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First-principles study of the effect of nitrogen vacancies on the decomposition pattern in cubic Ti$_{1-x}$Al$_x$N$_{1-y}$

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The effect of nitrogen substoichiometry on the isostructural phase stabilities of the cubic Ti$_{1-x}$Al$_x$N$_{1-y}$ 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$_x$N$_y$ 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$_{1-\delta}$ (0 < \delta < 1) while Al tends to form nitrogen-free fcc-Al or Al–Ti alloys. © 2008 American Institute of Physics.

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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 valence 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$_x$N$_{1-y}$. 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$_x$N$_{1-y}$ 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 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 $\Delta x$ and $\Delta y$ can be both negative and positive independent of each other) can be written as

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

(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 $\Delta E$ has the largest negative value. Figure 3 shows the results where the arrows point in the preferred decomposition direction and their length is proportional to $\Delta E$. 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 accumulated 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.\textsuperscript{13} We predict that this effect works together with the decomposition mechanism of stoichiometric Ti\textsubscript{1-x}Al\textsubscript{x}N 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\textsubscript{1-x}Al\textsubscript{x}N 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\textsubscript{N}\textsuperscript{=} 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. \textsuperscript{14} where epitaxial thin film samples of the composition Ti\textsubscript{0.66}Al\textsubscript{0.34}N\textsubscript{0.49} (Ref. \textsuperscript{15}) were found to decompose into what was inferred to be TiN\textsubscript{1+} and AlN\textsubscript{1+}. We propose that these phases more likely have compositions close to TiN\textsubscript{0.82} and Ti\textsubscript{0.18}Al\textsubscript{0.82} the latter possibly with an ordering tendency towards the Ti\textsubscript{0.25}Al\textsubscript{0.75} DO\textsubscript{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\textsubscript{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\textsubscript{N} defect in Ti\textsubscript{0.5}Al\textsubscript{0.5}N and one N impurity in a fcc-Ti\textsubscript{0.5}Al\textsubscript{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\textsubscript{N} to Ti neighbors. V\textsubscript{N} surrounded by five Ti neighbors (1 Al) is 0.67 eV lower in energy compared to a V\textsubscript{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\textsubscript{N}.

In conclusion, we have calculated the total energies for the cubic solid solution of Ti\textsubscript{1-x}Al\textsubscript{x}N\textsubscript{1-y} for a dense mesh with 0\leq x, y \leq 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\textsubscript{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\textsubscript{3}AlN pervoskite, ordered compounds with the corresponding local atomic coordination.

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\textsuperscript{8}We have used a combination of our LSGF values for the energy of TiN and fcc Ti with the PAW formation energy of TiN to get the value of E(N\textsubscript{N}).
\textsuperscript{15}This is the notation used in this work with two different sublattices, the total composition given in Ref. \textsuperscript{14} is Ti\textsubscript{0.44}Al\textsubscript{0.23}N\textsubscript{0.33}. 