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First-principles study of the effect of nitrogen vacancies on the decomposition pattern in cubic $Ti_{1-x}Al_xN_{1-y}$

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The effect of nitrogen substoichiometry on the isostructural phase stabilities of the cubic $Ti_{1-x}Al_xN_{1-y}$ system has been investigated using first-principles calculations. The preferred isostructural decomposition pattern in these metastable solid solutions was predicted from the total energy calculations on a dense concentration grid. Close to the stoichiometric $Ti_{1-x}Al_xN_1$ limit, N vacancies increase the tendency for phase separation as N sticks to Al while the vacancies prefers Ti neighbors. For nitrogen depleated conditions, N sticks to Ti forming TiN_δ $(0<\delta<1)$ while Al tends to form nitrogen-free fcc-Al or Al–Ti alloys. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2838747]

TiAlN is widely used in hard coating applications. The NaCl-structure solid solutions $Ti_{1-x}Al_xN$ have superior properties compared to TiN and is used by the cutting tool industry. The inclusion of Al provides oxidation resistance to the film which extends its lifetime in air-exposed operations. The system exhibits age hardening at high Al concentrations, up to $x\approx 0.67$, above which hexagonal AlN cannot be avoided.[1] This behavior has been explained by coherent isostructural decomposition (CID) into cubic AlN and Ti-rich $Ti_{1-x}Al_xN$ domains.[2,3] However, the effect of nitrogen off stoichiometry and especially N vacancies (V_N) has not yet been systematically considered in this system.

In this work, we address nitrogen substoichiometry and its effect on the chemical driving force for CID in the NaCl based solid solution $Ti_{1-x}Al_xN_{1-y}$ system using *ab initio* calculations. We have calculated the total energy of the random solid solution for the whole range $0\leqslant x,y\leqslant 1$ with steps of $\Delta x,y=0.125$ giving a mesh of 81 different compositions. Even though such solutions in the NaCl structure are thermodynamically unstable over a wide range of compositions, e.g., ground state AlN has the wurtzite structure and pure Ti crystallizes in the hcp structure, the scope is relevant for two reasons. Firstly, thin film deposition techniques can be employed to synthesize metastable systems far away from thermodynamic equilibrium and allow studies of CID. Secondly, general trends might be observed which is useful for better physical understanding of the TiAlN system including in a common framework, important material systems such as $Ti_{1-x}Al_xN$, $Ti_{n+1}AlN_n$(n=1–3), MAX phases[4] and Ti–Al intermetallics.

We have used the order-N, locally-self-consistent Green's function (LSGF) method[5,6] together with the generalized gradient approximation[7] for the exchange-correlation functional to solve the electronic structure problem for the solid solutions. The local interaction zone for the LSGF calculations included two nearest neighbor shells. Local relaxation of the N atoms were considered using the independent sublattice model[3] while the small relaxation of the metal atoms were neglected. Each supercell, consisting of 648 metal atom sites and 648 nitrogen/V_N sites, were created in order to mimic a completely random distribution in the solution phase.[3] To increase the space filling of the B1 structure, two empty spheres have been introduced in each unit cell. The calculations of formation energies for the entire concentration grid was performed with respect to fcc-Al, fcc-Ti, and N_2 molecules.[8] Short-range-order effects were studied using a projector augmented wave (PAW) method as implemented in the VASP package[9–11] to calculate formation energies for V_N and nitrogen impurities differently coordinated in a $Ti_{0.5}Al_{0.5}N$ system and in an fcc-$Ti_{0.5}Al_{0.5}$ alloy, respectively. We used supercells with 16 metal atoms arranged to mimic a random distribution.[3] In those calculations, all atomic positions were relaxed while the volume was kept fixed at the calculated volume of the defect-free supercell. The formation energies in this case was calculated with respect to the defect free supercell and chemical reservoir consisting of N_2 molecules at 0 K.

Panel (a) of Fig. 1 shows the calculated mixing enthalpies of $Ti_{1-x}Al_xN_{1-y}$ with respect to TiN_{1-y} and AlN_{1-y} (Ti–Al mixing) at fixed levels of V_N. Panel (b) shows the mixing enthalpies with respect to $Ti_{1-x}Al_xN$ and $Ti_{1-x}Al_x$ (N-V_N mixing) at different fixed Ti-to-Al ratios. The mixing enthalpy of stoichiometric $Ti_{1-x}Al_xN$ is in quantitative agree-

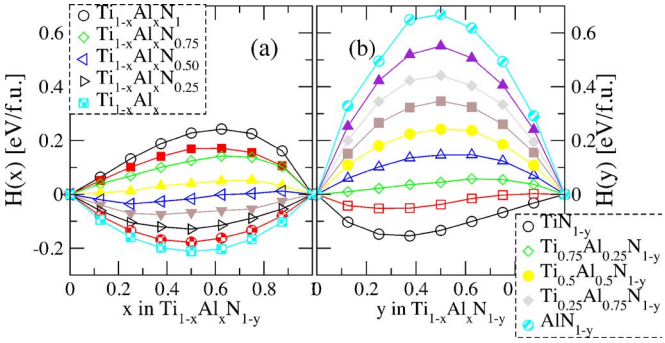

FIG. 1. (Color online) (a) Mixing enthalpy of $Ti_{1-x}Al_xN_{1-y}$ as a function of Al content x, for different fixed fractions of N between $y=0$ and $y=1$, relative to TiN_{1-y} and AlN_{1-y}. (b) Mixing enthalpy of $Ti_{1-x}Al_xN_{1-y}$ as a function of N content $(1-y)$ for different fixed Ti-to-Al ratios, relative to $Ti_{1-x}Al_xN_1$ and fcc $Ti_{1-x}Al_x$.

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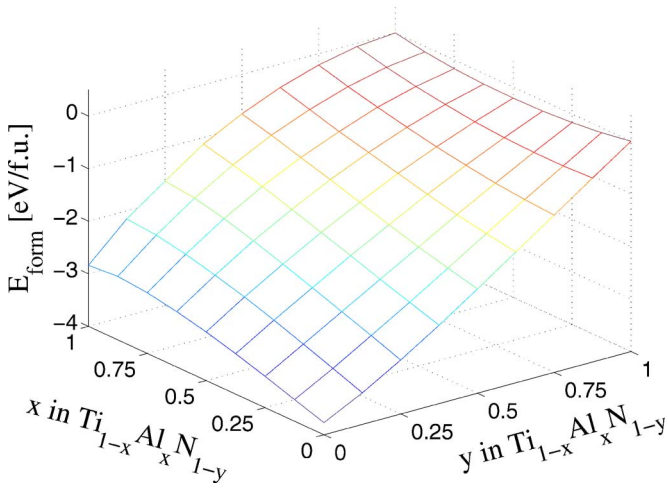

FIG. 2. (Color online) Formation energy of $Ti_{1-x}Al_xN_{1-y}$ in the *x*-*y* composition space.

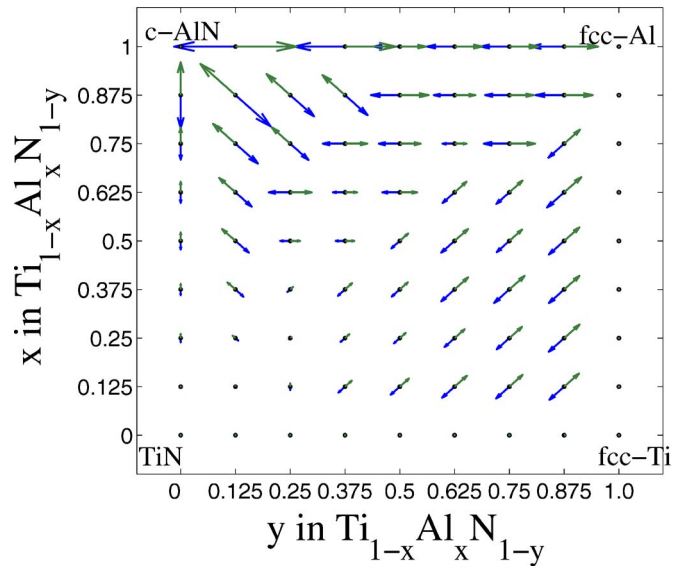

FIG. 3. (Color online) Energetically prefered decomposition pattern of $Ti_{1-x}Al_xN_{1-y}$ in *x*-*y* composition space. The arrows point in the direction in which a phase separation would be most energetically favorable. Their length indicate the magnitude of this energy. Just a dot indicates that there is no chemical driving force for nucleation-free phase separation. The directions of the arrows are approximate. The optimal direction can be in between the directions considered here.

ment with Ref. 3. For the N-free samples, our LSGF value of the enthalpy at $x=0.50$ is -0.211 eV/f.u. This can be compared with the value of our PAW calculation of the relaxed fcc-$Ti_{0.5}Al_{0.5}$ supercell which is -0.276 eV/f.u. The latter compare well with the value in Ref. 12, ≈ -0.286 eV/f.u. The small difference between our LSGF and PAW calculations is believed to be due to the neglect, in the former case, of local relaxations of metal atoms and the presence of an empty nitrogen sublattice which gives a slight artificial decrease in metal-metal interactions. The errors due to both those two sources are largest on the nitrogen-free border and we thus have an estimate of their maximum value.

Panel (a) of Fig. 1 shows a transition from large positive mixing enthalpies for the nitride system toward large negative mixing enthalpies for the transition metal alloy. In the nitride case, the positive mixing enthalpy and its nonsymmetric shape is explained by the electronic mismatch between TiN and AlN leading to an unfavorable localization of Ti nonbonding states.[3] When the N is removed the bondings of the system is gradually changing to the metallic situation of the Ti–Al intermetallics which forms stable compounds. Panel (b) shows a transition from negative mixing enthalpies in TiN_{1-y} toward the large positive mixing enthalpies in AlN_{1-y}. TiN is a very stable compound due to the N *p*-Ti *d* hybridization. However, the system is tolerant for off stoichiometry due to flexibility of the metallic states around the Fermi level to incorporate V_N states, leading to a negative mixing enthalpy. The B1 AlN considered in this work is a semiconductor and any V_N will disturb the balance of valance and cost energy, leading to a high mixing enthalpy.

Knowing the shape of the "psuedobinary" mixing enthalpy curves is, however, not enough to determine preferred decomposition patterns in the two dimensional composition space of $Ti_{1-x}Al_xN_{1-y}$. One has to consider also the possibility for an intersublattice coupling. We have thus considered our total energies as a function of two independent concentration variables *x* and *y*.

In Fig. 2, the formation energy of $Ti_{1-x}Al_xN_{1-y}$ is shown as a function of *x* and *y*. It reveals that a simultaneous consideration of the *x* and *y* degrees of compositional freedom gives rise to a complicated curvature of the energy surface. The energy gain or loss *per concentration change unit* by any spontaneous fluctuation in composition separating the system into two subsystems with compositions $x+\Delta x, y+\Delta y$ and $x-\Delta x, y-\Delta y$ (where Δx and Δy can be both negative and positive independent of each other) can be written as

$$\Delta E = \frac{E(x+\Delta x, y+\Delta y) + E(x-\Delta x, y-\Delta y) - 2E(x,y)}{2(|\Delta x| + |\Delta y|)}. \tag{1}$$

We have calculated this quantity numerically using for each (x,y) point the values from the eight points $(x \pm 0.125, y)$, $(x, y \pm 0.125)$, and $(x \pm 0.125, y \pm 0.125)$ surrounding it (except for at the perimeters where only one dimension of separation is possible) thus giving a measure on the energy gained by a small fluctuation in four different directions ($\hat{x}$, $\hat{y}$, $\hat{x}+\hat{y}$, and $\hat{x}-\hat{y}$). Other directions, e.g., $2\hat{x}+\hat{y}$, were not studied since their numerical derivation would involve a larger compositional offset. Note that our purpose is to find the driving force for spontaneous decomposition, without nucleation processes. We identify that this driving force is strongest in the direction in which ΔE has the largest negative value. Figure 3 shows the results where the arrows point in the preferred decomposition direction and their length is proportinal to ΔE. At 0 K, the solid solution is unstable toward small fluctuations in the concentration over almost the entire range of *x* and *y* values. The transition metal line and the TiN_{1-y} line are the two exceptions. However, three major regimes of different preferred decomposition directions can be identified.

(1) Close to the stoichiometric nitride case and particularly at the medium and high Al content, the V_N are acumulated in Ti-rich regions while N sticks to Al. This tendency can be explained following the argument above that formations of V_N in AlN is unfavorable due to the semiconducting character of its bonding, while TiN can

accommodate them, as experimentally observed.[13] We predict that this effect works together with the decomposition mechanism of stoichiometric $Ti_{1-x}Al_xN$ and should enhance the tendency for CID. This is indicated by the fact that the arrows on the row of compositions $y=0.125$ is longer than the one in the stoichiometric case $y=0.00$. Decreasing the N content can thus not be used as a way of stabilizing solid solution $Ti_{1-x}Al_xN$ at high Al content. It would instead be a way to enhance the decomposition tendency in situations where such behavior is desired.

(2) In the N-poor, Ti-rich region, N sticks to Ti while Al is accumulated in the V_N-rich regions eventually forming metallic Al or an Al–Ti alloy. The chemical driving force for this separation is strong even if one compares with the nitride case of the same Ti-to-Al ratio. The fact that Ti binds stronger to nitrogen than Al under N-poor conditions is connected with the discussion of the nitride case: Al can form stoichiometric AlN but between such compounds and metallic Al, all compositions are unfavorable due to the drastic incompatibility of the free electron like electronic structure of Al and the semiconducting structure of AlN. This suggests a partial reinterpretation of the findings in Ref. 14 where epitaxial thin film samples of the composition $Ti_{0.66}Al_{0.34}N_{0.49}$ (Ref. 15) were found to decompose into what was inferred to be $TiN_{y'}$ and $AlN_{y''}$. We propose that these phases more likely have compositions close to $TiN_{0.82}$ and $Ti_{0.18}Al_{0.82}$ the latter possibly with an ordering tendency towards the $Ti_{0.25}Al_{0.75}$ DO_{22} compound.

(3) In between the N-rich and the N-poor/Ti-rich regimes, at high Al content, there is a region where the tendency for separation along the N-V_N direction is dominating. This region corresponds to the energetically most unstable compositions where no reports of synthesized stable or metastable phases exist.

In order to investigate possible local interactions between the metal and N sublattices, we have calculated the formation energies of one V_N defect in $Ti_{0.5}Al_{0.5}N$ and one N impurity in a fcc-$Ti_{0.5}Al_{0.5}$ alloy, both as a function of the local environment of the defect. In the nitride case, there is a clear preference for the V_N to Ti neighbors. V_N surrounded by five Ti neighbors (1 Al) is 0.67 eV lower in energy compared to a V_N surrounded by five Al (1 Ti). In the transition metal alloy, the trend is reversed and the corresponding N impurity has a strong preference for Ti neighbors. A N impurity surrounded by five Ti (1 Al) are more than 2.45 eV lower in energy compared to the N impurity surrounded by five Al (1 Ti). These calculations reveal the strong effect of local environment on the interaction between the metal and nitrogen sublattices. Such interactions enhance CID in the nitrogen-rich region by introducing an additional phase separation driving force as Ti clusters around V_N.

In conclusion, we have calculated the total energies for the cubic solid solution of $Ti_{1-x}Al_xN_{1-y}$ for a dense mesh with $0 \leqslant x, y \leqslant 1$ and identified preferred patterns for isostructural decomposition. We find that close to the stoichiometric nitride limit, a small amount of nitrogen vacancies are likely to enhance the tendency for phase separation through Ti clustering around V_N. On the other hand, in the nitrogen-poor, Ti-rich region N sticks to Ti while Al tend to form nitrogen-free Ti–Al alloys or compounds. The latter mechanism can be identified as the same driving force that stabilizes the hexagonal MAX phases and the cubic Ti_3AlN perovskite, ordered compounds with the corresponding local atomic coordination.

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