure method. Through a developed systematic approach, the enthalpy of formation of $Ti_2Al(C_{1-x},O_x)$ has been compared to all experimentally known competing phases, and has been found favorable for all C to O ratios at the composition of the MAX phase. A negative isostructural formation enthalpy has also been predicted for $Ti_2Al(C_{1-x},O_x)$. Altogether, the results indicate that a large amount of oxygen, at least up to x=0.75, might be present in the Ti₂AlC MAX-phase structure without decomposition of the material into its competing phases. Furthermore, an effect of an increased oxygen content is a corresponding increase in the bulk modulus and a change in electronic properties. These results are of importance for further understanding and identification of possible composition range of the MAX-phase oxycarbide, and hence for the prospect of tuning the material properties by a varying incorporation of oxygen.

I. INTRODUCTION

Ti₂AlC belongs to the so-called MAX phases, which are nanolaminated ternary compounds with the general composition $M_{n+1}AX_n$ (n=1–3), where M is an early transition metal, A is an A-group element, and X is either carbon or nitrogen.[1,2] These compounds were discovered in the 1960s (Ref. [2]) and have during the last few years gained an increased attention as they exhibit a unique combination of both ceramic and metallic properties, such as high-temperature oxidation resistance,[1,3] good electrical and thermal conductivity,[4,5] machinability,[1,6] and excellent damage and thermal tolerance.[7] Hence, there is a variety of potential applications ranging from electrical contacts to high-temperature components in a reactive environment. The MAX-phase properties stem from its highly anisotropic hexagonal crystal structure with layers of octahedral edge sharing M atoms separated from each other by layers of A. The X atoms are placed on the octahedral interstitial position between the close-packed layers of M.

Characteristic MAX-phase properties are likely to change when impurities and defects are present in the structure. Of special interest in this work is the 211 MAX phase Ti₂AlC, seen in Fig. 1, which has been thoroughly studied both experimentally[8–28] and theoretically.[6,12,15,19,21,22,29–46] Experimentally, substitutional incorporation of elements on the Ti sublattice was studied by hot isostatic pressing of (Ti,Nb)₂AlC, where Ti and Nb were found to create a solid solution with a hardness in between what is reported for Ti₂AlC and Nb₂AlC.[15,26] Meng *et al.*[27] used the same procedure and found Ti₂AlC to be strengthened by substituting Ti with V to form a (Ti,V)₂AlC solid solution. Correspondingly, substitution of N on the C site, as investigated by use of hot isostatic pressing, resulting in a harder and more brittle material.[9,28] Theoretical studies based on *ab initio* calculations concern partial substitution of elements in Ti₂AlC.

Sun *et al.*[42] investigated the solubility of V and Cr in Ti₂AlC and found a miscibility gap for the (Cr,Ti)₂AlC system. Wang and Zhou investigated the elastic stiffness of Ti₂AlC upon partial substitution of V or Cr on the Ti sublattice, resulting in a bulk modulus in between those of the pure MAX phases, and c_{44} values varying with valence electron concentration.[46] The incorporation of defects in Ti₂AlC have also been studied, showing that introduction Ti, Al, or C monovacancies is possible, which is stated to be an effect of the material's tendency to redistribute electrons to maintain its phase stability.[43,45] Recently, Liao *et al.*[44] predicted that
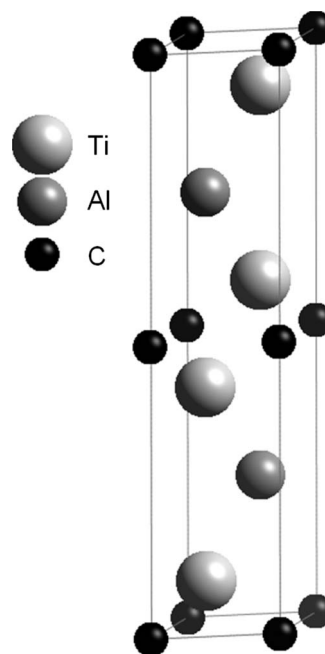

FIG. 1. Unit cell of Ti₂AlC.

impurities of O or N affect the Al vacancy formation energy in Ti$_2$AlC.

The few reports on defects in MAX-phase thin films mainly concern structural defects. Only recent studies have started focusing on (unintentional) impurity incorporation, and the effects thereof. However, recent experimental work on arc-deposited Ti$_2$AlC showed oxygen incorporation while maintaining the characteristic nanolaminated MAX-phase structure. There were also strong indications of O positioned on the C lattice positions.[47] Further evidence of O substituting for C have since then been presented based on electron-energy-loss spectroscopy and WIEN2K calculations,[48] and a new MAX-phase-related material, in part based on oxygen, is hence suggested. Motivated by these experimental findings we have used *ab initio* calculations to investigate the relative phase stability of Ti$_2$AlC upon oxygen incorporation in the form of a Ti$_2$Al(C,O) solid solution. Special care has been taken to treat the configurational degrees of freedom of such substitutionally disordered phases. This is achieved by usage of special quasirandom structures (SQS) method,[49,50] thus going beyond, in theoretical accuracy, all previous first-principles modeling of solid solutions in MAX phases. We have included the whole range of C to O ratios in Ti$_2$Al(C$_{1-x}$,O$_x$), including Ti$_2$AlO for the sake of completeness, although our main interest, as well as hitherto experimental work, has been focused on the C-rich regime. Furthermore we present a systematic scheme to search for the most critical combination of all known competing phases in terms of a linear optimization problem. Also investigated are the effects of oxygen on the MAX-phase properties, which is of importance since it gives an increased fundamental understanding of how material properties can be tuned by the incorporation of oxygen.

II. CALCULATION DETAILS

All calculations are based on the density-functional theory,[51] as implemented in the Vienna *ab initio* simulation package (VASP),[52,53] wherein the projector-augmented wave[54] method and the generalized gradient approximation[55] (GGA) for the exchange-correlation energy and one-electron potential are used. The convergence was 0.1 meV for the total energy. Reciprocal-space integration was performed within the Monkhorst-Pack scheme,[56] and plane-wave cutoff energy of 400 eV were used. A k-point grid of $23 \times 23 \times 7$ was used for the pure MAX-phases' ternaries (Ti$_2$AlC and Ti$_2$AlO) with unit cells containing eight atoms, and a grid of $5 \times 5 \times 5$ was used for the supercells of the quaternaries Ti$_2$Al(C$_{1-x}$,O$_x$), containing 128 atoms. These grids were
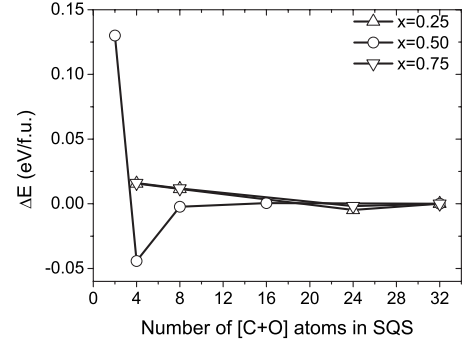

FIG. 2. Total energy per formula unit for Ti$_2$Al(C$_{1-x}$,O$_x$) SQS supercells of different size and with varying oxygen content x, relative to the 32 [C+O] atom cells.

chosen based on a convergence criterion below 0.05 meV per atom for the total energy as compared to, e.g., a $7 \times 7 \times 7$ k-point grid. The different structures were optimized with respect to cell volume, c/a ratio, and internal atomic positions.

An appropriate supercell needs to be chosen based on the criterion to mimic an atomic distribution in a random alloy. This is achieved by simulating a solid solution of C and O on the carbon sublattice by the so-called SQS method, as suggested by Zunger *et al.*,[49] and further extended by Alling *et al.*[57] The SQS method can briefly be described as a way of creating a structure with as many nearest-neighbor C-O bonds, next-nearest-neighbor C-O bonds, etc., as it should be in a completely random alloy. Hence, the method attempts to avoid *ad hoc* constructed supercells, which may lead to unpredictable results. Whether a supercell can be seen as random or not in the total-energy calculations is given by nature of the effective interactions in the system.[50,58] To accurately describe a random Ti$_2$Al(C$_{1-x}$O$_x$) system, supercells of different sizes were constructed for each composition x. The cell sizes varied from $1 \times 1 \times 1$ (two [C+O] atoms) up to $4 \times 2 \times 2$ (32 [C+O] atoms) unit cells. In Fig. 2 the total energy per formula unit of Ti$_2$Al(C$_{1-x}$O$_x$) is shown, relative to the 32 [C+O] SQS, for different cells with an oxygen content of $x = 0.25$, 0.50, and 0.75. A convergence in energy for the 32 [C+O] atom cell is evident. With increasing size of the supercell, the short-range order (SRO) parameters of the C-O sublattice can be optimized toward a random distribution of C and O, which for an ideal random alloy[50,57] are equal to zero. In Table I the SRO parameters of the method for SQS construction described in Ref. 57 are presented for the different supercells with 32 [C+O] atoms. The parameters are equal or close to zero for the first ten coordination

TABLE I. Short-range order (SRO) parameters for the C-O coordination shells, (Refs. 49 and 57) for Ti$_2$Al(C$_{1-x}$,O$_x$) supercells with 32 [C+O] atoms.

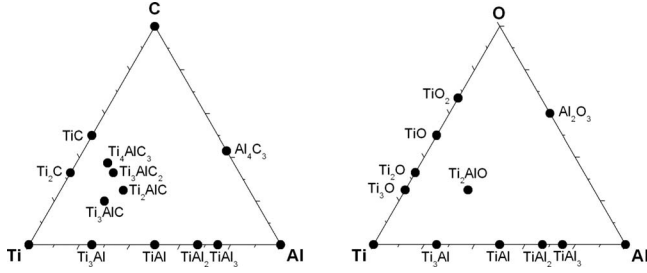| Fraction O	Shell									
	1	2	3	4	5	6	7	8	9	10
0.25, 0.75	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.11
0.50	0.00	0.00	0.00	0.00	0.00	0.00	−0.13	0.00	−0.08	0.00

FIG. 3. Phase diagram for Ti-Al-C (left) and Ti-Al-O (right) showing phases simulated in this work. Additional phases simulated, but not included in figure, are Ti$_2$Al(C$_{1-x}$,O$_x$) and Ti(C$_{1-x}$,O$_x$).

FIG. 4. Isostructural formation enthalpy of Ti$_2$Al(C$_{1-x}$,O$_x$) using Eq. (2).

shells. Therefore, all results presented for systems with $0.25 \leq x \leq 0.75$ will be based on the SQS containing 32 [C+O] atoms, if nothing else mentioned. The B1-Ti(C$_{1-x}$,O$_x$) solid solutions also included for comparison in the present work have been calculated using the SQS method and the structures presented in Ref. 57.

Both the dynamical and relative stabilities are of importance when discussing the stability of a specific compound. The dynamical stability is an intrinsic property where the energy of the system is at a minimum with respect to small perturbations of atomic positions. The relative stability is governed by the competition with other equilibrium phases in the system, which is the main focus of this work. A systematic search of the most competitive combination of phases at a given elemental composition b^{Ti}, b^{Al}, b^C, and b^O was performed using a linear optimization procedure of the form

$$\min E_{comp}(b^{Ti}, b^{Al}, b^C, b^O) = \sum_i^n x_i E_i, \qquad (1)$$

where x_i and E_i are the amount and energy of compound i, respectively, and E_{comp} is the energy we want to minimize subject to the constraints,

$$x_i \geq 0; \quad \sum_i^n x_i^{Ti} = b^{Ti}, \quad \sum_i^n x_i^{Al} = b^{Al},$$

$$\sum_i^n x_i^C = b^C, \quad \sum_i^n x_i^O = b^O.$$

Using Eq. (1) it is thus possible to find the combination of phases with lowest total energy as compared to, e.g., Ti$_2$AlC for which $b^{Ti}=2$, $b^{Al}=1$, $b^C=1$, and $b^O=0$. All energies are calculated for the equilibrium volume of each respective phase, thus setting the pressure-volume term of the enthalpies to zero.

In Fig. 3 all competing phases that have been included and simulated in this work can be found with the exception of the metal oxycarbides B1-Ti(C$_{1-x}$,O$_x$) and the quaternary phases Ti$_2$Al(C$_{1-x}$O$_x$). Included phases are all those found experimentally for systems containing Ti$_2$AlC, as given by, e.g., Refs. 18, 22, and 59, and those identified in phase diagrams for the Ti-Al-C (Refs. 60 and 61) and Ti-Al-O (Ref.
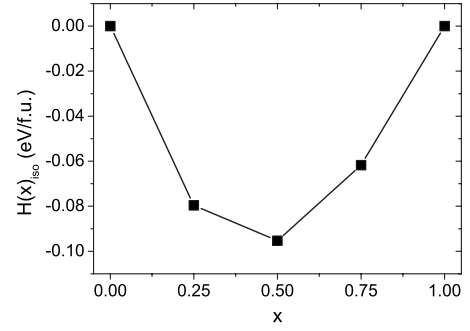
62) systems. In the latter, no Ti$_2$AlO phase can be found, and it is therefore treated as a hypothetical 211 MAX phase. It has previously been reported that oxidation of Ti$_2$AlC can result in formation of TiO$_2$ and Al$_2$O$_3$.[63] These compounds are included in the present investigation in the form of their low-temperature thermodynamically stable phase, serving as a "lowest energy" representation, and, as such, the most competitive phase. For TiO two structures has been calculated, B1-TiO and monoclinic TiO containing vacancies, (Ti$_5$Va$_1$)(O$_5$Va$_1$), according to Andersson *et al.*,[64] and references therein.

The effect of oxygen incorporation on the material properties was investigated by calculation of total density of states (TDOS). Furthermore, the bulk modulus was calculated by a least-squares fit of the volume energy using Birch-Murnaghan equation of states.[65]

III. RESULTS AND DISCUSSION

A. Phase stability of Ti$_2$AlC upon oxygen incorporation

In order to study the relative stability of Ti$_2$Al(C$_{1-x}$,O$_x$) in a systematic manner we first consider the stability with respect to its end products ($x=0$ and $x=1$) through the calculation of isostructural formation enthalpy $H(x)_{iso}$ as given by

$$H(x)_{iso} = E[\text{Ti}_2\text{Al}(\text{C}_{1-x},\text{O}_x)] - (1-x)E(\text{Ti}_2\text{AlC})$$
$$- xE(\text{Ti}_2\text{AlO}), \qquad (2)$$

where $E[\text{Ti}_2\text{Al}(\text{C}_{1-x},\text{O}_x)]$ is the total energy per formula unit of the SQS containing a fraction x of oxygen on the carbon sublattice, and where $E(\text{Ti}_2\text{AlC})$ and $E(\text{Ti}_2\text{AlO})$ are the total energy per formula unit of Ti$_2$AlC and Ti$_2$AlO, respectively. Note that all systems are considered to have underlying unit cell as shown in Fig. 1. The result is presented in Fig. 4 where it is clearly seen that the isostructural formation enthalpy is negative at all x, i.e., an indication of Ti$_2$Al(C$_{1-x}$,O$_x$) stability with respect to decomposition into its competing ternary phases. However, these latter phases need to be further investigated with respect to their decomposition.

The results from total-energy calculations of all competing phases are presented in Tables II and III, also including optimized structural parameters. The obtained energies are

TABLE II. Calculated total energies and lattice parameters for phases present in Ti-Al-C-O system. $Ti_2Al(C_{1-x},O_x)$ is not included.

Compound	Prototype	a (Å)	c (Å)	E (eV/f.u.)
Al_4C_3	$D7_1$	3.36	25.13	−43.340
Al_2O_3	Corundum	4.78	13.05	−37.477
Ti_3Al	$D0_{19}$	5.74	4.64	−28.153
TiAl	$L1_0$	3.98	4.08	−12.316
$TiAl_2$	Ga_2Hf	3.97	12.14	−16.538
$TiAl_3$	$D0_{22}$	3.84	4.31	−20.583
Ti_2C	$Ca_{33}Ge$	8.64		−26.583
TiC	B1	4.34		−18.529
$Ti(C_{0.75},O_{0.25})$	B1	4.33		−18.454
$Ti(C_{0.50},O_{0.50})$	B1	4.33		−18.219
$Ti(C_{0.25},O_{0.75})$	B1	4.32		−17.871
TiO	B1	4.29		−17.294
TiO	Monoclinic[a]			−17.732
Ti_3O		5.14	14.25	−33.818
Ti_2O	C6	3.96	2.63	−19.257
TiO_2	C4 (rutile)	4.66	2.97	−26.451
Al	A1	4.04		−3.745
C	A9 (graphite)	2.47	6.73	−9.215
Ti	A3	2.92	4.62	−7.762
Ti_3AlC	$CaTiO_3$ (perovskite)	4.18		−39.105
Ti_3AlC_2	Ti_3SiC_2 (312 MAX phase)	3.10	18.63	−49.884
Ti_4AlC_3	Ti_4AlN_3 (413 MAX phase)	3.09	23.61	−68.413

[a]Reference 64.

used for identification of possible energetically favorable phase combinations including also binaries and single element materials, as the Ti-Al-C and Ti-Al-O systems, followed by the quaternary Ti-Al-C-O system, are studied separately using Eq. (1).

Starting with the Ti-Al-C system, and hence Eq. (1) subject to the constraints $b^{Ti}=2$, $b^{Al}=1$, $b^{C}=1$, and $b^{O}=0$, (for Ti_2AlC), the combination of phases which gives the lowest energy are TiC and TiAl if ternaries are excluded. Including also ternaries, the most competitive candidates are Ti_3AlC_2 and TiAl. The formation enthalpy of Ti_2AlC can thus be calculated according to

$$H(x) = E(Ti_2AlC) - E(TiC) - E(TiAl) \qquad (3)$$

and

$$H(x) = E(Ti_2AlC) - \frac{1}{2}E(Ti_3AlC_2) - \frac{1}{2}E(TiAl) \qquad (4)$$

which is equal to −0.36 and −0.11 eV/f.u., respectively. This indicates that Ti_2AlC is stable with respect to decomposition into any of the competing phases.

Using the same procedure on the Ti-Al-O ternary system a similar result is found. The constraints for minimizing the energy, using Eq. (1), are $b^{Ti}=2$, $b^{Al}=1$, $b^{C}=0$, and $b^{O}=1$, (for Ti_2AlO). The most energetically favorable combination of binary or single element phases are TiAl and monoclinic vac-TiO, giving rise to an expression for the formation enthalpy of Ti_2AlO according to

$$H(x) = E(Ti_2AlO) - E(\text{vac-TiO}) - E(TiAl) \qquad (5)$$

with a result of −0.07 eV/f.u. Hence, also Ti_2AlO is stable with respect to decomposition into the competing phases. It should be noted that the formation enthalpy of Ti_2AlO with respect to its binaries is very small in contrast to Ti_2AlC, where the driving force to form the MAX phase is five times larger. Since the calculations are performed at 0 K, entropy effects may overtake this small energy at increasing temperatures. To experimentally revisit this so far hypothetical MAX phase at moderate temperatures is hence suggested. Also note that ternaries within the Ti-Al-O system seems somewhat less well explored as compared to the Ti-Al-C system, and no such phases to be included in this study have been identified.
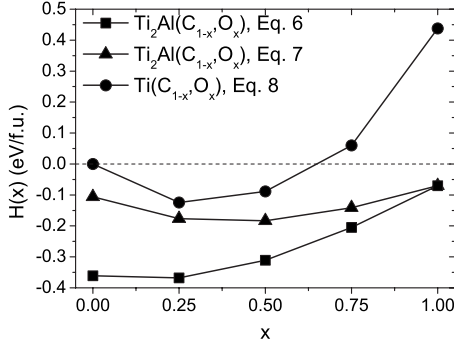
TABLE III. Experimental and theoretical values of equilibrium lattice parameters a and c, total energy E, volume V, and bulk moduli B for $Ti_2Al(C_{1-x},O_x)$.

x	a (Å)	c (Å)	E (eV/f.u.)	V (Å³/f.u.)	B (GPa)	Source
0.00	3.07	13.73	−31.206	56.02	140	This work
0.25	3.05	13.68	−31.014	54.97	145	This work
0.50	3.02	13.69	−30.757	53.94	151	This work
0.75	2.98	13.79	−30.452	52.97	155	This work
1.00	2.92	14.08	−30.118	52.04	161	This work
Ti_2AlC	3.06	13.6				Ref. 15. Experiment (EXAFS)
	3.04	13.59				Ref. 21. Experiment (XRD)
	3.056	13.62				Ref. 8. Experiment
	3.062	13.673			166	Ref. 42. Theory (VASP, GGA)
	3.053	13.640			137	Ref. 33. Theory (CASTEP, GGA)
	3.070	13.768			137	Ref. 35. Theory (WIEN2K, GGA)
	3.071	13.726			138	Ref. 40. Theory (VASP, GGA)

FIG. 5. Enthalpy of formation for $Ti_2Al(C_{1-x},O_x)$ using Eqs. (6) and (7), and for $B1-Ti(C_{1-x},O_x)$ using Eq. (8).

A most favorable combination of phases can be found also in the quaternary Ti-Al-C-O system, using Eq. (1) subject to the constraints $b^{Ti}=2$, $b^{Al}=1$, $b^C=1-x$, and $b^O=x$ where x is the oxygen content in $Ti_2Al(C_{1-x},O_x)$. The identified phases are, if only single elements and binaries are taken into account, TiAl, TiC, and vac-TiO. Including also ternaries, Ti_3AlC_2, TiAl and vac-TiO are the most competitive phases at all x. The formation enthalpy of $Ti_2Al(C_{1-x},O_x)$ can hence be calculated according to

$$H(x) = E[Ti_2Al(C_{1-x},O_x)] - (1-x)E(TiC) - xE(\text{vac-TiO})$$
$$- E(TiAl) \qquad (6)$$

and

$$H(x) = E[Ti_2Al(C_{1-x},O_x)] - \frac{1}{2}(1-x)E(Ti_3AlC_2)$$
$$- xE(\text{vac-TiO}) - \frac{1}{2}(1+x)E(TiAl) \qquad (7)$$

which for varying x results in curves as presented in Fig. 5. It should be noted that we have not taken into account the possibility of other (not yet identified) oxygen incorporated quaternaries such as $Ti_3Al(C,O)_2$ and $Ti_3Al(C,O)$. Moreover, rutile and alumina are the phases normally found in oxidation experiments when supply of oxygen are rather high.[63] In our case, simulating a condition where oxygen in strictly limited with respect to Ti and Al (and also C) the corresponding analysis for thermodynamic stability of $Ti_2Al(C_{1-x},O_x)$ at, e.g., $x=0.75$, in comparison with TiO_2, Al_2O_3, Ti_3Al, and Ti_3AlC gives a formation enthalpy of -0.37 eV/f.u., clearly marking the stability of the MAX phase oxycarbide. This is further supported by experimental observations of Al_2O_3 substrate decomposition upon TiC_x deposition, with resulting $Ti_2Al(C_{1-x},O_x)$ formation.[66] However, one should keep in mind that TiO_2 and Al_2O_3 are still the equilibrium products in the case of unlimited oxygen supply.

Since TiC and TiO are the binaries which are most likely present in the Ti-Al-C-O system, experimentally well-known metal oxycarbides, such as $B1-Ti(C_{1-x},O_x)$, might form. Its possible impact on the stability of $Ti_2Al(C_{1-x},O_x)$ can be obtained by replacing TiC and vac-TiO [through Eq. (1). identified as the most competing phases to also the ternary
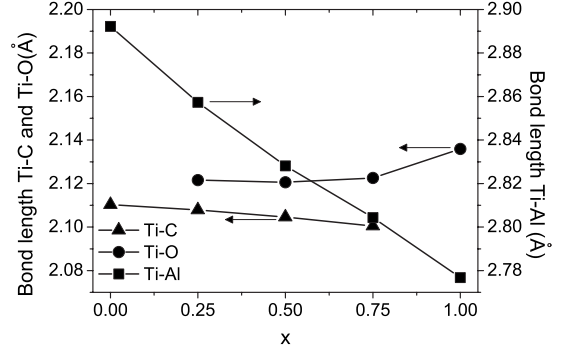
oxycarbide] in Eq. (6), where energetically favorable. Alternatively, the formation enthalpy of $Ti(C_{1-x},O_x)$ together with TiAl, at the MAX-phase composition 2:1:1, expressed as

$$H(x) = E[B1 - Ti(C_{1-x},O_x)] + E(TiAl) - (1-x)E(B1 - TiC)$$
$$- xE(\text{vac-TiO}) - E(TiAl) \qquad (8)$$

can be displayed together with Eqs. (6) and (7) in Fig. 5 [the form of Eq. (8) is chosen to simplify a direct comparison between Eqs. (6) and (8) through subtraction of the same set of phases]. The resulting graph shows that $Ti(C_{1-x},O_x)$ is stable with respect to decomposition into TiC and vac-TiO for x up to at least 0.5. However, since formation enthalpies of Eq. (8) are above those of Eq. (6) for all x, $Ti_2Al(C_{1-x},O_x)$ is the energetically favorable phase as compared to the metal oxycarbide $Ti(C_{1-x},O_x)$ in the presence of Al in the form of TiAl. Moreover, since the formation enthalpy of $Ti_2Al(C_{1-x},O_x)$, Eqs. (6) and (7), is negative for all x, it can be concluded that it is stable compared to all competing phases present in the Ti-Al-C-O system. This result strongly support the experimental findings of O incorporation into Ti_2AlC, and formation of $Ti_2Al(C_{1-x},O_x)$, apparently stable up to (at least) 900 °C.[47,48]

B. Structural parameters and properties of $Ti_2Al(C_{1-x},O_x)$

The calculated equilibrium values of the structural parameters of $Ti_2Al(C_{1-x},O_x)$ are presented in Table III together with the calculated bulk modulus. For $x=0$, i.e., for Ti_2AlC, the results are consistent with previously reported experimental and theoretical work. From the table it is evident that the lattice parameters change as oxygen is incorporated in Ti_2AlC with a decreasing as the oxygen content x increases and the lattice parameter c decreases for $x \leq 0.25$, followed by an increase up to $x=1.0$. Altogether this results in a volume decreasing linearly with increasing x. The average nearest-neighbor bond lengths of Ti-C, Ti-O, and Ti-Al are presented in Fig. 6. The change in bond length of Ti-C and Ti-O bonds is insignificant whereas the bond length of Ti-Al decreases almost linearly upon increasing O content, in total more than 0.1 Å. However, the hexagonal structure of the material is retained for all x.

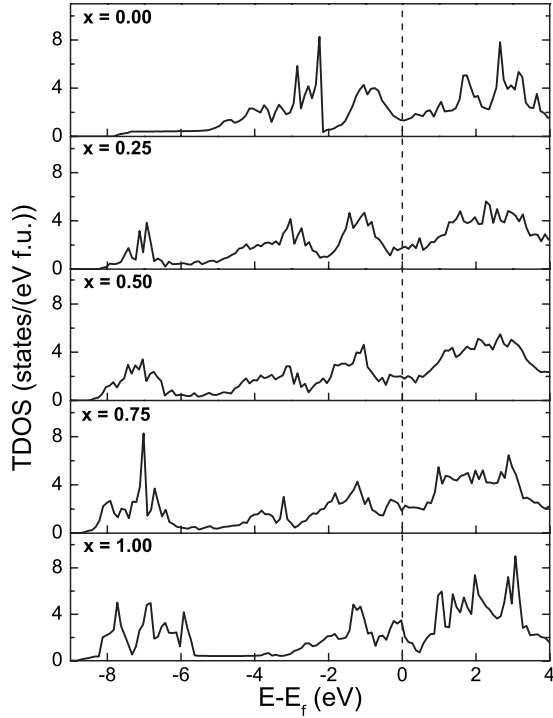Electronic-structure analysis was performed for $Ti_2Al(C_{1-x},O_x)$, presented in Fig. 7 as TDOS, for varying

FIG. 6. Calculated average bond length of Ti-C, Ti-O, and Ti-Al, as a function of oxygen content x in $Ti_2Al(C_{1-x},O_x)$.

FIG. 7. Calculated TDOS for $Ti_2Al(C_{1-x},O_x)$, for an increasing (from top to bottom) oxygen content, x. Dashed line indicates the Fermi energy.

FIG. 8. Number of states $N(E_f)$ at Fermi level E_f as a function of oxygen content x.

oxygen content x. The energy is given relative to the Fermi energy E_f. One can clearly see that the evolution of the electronic structure with increasing x shows nonrigid-band behavior. The spectral weight of states between -2 and -4 eV, corresponding to Ti d-C p hybrids, is decreasing while an increasing intensity due to primarily O p states is evident between -6 and -9 eV. Just below the Fermi level weak Ti d-Al p hybridization is observed. In Ti_2AlC a pseudogap between Ti d-C p and Ti d-Al p hybridizations is located at approximately -2 eV. As the oxygen content increases, the pseudogap is shifted to lower energies and at $x=0.75$ it is located at -3 eV.

For Ti_2AlC, the number of states $N(E_f)$ at the Fermi level E_f is located in a local minima which is consistent with a separation between bonding and antibonding states. As more O is added to the system more electrons are present, which results in an increased $N(E_f)$. For $x \leq 0.75$ E_f is in or close to a local minimum with $N(E_f)$ slowly increasing as O content increases, summarized in Fig. 8. For $x=1$, i.e., for Ti_2AlO, $N(E_f)$ has more then doubled compared to $x=0$ and exhibits a local maxima, which for some materials can be associated with a structural instability.[35] Whether or not the latter is valid for $Ti_2Al(C_{1-x},O_x)$ remains to be investigated. However, correlating this result to the calculated formation energies of $Ti_2Al(C_{1-x},O_x)$ in Fig. 5, where the quaternary is found to be stable at all x with respect to the most competitive combination of all considered phases, this work still suggests that $Ti_2Al(C_{1-x},O_x)$ should be stable up to (at least) $x=0.75$. Further studies on the electronic structure will presented elsewhere.

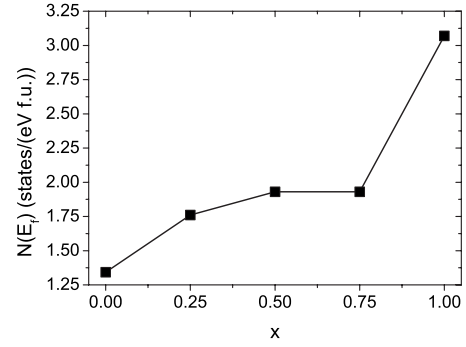The effect of oxygen on the mechanical properties is exemplified through calculations of bulk modulus, see Table III. An almost linear increase with increasing oxygen content x is evident, which means that the structure becomes more resistant against isotropic compression. This is an effect which can be correlated with the corresponding decrease in the Ti-Al bond lengths, as shown in Fig. 6.

Since no previous theoretical study of oxygen incorporation in Ti_2AlC has been reported, no direct comparison to our results is possible. In this work entropy terms have been neglected so no definite, conclusive predictions of phase stabilities at finite temperatures can be made. However, our result confirms the experimental observations of oxygen incorporation in Ti_2AlC,[47,48,66] and explains its formation and apparent stability even at elevated temperatures. It can also be noted that the disordered (in terms of oxygen substituting for carbon) MAX phase has a considerable configurational entropy which makes it more competitive at higher temperatures as compared to more ordered structures. According to the third law of thermodynamics, disordered phases cannot be the ground state at 0 K. This means that there should theoretically exist ordered $Ti_2Al(C,O)$ phases with lower energy than the solid solution. The search of such ground-state structures is beyond the scope of this work and besides ordering temperatures in related structures are reported to be below room temperature.[67]

IV. CONCLUSIONS

Through first-principles calculations, we have studied the phase stability of Ti_2AlC upon oxygen incorporation. A random distribution of oxygen on the carbon sublattice has been used, motivated by recent experimental identification of a new MAX-phase oxycarbide $Ti_2Al(C_{1-x}O_x)$. All experimentally known phases in the Ti-Al-C-O system have been taken into account for comparison, and our results show that a large amount of oxygen, at least up to $x=0.75$, may be present in the Ti_2AlC MAX-phase structure without decomposition of the material into its competing phases. Our study should not be directly related to experimental conditions where the supply of oxygen is unlimited, e.g., oxidation studies, since the present work focus on oxygen-included binary and ternary phases. An effect of an increased oxygen incorporation is a corresponding increase in the bulk modulus,

which can be correlated with indicated shorter and stronger Ti-Al bonds. The results of this study are of importance for identification of a range of possible elemental compositions in the MAX-phase oxycarbide, and hence for the possibility of tailoring the materials properties and expanding the use of Ti$_2$AlC in various applications. Furthermore, our developed systematic approach to investigate the phase stability of the MAX-phase material can be used also for a general material system.

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