PHYSICAL REVIEW B **80**, 214113 (2009)

Prediction of the stability of the $M_{n+1}AX_n$ phases from first principles

V. J. Keast, S. Harris, and D. K. Smith
School of Mathematical and Physical Sciences, The University of Newcastle, Callaghan, New South Wales 2308, Australia

(Received 15 June 2009; revised manuscript received 12 November 2009; published 18 December 2009)

One of the unusual features of the $M_{n+1}AX_n$ phases (where M is a transition metal, A is a group A element, X is carbon or nitrogen, and $n=1,2,3\ldots$) is that for a given M-A-X system, only certain values of n are found to occur and there is no systematic behavior between the different systems. Density-functional theory was used to verify the stability of the different phases by comparing their total energy to that of the appropriate competing phases. Five systems (Ti-Al-C, Ti-Si-C, Ti-Al-N, Ti-Si-N, and Cr-Al-C) were studied for $n=1-4$. Complete agreement with observed occurrences of these phases was found. Very small energy differences suggest that it may be possible to fabricate Ti_2SiC, Ti_2SiN, and Ti_3AlN_2 as metastable phases. None of the M_5AX_4 phases were predicted to occur and in all cases the α phases were found to be more energetically favorable than the β phases.

DOI: 10.1103/PhysRevB.80.214113 PACS number(s): 61.50.Lt, 61.66.Dk

I. INTRODUCTION

The existence of the so-called $M_{n+1}AX_n$ phases (where M is a transition metal, A is a group A element, X is carbon or nitrogen, and $n=1,2,3\ldots$) has been known for decades. The development of methods for phase-pure fabrication in both the bulk[1,2] and thin-film forms[3] has resulted in these materials receiving increased attention in recent years. Their unique combination of metallic and ceramic properties makes them of interest for possible applications in a variety of high-temperature applications or in other extreme environments. The usual compromise between high stiffness and good machinability does not need to be made for these materials. In addition the beneficial mechanical properties are maintained at high temperatures and the oxidation resistance is high. Some of the possible applications include but are not limited to: replacement in high-temperature applications for the Ni-based superalloys; wear and corrosion protection; heat exchangers; kiln components; and wear-resistant electrical contacts.[4]

This combination of metallic and ceramic properties arises from the crystal structure of these materials where ceramiclike M-X atomic layers with strong bonds are interleaved with A layers which are weakly bonded to M. As n increases, the number of M-X layers between the A layers increases as shown in Fig. 1. The space group is $P6_3/mmc$ and the atoms are located at the positions given in Table I. There is evidence that the M_3AX_2 and M_4AX_3 structures can occur with a different stacking of the layers—the α and β phases.[5–9] In addition, a mixture of alternating M_3AX_2 and M_4AX_3 or M_2AX layers have been observed in some samples.[10–15] No observations of M_5AX_4 structures have yet been reported and the stacking sequence, should it occur, is not known. The structure used in this paper is given in Table I which is consistent with the layer stacking found in the α phases, which are predominant.

One of the fascinating but rarely discussed aspects of this set of alloys is that, for a given M-A-X system, only certain values of n have been reported. For example, in the Ti-Si-C system, Ti_3SiC_2 is observed and Ti_2SiC is not whereas the opposite occurs in the Ti-Al-N system: Ti_2AlN is observed but Ti_3AlN_2 is not. There does not appear to be an obvious pattern or systematic behavior (see Table II) and this behavior has not yet been explained. It is not immediately clear why the insertion or removal of a transition-metal carbide or nitride layer should or should not be preferred in any particular system.

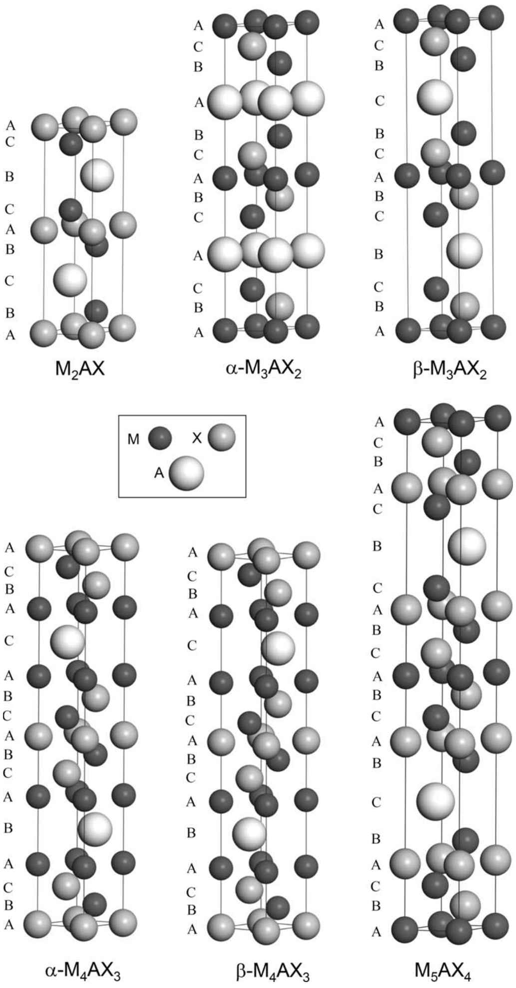

FIG. 1. Crystal Structures of the $M_{n+1}AX_n$ phases.

©2009 The American Physical Society

TABLE I. Atom positions (Wyckoff sites) for the $M_{n+1}AX_n$ phases.

M_2AX	$M(\frac{1}{3},\frac{2}{3},u)4f$		
	$A(\frac{2}{3},\frac{1}{3},\frac{1}{4})2d$		
	X (0,0,0) 2a		
α-M_3AX_2	$M1$ (0,0,0) 2a	β-M_3AX_2	$M1$ (0,0,0) 2a
	$M2(\frac{2}{3},\frac{1}{3},v)4f$		$M2(\frac{2}{3},\frac{1}{3},v)4f$
	$A(0,0,\frac{1}{4})2b$		$A(\frac{1}{3},\frac{2}{3},\frac{1}{4})2b$
	$X(\frac{1}{3},\frac{2}{3},u)4f$		$X(\frac{1}{3},\frac{2}{3},u)4f$
α-M_4AX_3	$M1(\frac{1}{3},\frac{2}{3},u)4f$	β-M_4AX_3	$M1(\frac{1}{3},\frac{2}{3},u)4f$
	$M2(0,0,w)4e$		$M2(0,0,w)4e$
	$A(\frac{1}{3},\frac{2}{3},\frac{1}{4})2c$		$A(\frac{2}{3},\frac{1}{3},\frac{1}{4})2c$
	$X1$ (0,0,0) 2a		$X1$ (0,0,0) 2a
	$X2(\frac{2}{3},\frac{1}{3},v)4f$		$X2(\frac{2}{3},\frac{1}{3},v)4f$
M_5AX_4	$M1$ (0,0,0) 2a		
	$M2(\frac{2}{3},\frac{1}{3},v)4f$		
	$M3(\frac{1}{3},\frac{2}{3},x)4f$		
	$A(\frac{2}{3},\frac{1}{3},\frac{1}{4})2d$		
	$X1(\frac{1}{3},\frac{2}{3},u)4f$		
	$X2(0,0.w)4e$		

Density-functional theory (DFT) has been used extensively to study the $M_{n+1}AX_n$ phases. These studies have included predictions of the structural parameters, formation energies, electronic structure, and elastic constants.[8,9,11,13,16–48] In general, good agreement with the available experimental data is observed; lattice parameters, elastic constants, and the electronic structure are well described. The DFT calculations have played an important role in understanding the origin of their unique physical properties. Despite the extensive number of calculations on this system of alloys, surprisingly little has been done to address the question of which of the possible phases can be expected to occur. The formation energy (the total energy minus the energy of the constituent elements) is usually found to be negative, favoring phase formation. However, this information alone is insufficient to predict the actual occurrence of the compounds. In order to answer this question, the calculated total energy must be compared to that of the competing phases as determined from the ternary phase diagrams. This process is necessary because, although a particular $M_{n+1}AX_n$ phase might be energetically favorable when compared to the starting elements, the phase will not be observed to occur if it is more energetically favorable to instead form two or more different compounds. The ternary phase diagrams can be used to identify which compounds may be observed instead. The few studies so far that have taken this approach have only had limited success when compared to the experimental observations.[13,18,49]

TABLE II. Reported occurrences of some of the $M_{n+1}AX_n$ phases (Ref. 4).

	M_2AX	M_3AX_2	M_4AX_3
Ti-Si-N	×	×	×
Ti-Al-N	✓	×	✓
Ti-Si-C	×	✓	✓[a]
Ti-Al-C	✓	✓	×
Cr-Al-C	✓	×	×

[a] Prepared using thin-film epitaxial growth (Ref. 13).

This paper uses DFT to calculate the energy of the $M_{n+1}AX_n$ phases of Table II and compares them to the energies of the appropriate competing phases as obtained from the ternary phase diagrams. Both the α and β structures are considered as are the M_5AX_4 structures.

II. COMPUTATIONAL METHODS

In order to calculate the phase stability for each of the $M_{n+1}AX_n$ alloys the competing phases involved must be identified. This was achieved through the use of the experimentally determined ternary phase diagrams in the literature.[50–53] The position of the $M_{n+1}AX_n$ alloys in the ternary diagram was determined and the competing phases identified from the nearby stable points on the diagram. The stoichiometry of the competing phases and the $M_{n+1}AX_n$ alloys was then used to derive the balance equations. In some cases there was some ambiguity about which set of competing phases to choose and so different combinations were considered. Some of these alternative combinations have been included in the results.

The DFT calculations were performed using the (linearized) augmented plane wave plus local orbitals method (L/APW+lo) within the WIEN2K software package.[54] The generalized gradient approximation (GGA) (Ref. 55) was used for the exchange-correlation potential. The plane-wave cutoff, defined by the product of the smallest atomic sphere radius times the magnitude of the largest reciprocal-lattice vector $R_{MT}K_{max}$, was set to 7.0 and a G_{max} (magnitude of the largest vector in the charge-density Fourier expansion) of 12 was used for all calculations. The atomic sphere radii (in Bohr) were taken as: Ti, Cr=1.9; Al, Si=1.8; and C=1.3; and N=1.5. They were kept constant for all calculations to ensure comparisons of total energy between different structures remained valid. The number of k points in the irreducible Brillouin zone was in the range of 80–150, depending on the size of the crystal cell. The number of k points was tested for convergence. Spin polarization was not included. The Ti-based systems are nonmagnetic and so spin polarization is unlikely to be significant. In the Cr-based systems the energy differences found here are quite large and the outcome in terms of phase stability is also unlikely to be influenced by the inclusion of spin polarization.

Structural optimizations were performed for all structures, including lattice parameters and internal coordinates (where applicable). Experimental structural parameters are available for many of the compounds in the calculations but not all. Calculated values must be used in order to ensure consistency between the results for all structures. Where optimization of several parameters was required, the optimization was cycled through the parameters until the changes in the total energy with optimization were too small to have any influence on the determination of phase stability. Usually two or three cycles were sufficient. The numerical value for the convergence criteria for both the structural parameters and the k points was usually better than 1–2 meV. This condition was slightly relaxed in some instances when the energy differences between the $M_{n+1}AX_n$ phase and the competing phases were on the order of 0.5 eV or greater.

III. RESULTS

Tables III and IV show the results for structural parameters and total energies of the competing phases and the $M_{n+1}AX_n$ phases, respectively. In all cases the structural parameters are in agreement with experimental data or previous calculations within the expected limits of accuracy of DFT. Table V shows the balance equations determined from the ternary phase diagrams for the systems of interest. The calculated energy difference ΔE between the $M_{n+1}AX_n$ phase (E_{MAX}) and the competing phases (E_{CP}) is derived from the results in Tables III and IV and is given in eV. Theoretical formation of a stable $M_{n+1}AX_n$ phase occurs when $\Delta E < 0$. With the exception of Ti_4SiC_3, the observed occurrences of the $M_{n+1}AX_n$ phases, as given in Table II, are confirmed by the calculations. In all cases the α structures are preferred over the β structures and no M_5AX_4 structures are predicted to occur.

IV. DISCUSSION

The calculations have had quite remarkable success in verifying the occurrences of the $M_{n+1}AX_n$ phases considered here. The success of the calculations is arguably greater than we might have anticipated, given that there are significant approximations in these kinds of DFT calculations. Firstly, the calculations are performed at 0 K and zero pressure: vibrational, entropy, and pressure effects are neglected. Secondly, kinetic effects are expected to play a significant role in whether a compound will occur. For example, it has been observed that intermediate phases are important in the bulk fabrication Ti_3SiC_2.[56,57] Finally, the calculations are unable to easily include the effect of vacancies, solid solutions, and nonstoichiometric alloys. It is possible that in some instances there will be a set of competing phases with a lower energy than those used. The V-Al-C system would be particularly challenging to study as the likely competing phases include a solid solution of Al in V up to 22% and a disordered ξ-VC_{1-x}.

The single exception to the success of the calculations is the result that Ti_4SiC_3 phase would not occur even though it has been observed in thin films. However, as it has not been observed by bulk fabrication methods, it is likely that the observed thin film Ti_4SiC_3 is a metastable phase. In this instance, our theoretical result is not in contradiction with the observation but serves to further emphasize the role that kinetic effects can sometimes play in experimental fabrication.

The phase stability in the Ti-Si-C system of $M_{n+1}AX_n$ phases has previously been studied by DFT.[13] In that work both the Ti_2SiC ($\Delta E = -0.008$ eV/atom) and Ti_4SiC_3 ($\Delta E = -0.029$ eV/atom) were calculated to occur. The main difference between their calculations and those presented here is that we have included Ti_5Si_3C as a competing phase. Here, we have found that Ti_2SiC would not occur, in agreement with experimental observation. Consistent with a previous study, β-Ti_3SiC_2 is not predicted to form.[9] We have also confirmed that the β-$M_{n+1}AX_n$ structures are not energetically preferred for any of the systems investigated here.

It should be noted that the differences in energy between the $M_{n+1}AX_n$ phases and the competing phases are sometimes very small and are close to the expected level of accuracy of the calculations. The very small theoretical energy differences for phase formation in some alloys and the experimental observation of a metastable Ti_4SiC_3 suggest the possibility that a number of phases, not previously observed, could also be fabricated as metastable phases. On the basis of our calculations, the phases that may warrant further efforts at thin-film fabrication are Ti_2SiC, Ti_2SiN, and Ti_3AlN_2.

The results suggest that the dominant contribution to the phase stability is the total electronic energy. It has not been necessary to include the effect of temperature to obtain agreement with the experimental occurrences of these phases. At first this might seem very surprising, given that fabrication of the alloys usually occurs at high temperature. However, the $M_{n+1}AX_n$ phases, once formed, are stable and do not decompose if they are slowly cooled. This supports the finding here that the role of temperature in the equilibrium phase stability is not large. For the systems considered in this work, the materials are highly ordered. For other systems, where nonstoichiometric and disordered compounds play a significant role, the temperature dependence of the ordering behavior would add an additional complication in the determination of phase formation.

In has been shown previously that the inclusion of temperature can change the stability from the α to the β phases in Ti_3SiC_2 and Ta_3AlC_2 for temperatures above 1000 K,[58,59] suggesting that calculations at elevated temperatures are necessary. However it should also be noted that it is the α phase that usually is fabricated. The β phase has been seen in electron microscopy images and is believed to be produced by transformation during sample preparation.[7] It may be possible to understand why it has not been necessary to include temperature in this work by recognizing that the local atomic arrangements and bonding in the $M_{n+1}AX_n$ phases and the competing phases are very similar (as opposed to the case for the α and β phases). As a consequence, the difference between the temperature dependence of the phonons is anticipated to be very small and so the influence of temperature on phase stability will also be small. Ideally, temperature effects should be included for highest accuracy calculations. However, this additional accuracy is computationally prohibitive for the 40+ compounds studied here. Such calculations may be of interest in the future to explore the decomposition behavior at high temperatures and the role of intermediate phases.

As n increases, the overall trend across each of the series studied here is that the formation of the $M_{n+1}AX_n$ phase becomes less energetically favorable. However the widespread validity of this observation remains in doubt. There are the notable exceptions of Ti_3SiC_2 and Ti_4AlN_3. In addition, if it were generally true, then we may expect that more M_3AX_2 than M_4AX_3 phases could be fabricated, in contradiction with

TABLE III. Results of the DFT calculations for all competing phases considered in this work. Optimized structural parameters and the total energy (per formula unit) are given.

	Space group	Lattice parameters (Å)	Atom positions	Total energy (Ry)
TiSi	*Pnma*	$a=6.57$ $b=3.64$ $c=4.98$	Ti$(0.177,\frac{1}{4},0.129)4c$ Si$(0.044,\frac{1}{4},0.647)4c$	−2287.8154
$TiSi_2$	*Fddd*	$a=8.29$ $b=4.81$ $c=8.58$	Ti$(\frac{1}{8},\frac{1}{8},\frac{1}{8})8a$ Si$(0.462,\frac{1}{8},\frac{1}{8})16e$	−2867.8992
TiN	*Fm*-3*m*	$a=4.25$	Ti (0,0,0) 4a N$(\frac{1}{2},0,0)4b$	−1817.4124
TiAl	*P*4/*mmm*	$a=2.82$ $c=4.06$	Ti (0,0,0) 1a Al$(\frac{1}{2},\frac{1}{2},\frac{1}{2})1d$	−2193.3292
$TiAl_3$	*I*4/*mmm*	$a=3.85$ $c=8.57$	Ti (0,0,0) 2a Al$(0,0,\frac{1}{2})2b$ Al$(0,\frac{1}{2},\frac{1}{4})4d$	−3164.6704
TiC	*Fm*-3*m*	$a=4.34$	Ti (0,0,0) 4a C$(\frac{1}{2},0,0)4b$	−1783.9685
Ti_3AlC	*Pm*-3*m*	$a=4.18$	Ti$(0,\frac{1}{2},\frac{1}{2})$3c Al (0,0,0) 1a C$(\frac{1}{2},\frac{1}{2},\frac{1}{2})1b$	−5684.9885
Ti_3AlN	*Pm*-3*m*	$a=4.12$	Ti$(0,\frac{1}{2},\frac{1}{2})3c$ Al (0,0,0) 1a N$(\frac{1}{2},\frac{1}{2},\frac{1}{2})1b$	−5718.4253
Ti_5Si_3N	$P6_3/mcm$	$a=7.43$ $c=5.16$	Ti1$(\frac{1}{3},\frac{2}{3},0)4d$ Ti2$(0.228,0,\frac{1}{4})6g$ Si$(0.591,0,\frac{1}{4})6g$ C (0,0,0) 2b	−10388.6114
Ti_5Si_3C	$P6_3/mcm$	$a=7.48$ $c=5.17$	Ti1$(\frac{1}{3},\frac{2}{3},0)4d$ Ti2$(0.231,0,\frac{1}{4})6g$ Si$(0.593,0,\frac{1}{4})6g$ C (0,0,0) 2b	−10355.1673
C	$P6_3/mmc$	$a=2.46$ $c=6.80$	C1$(0,0,\frac{1}{4})2b$ C2$(\frac{1}{3},\frac{2}{3},\frac{1}{4})2c$	−76.2065
Cr_2Al	*I*4/*mmm*	$a=2.97$ $c=8.51$	Cr (0,0,0) 2a Al (0,0,0.317) 4e	−4689.2085
Cr_3C_2	*Pnma*	$a=5.50$ $b=2.80$ $c=11.45$	Cr1$(0.018,\frac{1}{4},0.404)4c$ Cr2$(0.186,\frac{1}{4},0.774)4c$ Cr3$(0.867,\frac{1}{4},0.931)4c$ C1$(0.099,\frac{1}{4},0.204)4c$ C2$(0.237,\frac{1}{4},0.952)4c$	−6457.8084
Al_4C_3	*R*-3*m*	$a=3.36$ $c=25.10$	Al1 (0,0,0.294) 6c Al2 (0,0,0.130) 6c C1 (0,0,0) 3a C2 (0,0,0.217) 6c	−2171.2476

the current status in these materials. Further theoretical studies across more systems than the five studied here would be needed to decide whether this is a general trend with a few exceptions or not a trend at all.

Hug[22] has constructed scheme for discussion of likely formation of when $n=2$. As filling of the p states for the A atom increases the likelihood of phase formation decreases but with a number of exceptions. One of the most notable excep-

TABLE IV. Results of the DFT calculations for $M_{n+1}AX_n$ phases considered in this work. Optimised structural parameters and the total energy (per formula unit) are given.

	Lattice parameters (Å)	Internal parameters	Total energy (Ry)
Ti_2SiN	$a=2.99$ $c=12.88$	$u=0.092$	−4105.2276
α-Ti_3SiN_2	$a=2.99$ $c=17.84$	$u=0.069$ $v=0.136$	−5922.6369
β-Ti_3SiN_2	$a=2.96$ $c=18.09$	$u=0.068$ $v=0.136$	−5922.6214
α-Ti_4SiN_3	$a=3.00$ $c=22.58$	$u=0.055$ $v=0.109$ $w=0.160$	−7740.0482
β-Ti_4SiN_3	$a=2.99$ $c=22.87$	$u=0.055$ $v=0.107$ $w=0.159$	−7740.0288
Ti_5SiN_4	$a=2.99$ $c=27.71$	$u=0.045$ $v=0.089$ $w=0.133$ $x=0.176$	−9557.4561
Ti_2AlN	$a=2.99$ $c=13.64$	$u=0.085$	−4010.7842
α-Ti_3AlN_2	$a=3.00$ $c=18.49$	$u=0.068$ $v=0.129$	−5828.1954
β-Ti_3AlN_2	$a=2.99$ $c=18.67$	$u=0.067$ $v=0.128$	−5828.1832
α-Ti_4AlN_3	$a=3.00$ $c=23.51$	$u=0.054$ $v=0.106$ $w=0.154$	−7645.6191
β-Ti_4AlN_3	$a=2.98$ $c=23.60$	$u=0.054$ $v=0.105$ $w=0.154$	−7645.6078
Ti_5AlN_4	$a=3.00$ $c=28.44$	$u=0.043$ $v=0.087$ $w=0.130$ $x=0.170$	−9463.0186
Ti_2SiC	$a=3.06$ $c=12.84$	$u=0.092$	−4071.7936
α-Ti_3SiC_2	$a=3.08$ $c=17.74$	$u=0.072$ $v=0.135$	−5855.7713
β-Ti_3SiC_2	$a=3.05$ $c=18.09$	$u=0.071$ $v=0.133$	−5855.7474
α-Ti_4SiC_3	$a=3.08$ $c=22.70$	$u=0.053$ $v=0.112$ $w=0.160$	−7639.7389
β-Ti_4SiC_3	$a=3.06$ $c=23.06$	$u=0.053$ $v=0.110$ $w=0.158$	−7639.7142
Ti_5SiC_4	$a=3.08$ $c=27.66$	$u=0.045$ $v=0.088$ $w=0.136$ $x=0.175$	−9423.7051
Ti_2AlC	$a=3.07$ $c=13.64$	$u=0.084$	−3977.3373
α-Ti_3AlC_2	$a=3.08$ $c=18.61$	$u=0.068$ $v=0.127$	−5761.3155
β-Ti_3AlC_2	$a=3.07$ $c=18.83$	$u=0.069$ $v=0.126$	−5761.2994
α-Ti_4AlC_3	$a=3.08$ $c=23.51$	$u=0.052$ $v=0.108$ $w=0.155$	−7545.2811
β-Ti_4AlC_3	$a=3.07$ $c=23.71$	$u=0.051$ $v=0.107$ $w=0.153$	−7545.2644
Ti_5AlC_4	$a=3.08$ $c=28.56$	$u=0.044$ $v=0.085$ $w=0.132$ $x=0.170$	−9329.2486
Cr_2AlC	$a=2.84$ $c=12.70$	$u=0.085$	−4765.4734
α-Cr_3AlC_2	$a=2.86$ $c=17.42$	$u=0.070$ $v=0.129$	−6943.4396
β-Cr_3AlC_2	$a=2.86$ $c=17.51$	$u=0.070$ $v=0.127$	−6943.4331
α-Cr_4AlC_3	$a=2.89$ $c=22.04$	$u=0.055$ $v=0.108$ $w=0.152$	−9121.4140
β-Cr_4AlC_3	$a=2.89$ $c=22.08$	$u=0.055$ $v=0.108$ $w=0.151$	−9121.4072
Cr_5AlC_4	$a=2.88$ $c=26.83$	$u=0.044$ $v=0.089$ $w=0.134$ $x=0.170$	−11299.3779

tions to the general behavior in this system of alloys is the most widely studied material of Ti_3SiC_2. It is the only known $M_{n+1}AX_n$ phase with Si as the A element. It is also the only known system where $n>1$ occurs when $n=1$ does not. This suggests that Ti_3SiC_2 is unusually and unexpectedly stable.

The calculation of an energetically favorable phase formation in a system of alloys is not in itself an explanation of why one set of compounds is preferred over another. It is rare in the literature that the reasons why any particular arrangement of atoms is energetically favorable are discussed. Simple metallic or covalent models are available but are normally used to differentiate between crystal structures of the same composition not to compare an alloy with a combination of competing phases. In addition, simple and intuitive models that can be used for purely covalent or purely metallic systems are difficult to apply for the anisotropic and mixed bonding found in the $M_{n+1}AX_n$ phases. The uniqueness of the bonding in these materials gives them their unusual and beneficial properties but at the same makes them difficult to understand in terms of the conventional models for describing phase stability.

One of the motivations for this work was to see if it were possible to find any underlying principles or trends that could be used to predict phase formation for different value of n. To achieve this aim we have analyzed factors such as the valence charge density, bond distances, charge within the muffin-tin spheres, and the relative energy of features in the density of states. These analyses have, as yet, all failed to reveal any correlations or systematic behavior. In all cases the differences between all of these quantities is very subtle. This would suggest that verification and prediction of phase formation in this set of alloys will always require full DFT calculations. To explore this issue further, it would be desirable to quantitatively calculate bond energies for the different compounds. Unfortunately, the arbitrariness in the exact energy position in the calculations makes this task impossible. Within a calculation, all energies are with reference to a zero point that is defined as the average of the potential in the interstitial region. This does not influence the value of the total energy but makes the comparison of absolute energies between different structures difficult.

TABLE V. Balance equations used to determine the phase stability of the $M_{n+1}AX_n$ alloys and the energy difference, ΔE, between the $M_{n+1}AX_n$ phase (E_{MAX}) and the competing phases (E_{CP}). $\Delta E < 0$ implies a stable $M_{n+1}AX_n$ phase.

System	Balance equations	$\Delta E = E_{\mathrm{MAX}}$-$E_{\mathrm{CP}}$ (eV)
Ti-Si-N	$Ti_2SiN \leftrightarrow TiSi + TiN$ or	0.003
	$Ti_2SiN \leftrightarrow \frac{4}{5}TiN + \frac{1}{5}TiSi_2 + \frac{1}{5}Ti_5Si_3N$	0.061
	$Ti_3SiN_2 \leftrightarrow TiSi + 2TiN$ or	0.044
	$Ti_3SiN_2 \leftrightarrow \frac{9}{5}TiN + \frac{1}{5}TiSi_2 + \frac{1}{5}Ti_5Si_3N$	0.102
	$Ti_4SiN_3 \leftrightarrow TiSi + 3TiN$ or	0.061
	$Ti_4SiN_3 \leftrightarrow \frac{13}{5}TiN + \frac{1}{5}TiSi_2 + \frac{1}{5}Ti_5Si_3N$	0.119
	$Ti_5SiN_4 \leftrightarrow TiSi + 4TiN$	0.122
Ti-Al-N	$Ti_2AlN \leftrightarrow TiAl + TiN$ or	−0.580
	$Ti_2AlN \leftrightarrow \frac{2}{5}Ti_3AlN + \frac{1}{5}TiAl_3 + \frac{3}{5}TiN$	−0.443
	$Ti_3AlN_2 \leftrightarrow Ti_2AlN + TiN$ or	0.017
	$Ti_3AlN_2 \leftrightarrow \frac{1}{2}Ti_2AlN + \frac{1}{2}Ti_4AlN_3$	0.085
	$Ti_4AlN_3 \leftrightarrow Ti_2AlN + 2TiN$	−0.136
	$Ti_5AlN_4 \leftrightarrow Ti_4AlN_3 + TiN$	0.176
Ti-Si-C	$Ti_2SiC \leftrightarrow \frac{4}{9}Ti_3SiC_2 + \frac{1}{9}TiSi_2 + \frac{1}{9}Ti_5Si_3C$	0.014
	$Ti_3SiC_2 \leftrightarrow \frac{9}{5}TiC + \frac{1}{5}TiSi_2 + \frac{1}{5}Ti_5Si_3C$	−0.202
	$Ti_4SiC_3 \leftrightarrow Ti_3SiC_2 + TiC$	0.012
	$Ti_5SiC_4 \leftrightarrow Ti_3SiC_2 + 2TiC$	0.043
Ti-Al-C	$Ti_2AlC \leftrightarrow TiAl + TiC$ or	−0.540
	$Ti_2AlC \leftrightarrow \frac{2}{5}Ti_3AlC + \frac{1}{5}TiAl_3 + \frac{3}{5}TiC$	−0.364
	$Ti_3AlC_2 \leftrightarrow Ti_2AlC + TiC$	−0.131
	$Ti_4AlC_3 \leftrightarrow Ti_3AlC_2 + TiC$	0.039
	$Ti_5AlC_4 \leftrightarrow Ti_3AlC_2 + 2TiC$	0.052
Cr-Al-C	$Cr_2AlC \leftrightarrow Cr_2Al + C$ or	−0.795
	$Cr_2AlC \leftrightarrow \frac{8}{25}Cr_3C_2 + \frac{3}{25}Al_4C_3 + \frac{13}{25}Cr_2Al$	−0.498
	$Cr_3AlC_2 \leftrightarrow Cr_2AlC + \frac{1}{3}Cr_3C_2 + \frac{1}{3}C$ or	0.528
	$Cr_3AlC_2 \leftrightarrow \frac{9}{13}Cr_2AlC + \frac{7}{13}Cr_3C_2 + \frac{1}{13}Al_4C_3$	0.474
	$Cr_4AlC_3 \leftrightarrow \frac{5}{13}Cr_2AlC + \frac{42}{39}Cr_3C_2 + \frac{2}{13}Al_4C_3$	0.836
	$Cr_5AlC_4 \leftrightarrow \frac{1}{13}Cr_2AlC + \frac{21}{13}Cr_3C_2 + \frac{3}{13}Al_4C_3$	1.341

However, it may be anticipated that further studies across additional *M-A-X* series may prove more revealing. Systems based on Nb, Ta, Ga, and Ge are good candidates for further study. Given that this study of just five series required full structural optimization and energy minimization of over 40 compounds, the task ahead is quite challenging. In some cases, where the energy differences are quite small, considerable care and effort needs to be taken with the accuracy of the calculations.

V. CONCLUSION

DFT was used to calculate the total energy of $M_{n+1}AX_n$ phases and their competing phases as established from the ternary phase diagrams. Agreement with the observed stability of these phases was found in all cases. The α phases were found to be preferred over the β phases and M_5AX_4 phases are not expected. The results also suggest that Ti_2SiC, Ti_2SiN, and Ti_3AlN_2 have the potential to be produced as metastable compounds.

---

[1] M. W. Barsoum, D. Brodkin, and T. El-Raghy, Scr. Mater. **36**, 535 (1997).

[2] M. W. Barsoum and T. El-Raghy, J. Am. Ceram. Soc. **79**, 1953 (1996).

[3] J.-P. Palmquist, U. Jansson, T. Seppänen, P. O. Å. Persson, J. Birch, L. Hultman, and P. Isberg, Appl. Phys. Lett. **81**, 835 (2002).

[4] M. W. Barsoum, Prog. Solid State Chem. **28**, 201 (2000).

[5] M. W. Barsoum, L. Farber, I. Levin, A. Procopio, T. El-Raghy, and A. Berner, J. Am. Ceram. Soc. **82**, 2545 (1999).

[6] P. Eklund, J.-P. Palmquist, J. Howing, D. Trinh, T. El-Raghy, H. Högberg, and L. Hultman, Acta Mater. **55**, 4723 (2007).

[7] L. Farber, I. Levin, M. W. Barsoum, T. El-Raghy, and T. Tzenov, J. Appl. Phys. **86**, 2540 (1999).

[8] T. Liao, J. Wang, and Y. Zhou, J. Phys.: Condens. Matter **18**, 6183 (2006).

[9] J. Y. Wang and Y. C. Zhou, Phys. Rev. B **69**, 144108 (2004).

[10] H. Hogberg, L. Hultman, J. Emmerlich, T. Joelsson, P. Eklund, J. M. Molina-Aldareguia, J.-P. Palmquist, O. Wilhelmsson, and U. Jansson, Surf. Coat. Technol. **193**, 6 (2005).

[11] Z. Lin, M. Zhuo, Y. Zhou, Meishuan Li, and Jingyang Wang, J. Am. Ceram. Soc. **89**, 3765 (2006).

[12] Z. J. Lin, M. J. Zhuo, Y. C. Zhou, M. Li, and J. Wang, Acta Mater. **54**, 1009 (2006).

[13] J.-P. Palmquist, S. Li, P. O. A. Persson, J. Emmerlich, O. Wilhelmsson, H. Högberg, M. I. Katsnelson, B. Johansson, R. Ahuja, O. Eriksson, L. Hultman, and U. Jansson, Phys. Rev. B **70**, 165401 (2004).

[14] O. Wilhelmsson, J.-P. Palmquist, E. Lewin, J. Emmerlich, P. Eklund, P. O. Å. Persson, H. Högberg, S. Li, R. Ahuja, O. Eriksson, L. Hultman, and U. Jansson, J. Cryst. Growth **291**, 290 (2006).

[15] Y. Zhou, F. Meng, and J. Zhang, J. Am. Ceram. Soc. **91**, 1357 (2008).

[16] R. Ahuja, O. Eriksson, J. M. Wills, and B. Johansson, Appl. Phys. Lett. **76**, 2226 (2000).

[17] A. Bouhemadou, Physica B (Amsterdam) **403**, 2707 (2008).

[18] C. M. Fang, R. Ahuja, and O. Eriksson, J. Appl. Phys. **101**, 013511 (2007).

[19] C. M. Fang, R. Ahuja, O. Eriksson, S. Li, U. Jansson, O. Wilhelmsson, and L. Hultman, Phys. Rev. B **74**, 054106 (2006).

[20] B. Holm, R. Ahuja, and B. Johanssen, Appl. Phys. Lett. **79**, 1450 (2001).

[21] B. Holm, R. Ahuja, S. Li, and Börje Johansson, J. Appl. Phys. **91**, 9874 (2002).

[22] G. Hug, Phys. Rev. B **74**, 184113 (2006).

[23] G. Hug and E. Fries, Phys. Rev. B **65**, 113104 (2002).

[24] G. Hug, M. Jaouen, and M. W. Barsoum, Phys. Rev. B **71**, 024105 (2005).

[25] T. Liao, J. Wang, and Y. Zhou, Phys. Rev. B **73**, 214109 (2006).

[26] S. E. Lofland, J. D. Hettinger, K. Harrell, P. Finkel, S. Gupta, M. W. Barsoum, and G. Hug, Appl. Phys. Lett. **84**, 508 (2004).

[27] M. Magnuson, M. Mattesini, O. Wilhelmsson, J. Emmerlich, J. P. Palmquist, S. Li, R. Ahuja, L. Hultman, O. Eriksson, and U. Jansson, Phys. Rev. B **74**, 205102 (2006).

[28] M. Magnuson, J.-P. Palmquist, M. Mattesini, S. Li, R. Ahuja, O. Eriksson, J. Emmerlich, O. Wilhelmsson, P. Eklund, H. Högberg, L. Hultman, and U. Jansson, Phys. Rev. B **72**, 245101 (2005).

[29] M. Magnuson, O. Wilhelmsson, J.-P. Palmquist, U. Jansson, M. Mattesini, S. Li, R. Ahuja, and O. Eriksson, Phys Rev. B **74**, 195108 (2006).

[30] N. I. Medvedeva, D. L. Novikov, A. L. Ivanovsky, M. V. Kuznetsov, and A. J. Freeman, Phys. Rev. B **58**, 16042 (1998).

[31] D. Music, Z. Sun, R. Ahuja, and J. M. Schneider, Phys. Rev. B **73**, 134117 (2006).

[32] D. Music, Z. Sun, and J. M. Schneider, Phys. Rev. B **71**, 092102 (2005).

[33] D. Music, Z. Sun, and J. M. Schneider, Solid State Commun. **133**, 381 (2005).

[34] D. Music, Z. Sun, and J. M. Schneider, Solid State Commun. **137**, 306 (2006).

[35] D. Music, Z. Sun, A. A. Voevodin, and Jochen M. Schneider, J. Phys.: Condens. Matter **18**, 4389 (2006).

[36] D. Music, Z. Sun, A. A. Voevodin, and Jochen M. Schneider, Solid State Commun. **139**, 139 (2006).

[37] J. M. Schneider, R. Mertens, and D. Music, J. Appl. Phys. **99**, 013501 (2006).

[38] J. M. Schneider, Z. Sun, R. Mertens, Fatih Uestel, and Rajeev Ahuja, Solid State Commun. **130**, 445 (2004).

[39] Z. Sun, R. Ahuja, S. Li, and Jochen M. Schneider, Appl. Phys. Lett. **83**, 899 (2003).

[40] Z. Sun, S. Li, R. Ahuja, and Jochen M. Schneider, Solid State Commun. **129**, 589 (2004).

[41] Z. Sun, D. Music, R. Ahuja, S. Li, and J. M. Schneider, Phys. Rev. B **70**, 092102 (2004).

[42] Z. Sun, D. Music, R. Ahuja, and Jochen M. Schneider, J. Phys.: Condens. Matter **17**, 7169 (2005).

[43] Z. Sun, D. Music, R. Ahuja, and J. M. Schneider, Phys. Rev. B **71**, 193402 (2005).

[44] Z. Sun, D. Music, R. Ahuja, and Jochen M. Schneider, J. Phys.: Condens. Matter **17**, L15 (2005).

[45] J. Wang, J. Wang, Y. Zhou, and C. Hu, Acta Mater. **56**, 1511 (2008).

[46] J. Wang and Y. Zhou, Phys. Rev. B **69**, 214111 (2004).

[47] J. Y. Wang and Y. C. Zhou, J. Phys.: Condens. Matter **15**, 1983 (2003).

[48] J. A. Warner, S. K. R. Patil, S. V. Khare, and K. C. Masiulaniec, Appl. Phys. Lett. **88**, 101911 (2006).

[49] A. Grechnev, S. Li, R. Ahuja, O. Eriksson, U. Jansson, and O. Wilhelmsson, Appl. Phys. Lett. **85**, 3071 (2004).

[50] Y. S. Han, K. B. Kalmkov, S. F. Dunaev, and A. I. Zaitsev, J. Phase Equilib. Diffus. **25**, 427 (2004).

[51] X. Ma, C. Li, and W. Zhang, J. Alloys Compd. **394**, 138 (2005).

[52] M. A. Pietzka and J. C. Schuster, J. Phase Equilib. **15**, 392 (1994).

[53] W. J. J. Wakelkamp, F. J. J. van Loo, and R. Metselaar, J. Eur. Ceram. Soc. **8**, 135 (1991).

[54] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Technische Universität Wien, Austria, 2001).

[55] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[56] E. H. Kisi, E. Wu, J. S. Zobec, Jennifer S. Forrester, and Daniel P. Riley, J. Am. Ceram. Soc. **90**, 1912 (2007).

[57] D. P. Riley, E. H. Kisi, T. C. Hansen, and Alan W. Hewat, J. Am. Ceram. Soc. **85**, 2417 (2002).

[58] D. Music, J. Emmerlich, and J. M. Schneider, J. Phys.: Condens. Matter **19**, 136207 (2007).

[59] Z. Sun, J. Zhou, D. Music, R. Ahuja, and J. Schneider, Scr. Mater. **54**, 105 (2006).