Anharmonicity changes the solid solubility of a random alloy at high temperatures

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We have developed a method to accurately and efficiently determine the vibrational free energy as a function of temperature and volume for substitutional alloys from first principles. Taking Ti1−xAlxN alloy as a model system, we calculate the isostructural phase diagram by finding the global minimum of the free energy, corresponding to the true equilibrium state of the system. We demonstrate that the anharmonic contribution and temperature dependence of the mixing enthalpy have a decisive impact on the calculated phase diagram of a Ti1−xAlxN alloy, lowering the maximum temperature for the miscibility gap from 6560 K to 2860 K. Our local chemical composition measurements on thermally aged Ti0.5Al0.5N alloys agree with the calculated phase diagram.

When discussing the solubility of a random alloy, the configurational entropy is always taken into account, but the effect of temperature associated with lattice vibrations (the vibrational contribution to the free energy) is often neglected. It has been experimentally shown [1–3] that the vibrational and configurational entropies are comparable in the cases of fcc Ni3Al and Cu3Au, and bcc Fe3Al. Theoretical studies draw the same conclusion — that lattice vibrations cannot be ignored [4–8]. High quality phonon spectra can be computed in the framework of density functional perturbation theory (DFPT) [9], but the introduction of substitutional disorder as in an alloy causes the cost of such calculations to escalate rapidly. In this work, we propose a formally exact method of computing the vibrational free energy of a configurationally disordered solid, which has an efficiency comparable to the state-of-the art methods that only apply to ordered solids. Moreover, the method has the advantage of taking into account anharmonicity of the lattice vibrations and therefore remains valid at temperatures for which the quasi-harmonic approximation breaks down.

We demonstrate the accuracy of our technique in a study of decomposition thermodynamics of Ti1-xAlxN alloys [10, 11], a system for which lattice vibrations underpin an unusual and technologically useful isostructural decomposition [12]. Metastable Ti1-xAlxN coatings are ideal for use in the manufacture of cutting tools due to their characteristic age hardening during use. Metastable cubic TiAlN undergoes spinodal decomposition to form nano-scale domains of cubic TiN and AlN, through which extra stress is required to propagate dislocations [10, 13, 14]. Remarkably, calculated values of the maximum temperature for the miscibility gap vary between approximately 6050 and 9000 K [15–17], depending on the methodological details. Within the Debye-Grüneisen approximation, Wang et al. [15] obtained a maximum temperature of 3790 K for the miscibility gap of. These are well above the dissociation temperatures of TiN and AlN, however, but cutting tools may reach temperatures of up to 1300 K [18], at which point vibrations could be of considerable importance and are subject to the effects of thermal expansion and anharmonicity. We note that existing studies either neglect or use an incomplete description of the vibrational contribution to the free energy, since the methodological challenge and computational efforts required to calculate the phonon spectra of a substitutionally disordered solid using ab initio approaches are considerable.

In this Letter, we propose a computationally tractable method for the treatment of vibrational free energy of a random alloy, and use it to perform accurate first-principles calculations of the vibrational free energy of B1 Ti1−xAlxN alloy, our model system. The theoretical miscibility gap has a maximum temperature of 2860 K, and the solubility limit of Al in TiN at intermediate temperatures is increased in comparison to calculations which neglect the effect of lattice vibrations. This result is supported by our atom probe tomography experiments, demonstrating that the combination of anharmonic lattice vibrations and configurational disorder has a decisive influence on the solubility of this system.

Our method employs the temperature dependent effective potential (TDEP) method [19, 20] to compute the vibrational contribution to the free energy. When constructing the phase diagram we return to the originally ideas of Gibbs [21] — we minimize the Gibbs free energy to obtain the stable alloy compositions at equilibrium. We perform atom probe tomography experiments, exploiting the high spatial and chemical resolutions to de-
pict the decomposition of a supersaturated solid solution of TiAlN with an alloy composition inside the miscibility gap, thus verifying the predicted phase diagram.

Phase stability at constant temperature and volume is determined by the Helmholtz free energy $F$, which can be expressed as the sum of the free energy of a model system $F_m$ and a correction term based on the Kirkwood coupling theorem [22], where $U_m$ and $U$ are potential energies of model and real system respectively.

$$F = F_m + \int_{\Delta F}^{1} (U_m - U) \frac{d\lambda}{\lambda}.$$  (1)

Eq. 1 is formally exact for any choice of the model system. In practice, calculating $\Delta F$ can be very difficult [23], so our strategy will be to choose the model system with the smallest possible $\Delta F$. Ideally, it should be within the error bars of ab initio calculations.

Our model system consists of atoms distributed on the sites of a special quasirandom structure [24] (SQS) supercell simulating the solid solution. These atoms, however, interact with effective force constants which have full symmetry of the underlying crystal lattice. Lattice vibrations of the model system are described by a temperature dependent (TDEP) model Hamiltonian [19, 20]:

$$\hat{H} = U_0 + \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{ij} \Phi_{ij} \epsilon_{ij},$$  (2)

where $p_i$ and $u_i$ are the momentum and displacement of atom $i$, $\Phi_{ij}$ are the second order effective force constant tensors, which relate the displacement of atom $j$ to the force $f_j$ exerted on atom $i$. The TDEP method allows us to fit parameters of the model Hamiltonian to results of ab initio molecular dynamics simulations carried out for the real system of interest.

In the model Hamiltonian (Eq. 2), the translational and spatial symmetry of the underlying crystal lattice are imposed by treating the components of the alloy as symmetry equivalent, and the real interactions present in DFT are mapped to effective interactions expressed by the interatomic effective alloy force constants $\Phi_{ij}$ corresponding to the underlying crystal lattice, B1 in case of Ti$_{1-x}$Al$_x$N. Imposing the symmetry reduces the number of independent components in $\Phi_{ij}$ considerably, making the method numerically efficient [20]. It differs from the virtual crystal approximation [25], in which there is no distinction between atomic species. In our approach, the forces are obtained from calculations of the real disordered system as described by the SQS and only then mapped onto effective force constants in a system with randomly distributed masses. Note that the accuracy of the free energy calculations can always be improved, for example, by using a more complex model Hamiltonian, although this is not necessary for our model system.

We recomputed free energies of Ti$_{0.5}$Al$_{0.5}$N using the formally exact thermodynamic integration technique (UP-TILD) [23] to verify that our choice of model Hamiltonian was sufficiently accurate. The correction to the free energy (Eq. 1) at 1500 K and a fixed volume close to the equilibrium volume was calculated to be $\sim 5$ meV/atom (see supplementary material). In addition, we compared our method with phonon calculations on the SQS within the harmonic approximation at the equilibrium volume corresponding to $T = 0$ K for alloys with different compositions. In this case, nonsymmetrized, force constants were extracted, and the difference in free energy were within 8 meV/atom at 1500 K.

In order to find the effective force constant matrix that best represents the Born-Oppenheimer potential energy surface, we minimize the difference in forces between the model system and the SQS model of a real alloy, computing the latter by means of ab initio molecular dynamics (see supplementary material).

Density functional theory (DFT) calculations give us an efficient way of determining the internal energy and the electronic contribution to the entropy via the Mermin functional [26]. The configurational entropy is estimated using the mean-field approximation [27]. Short-range clustering effects in Ti$_{1-x}$Al$_x$N have been shown to be significant and similar in magnitude to the mean field contribution at temperatures below 3500 K [17]. In principle, such clustering effects should be included in the free energy calculations. However, in Ti$_{1-x}$Al$_x$N they were found to predominantly impact the AlN-rich compositions, having little effect on the solubility limits in the TiN-rich region, and only moderately decrease the maximum temperature of the miscibility gap. For these reasons, short-range clustering are not included in our calculations.

It is convenient to decompose the Helmholtz free energy into vibrational (“vib”), configurational (“config”) and electronic terms (“el”):

$$F = U - TS = F_{el} + F_{vib} + F_{config}$$  (3)

Using the force constants in Eq. 2, we can calculate the phonon density of states $g(\omega, T)$, which is used to compute the vibrational contribution to the Helmholtz free energy:

$$F_{vib}(\omega, T) = \int_{0}^{\infty} g(\omega, T)[k_B T \ln \left(1 - \exp \left(-\frac{\hbar \omega}{k_B T}\right)\right) + \frac{\hbar \omega}{2}]d\omega.$$  (4)

In our case $g(\omega, T)$ is strongly temperature dependent and includes anharmonic effects and thermal expansion.
Concentration $x$ in Ti$_{1-x}$Al$_x$N (at. %)

Solid solution
Binodal
Spinodal
Miscibility gap

FIG. 1. (Color online) Calculated phase diagram for B1-
Ti$_{1-x}$Al$_x$N random alloy. The yellow region corresponds to
the solid solution, and the green area to the miscibility gap.
The difference between the dotted and solid lines shows the
effect of including the vibrational entropy for binodal using
the TDEP method. The dash-dotted line corresponds to the
spinodal metastable region including the anharmonic contribu-
tion. The dashed line in solid solution region corresponds
to the spinodal line without vibrational contribution.

(see supplementary material). We construct the Gibbs
free energy ($G = F + PV$) from the Helmholtz free energy
surface, where $P = -dF/dV$. At constant temperature
and pressure it is a necessary and sufficient condition for
a system to have the minimum Gibbs free energy in order
to be at the equilibrium state. The Gibbs free energy of
mixing is given by,

$$G_{\text{mix}}(T, x) = G_{\text{T}_1-x\text{Al}_x\text{N}} - (1 - x)G_{\text{TIN}} - xG_{\text{AIN}}, \quad (5)$$

where $x$ is the fraction of AlN.

We reconstruct the concentration-temperature phase
diagram at zero pressure by a direct minimization of
$G_{\text{mix}}$ at each temperature and global composition on a
grid (see supplementary material). We determine the
spinodal from the condition ($\frac{\partial^2 G_{\text{mix}}}{\partial x^2} < 0$).

The calculated phase diagram is compared with one
neglecting lattice vibrations in Fig. 1. The difference
in both the spinodal region and the miscibility gap is
dramatic. By including the vibrational contribution to
the free energy, the maximum of the miscibility gap is
lowered from 6560 K to 2860 K. The roots of the sec-
ond derivative of the total Gibbs free energy below 1000
K depend on the fitting function, in this case third or-
der Redlich-Kister polynomials [28] (gray lines of spin-
odal). To understand this dramatic shift in the phase
diagram we consider each contribution to the free energy
separately and compare them with free energies that ex-
clude anharmonic effects (harmonic approximation) and
include only volume dependence at $T = 0$ K from TDEP
(quasi-harmonic approximation).

The Gibbs free energy of mixing the Ti$_{0.5}$Al$_{0.5}$N alloy
is decomposed into components in Fig. 2. The mixing en-
thalpy increases slightly with a temperature. The green
dashed and black lines show the effect of including ther-
mal expansion. The blue line is the phonon free energy
calculated using our new method, and it includes the
temperature dependence of the force constants and ther-
mal expansion. The configurational contribution behaves
linearly with $T$, as expected from the mean-field theory.
On the other hand, the vibrational contribution behaves
non-linearly, becoming comparable to the configurational
contribution at high temperatures due to anharmonicity.
Note that the temperature dependence of the force con-
stants and the thermal expansion effects are similar in
magnitude. Together, these effects strongly suppress the
miscibility gap and spinodal region of Ti$_{1-x}$Al$_x$N alloys.

Experimental verification of theoretical phase diagram
(Fig. 1) is a challenging task. Because of the high melting
temperature of TiN, its alloys are synthesized by thin-
film deposition techniques, often followed by an anneal-
ing. Due to the explicit out-of-equilibrium nature of this
metastable transformation, direct information from equi-
librium experiments is not available, so we adopted the
following strategy. 4 µm thick TiAIN films with equal
amounts of Ti and Al ($x = 0.5$) were deposited by cat-
thodic arc evaporation, resulting in a nearly uniform solid
solution [29]. Our theoretical predictions suggest that
when diffusion is activated this alloy will phase segregate through spinodal decomposition. To study this effect, a set of samples was prepared by annealing the TiAlN films at 1073 K for 2, 4, 12 and 100 hours in an argon atmosphere. The evolved microstructures where then examined by atom probe tomography.

Fig. 3 shows 2D compositional maps of 2 nm thick slices through the reconstructed 3D atom probe specimen of the annealed samples. The initially homogeneous cubic solid solution decomposes isostructurally forming cubic Ti- and Al-rich domains during the first 12 hours. After 100 hours, the metastable cubic AlN-rich phase has to a large extent transformed to its stable wurtzite phase [18]. During the first 12 hours the evolution of the microstructure and the chemical segregation becomes gradually more pronounced, which is consistent with the spinodal decomposition [30]. After 100 hours the microstructure is coarser.

The phase diagram (Fig. 1) shows a substantial shift of the solubility at 1073 K compared to the predictions excluding vibrational effects, especially for the solubility of Al in TiN. In order to experimentally verify this, we extracted the maximum and minimum local composition in the decomposed microstructure by constructing histograms of the concentrations in 1 nm$^3$ bins throughout the sample. These two local compositional extrema are plotted in Fig. 4 as a function of annealing time, and demonstrate the timescale and decomposition path of the alloy. The solubility of Al in TiN at 1073 K tends to a final solubility of $\sim 2\%$ according to the theoretical phase diagram. The solubility limit for Ti in cubic AlN could not be determined experimentally since it was not reached prior to the onset of wurtzite AlN formation. However, the experimental data for Ti in cubic AlN asymptotically approaches the theoretical value ($x = 1$).

In summary, we present an accurate technique for calculating the vibrational contribution to the Gibbs free energy for random alloys. We reconstruct the phase diagram of a model Ti$_{1-x}$Al$_x$N alloy, and demonstrate that in this system, the vibrational mixing phonon free energy is large and comparable to the configurational entropy. As a result, we find a dramatic decrease of the maximum temperature for the miscibility gap, from 6560 K to 2860 K, as well as an increase AlN of solubility in TiN as compared to calculations which neglect lattice vibrations. Atom probe tomography experiments on annealed Ti$_{0.5}$Al$_{0.5}$N samples are in line with our theoretical predictions demonstrating a finite AlN content in the TiN rich compositions after 100 h of annealing at 1073 K.

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METHODOLOGICAL DETAILS

In order to find the effective force constant matrix that best represents the Born-Oppenheimer potential energy surface, we minimize the difference in forces between the model system and the SQS model of a real alloy, computing the latter by means of ab initio molecular dynamics (AIMD). We seek the linear least squares solution for the force constants $\Delta \overline{\Phi}_{ij}$ that minimize the difference in forces $\Delta F$ between AIMD and our Hamiltonian form $\{F^m_t\}$.

$$\min_{\Delta \overline{\Phi}} \Delta F = \frac{1}{N_t} \sum_{t=1}^{N_t} |F^\text{MD}_t - F^\text{H}_t|^2$$

$$\min_{\Delta \overline{\Phi}} \Delta F = \frac{1}{N_t} \sum_{t=1}^{N_t} |F^\text{MD}_t - \overline{\Phi}_{ij}^\text{eff} U^\text{MD}_t|^2,$$  \hfill (1)

where $\{U^\text{MD}_t\}$ and $\{F^\text{MD}_t\}$ are sets of displacements and forces from AIMD respectively.

COMPUTATIONAL DETAILS

Canonical ensemble ab initio molecular dynamics simulations were performed using the projector-augmented wave (PAW) method [1] as implemented in VASP[2–5] over a range of temperatures, volumes, and concentrations. The temperature was set with a Nosé thermostat [6, 7] with Fermi smearing corresponding to the simulation temperature. The plane wave energy cutoff was set to 600 eV and the Brillouin zone (BZ) was sampled at the Gamma point. The random alloy was generated using a special quasirandom structure (SQS) approach [8]. A 128 atom SQS (4 × 4 × 4) supercell was constructed, in which 64 atoms were metal and 64 were nitrogen. Three different SQS were generated, corresponding to different compositions of the random Ti$_{1-x}$Al$_x$N alloy, with B1 symmetry and $x = \{0.25, 0.5, 0.75\}$. 128 atoms SQS was generated trying to mimic the SRO parameters of perfect random alloys for the first 7 coordination shells for pair interactions with extra focus on the first 5.

A subset of uncorrelated samples from the AIMD simulations was selected and upscaled to high accuracy with a 3 × 3 × 3 k-point mesh for the BZ integration. The effective force constants were found to be smooth and easily interpolated across the whole concentration interval, giving the phonon DOS as a continuous function of concentration, volume and temperature.

THERMODYNAMIC INTEGRATION

A Langevin thermostat was used to control the temperature and break the mode-locking. The numerical integration over coupling parameter $\lambda$ was carried out over 5 discrete steps, and the MD simulations were run for $\sim$100 000 timesteps with k-point sampling at the Gamma-point only. A set of uncorrelated snapshots was selected from AIMD and upscaled to high accuracy with a 3 × 3 × 3 k-point mesh to ensure convergence for $\Delta F$.

PHONON DENSITY OF STATES

In our case the dramatic difference in phonon free energy comes directly from anharmonic behaviour of phonon density of states. The part of the phonon density of states at low frequencies (see Fig. 1 ) contributes most to the shift in the free energy at high temperatures.

PHASE DIAGRAM RECONSTRUCTION

$G_{\text{mix}}(x)$ is defined as a function of the vector $x$ in a composition space. In general case at a given pressure and temperature, a mixture of $N_c$ atomic species, or components, may split into $N_p$ distinct phases. We define a $N_c \times N_p - 1$ grid of compositions $x$ with elements $x_{ik}$, where element $x_{ik}$ is an atomic fraction of component $i$ in phase $k$. The solution must satisfy two constraints [9]: the component material balance constraint and the positive value of the atomic fraction of components in the
This is a convenient methodology since no assumptions about reactions are necessary, and the constraints are easy to identify. There is also no need to have $G$ defined across the entire concentration interval if we have a many phase system, which removes complications such as the presence of dynamically unstable phases. Furthermore the proposed technique removes the need to numerically calculate derivatives of the Gibbs free energy needed in state-of-the-art methods for constructing phase diagrams, a procedure that is notoriously sensitive to numerical noise. Of course in our case, we still determine the spinodal from the condition $\left(\frac{\partial^2 G_{\text{mix}}}{\partial x^2}\right)_{T} \leq 0$.

**EXPERIMENTAL DETAILS**

Atom probe tomography (APT) samples were prepared in a dual-beam focused ion beam/scanning electron microscopy workstation (FIB/SEM) (Helios NanoLab 600TM, FEI Company, USA) by the standard lift-out technique [11]. Laser Pulsed APT was carried out with a LEAPTM 3000X HR (CAMECA) at a repetition rate of 200 kHz, a specimen temperature of about 60 K, a pressure lower than $1 \times 10^{-10}$ Torr (1.33 $\times 10^{-8}$ Pa), and a laser pulse energy of 0.5 nJ. The evaporation rate of the specimen was 5 atoms per 1000 pulses. The positions and the time-of-flight of the ions coming into the detector are used to generate a three-dimensional reconstruction with IVASTM 3.6.6 software (CAMECA). The accuracy of atomic-scale of APT and concentration are discussed in literature [12–15]. Previous results demonstrate that it is now possible to obtain highly quantitative information from APT.

FIG. 1. (Color online) Phonon density of states for 300 K and 2700 K including thermal expansion and anharmonic effects.

$G(x) = \sum_{i=1}^{N_c} \sum_{k=1}^{N_p-1} x_{ik} G_{ik}.$

The mass balance constraint can be rewritten in matrix form $Ax = B$, or

$$\sum_{i=1}^{N_c} \sum_{k=1}^{N_p-1} a_{ei} x_{ik} = B,$$

where $e$ is an index of number of possible combinations of fractions of component $i$ and $a_{ei}$ are the matrix elements.

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where $e$ is an index of number of possible combinations of fractions of component $i$ and $a_{ei}$ are the matrix elements. B is a global concentration of component $i$ in the initial solid solution phase.

In our case we consider a Gibbs free energy of mixing. It can be done as alternative to the Gibbs free energy. We have two phases or distinct regions ($k=2$), where one region is a solid solution of Ti$_{1-x}$Al$_x$N and another region is a miscibility region.

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