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High pressure and high temperature stabilization of cubic AlN in $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$

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In the present work, the decomposition of unstable arc evaporated $\text{Ti}_{0.6}\text{Al}_{0.4}\text{N}$ at elevated temperatures and quasihydrostatic pressures has been studied both experimentally and by first-principles calculations. High pressure and high temperature (HPHT) treatment of the samples was realized using the multi anvil press and diamond anvil cell techniques. The products of the HPHT treatment of $\text{Ti}_{0.6}\text{Al}_{0.4}\text{N}$ were investigated using x-ray diffractometry and transmission electron microscopy. Complimentary calculations show that both hydrostatic pressure and high temperature stabilize the cubic phase of AlN, which is one of the decomposition products of $\text{Ti}_{0.6}\text{Al}_{0.4}\text{N}$. This is in agreement with the experimental results which in addition suggest that the presence of Ti in the system serves to increase the stability region of the cubic c-AlN phase. The results are industrially important as they show that $\text{Ti}_{0.6}\text{Al}_{0.4}\text{N}$ coatings on cutting inserts do not deteriorate faster under pressure due to the cubic AlN to hexagonal AlN transformation. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4790800>]

I. INTRODUCTION

$\text{Ti}_{1-x}\text{Al}_x\text{N}$ has been used as a protective coating in cutting applications since the 1980s^{1,2} and in comparison with TiN, its high temperature properties are outstanding. This is mainly due to improved oxidation resistance and age hardening occurring at elevated temperatures that results in an increase in hardness compared to as-deposited $\text{Ti}_{1-x}\text{Al}_x\text{N}$ despite the stress relaxation at high temperature often seen in physical vapor deposited films.³ The age hardening effect has its origin in the isostructural spinodal decomposition of the unstable cubic (B1) c- $\text{Ti}_{1-x}\text{Al}_x\text{N}$ into coherent c-TiN and c-AlN rich domains of nanometer size.^{4,5} The differences in elastic properties,⁶ in combination with coherency strains at the domain borders due to the lattice mismatch,⁷ hinder effectively dislocation movements. With increasing temperatures, the domains grow⁸ whereupon the c-AlN transforms into its stable hexagonal wurtzite (B4) structure, h-AlN. These larger precipitates are incoherent with the TiN-matrix and the net effect of this second decomposition step is deterioration of the coating's mechanical properties.⁹

The decomposition process described above is valid at atmospheric pressure and the behavior of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ is so far unknown at simultaneous high pressure and high temperature (HPHT) conditions. Theoretical studies^{10,11} suggest a promoted spinodal decomposition and a suppression of the c-AlN to h-AlN transformation in $\text{Ti}_{1-x}\text{Al}_x\text{N}$ at elevated hydrostatic pressures. Due to a shoulder on the spinodal,¹¹ the effect of pressure on the spinodal decomposition is believed to be largest at an Al-content around 0.4. The pres-

sure dependent stability of pure AlN has been studied both experimentally¹² and theoretically.^{13,14} According to these studies,¹²⁻¹⁴ c-AlN is stable at hydrostatic pressures above 12–17 GPa. Siegel *et al.*¹⁵ used first-principles calculations to theoretically predict the equilibrium line between c-AlN and h-AlN in the AlN PT phase diagram. It was found that the cubic phase has a broad stability field at HP and HT. Hence, an increase in temperature under certain pressures may stabilize the cubic phase, which is not the case at ambient pressure.

Taking into account that so far the HPHT behavior of the ternary $\text{Ti}_{1-x}\text{Al}_x\text{N}$ has not been studied, we here present results from a series of HPHT experiments on $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ using multi-anvil (MA) press and diamond anvil cell (DAC) techniques. In addition, we have calculated a phase diagram for AlN using *ab-initio* theory as implemented in Quantum Espresso (QE)¹⁶ package, which allows for simulations of phonon dispersion relations through the linear response method.¹⁷

II. MATERIAL AND METHODS

A. Experimental details

$\text{Ti}_{0.6}\text{Al}_{0.4}\text{N}$ coatings were grown in a commercial Sulzer Metaplas MZR323 reactive cathodic arc evaporation system in a 4.5 Pa N_2 atmosphere, with a substrate temperature of $\sim 500^\circ\text{C}$ and a substrate bias of -40 V . The coatings were grown on ultrasonically cleaned and Ar ion etched thin foils of iron mounted in front of the TiAl (Ti:0.60, Al:0.40) compound cathodes yielding an equivalent metal ratio in the as-deposited coatings. After deposition, the coated iron sheets were dissolved in 64% hydrochloric acid releasing the remaining coating in the form of flakes. The $\text{Ti}_{0.6}\text{Al}_{0.4}\text{N}$

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flakes were washed in acetone and water, dried and eventually ground to a powder. The composition of the powder was investigated using a Leo 1550 Gemini scanning electron microscope operated at 20 kV and equipped with an energy dispersive x-ray spectrometer (EDS).

The MA experiments were performed in a 1000-ton (or 1200-ton) multi-anvil press at pressures between 8 GPa and 14 GPa and temperatures between 900 °C and 1900 °C, hereinafter referred to as $P_{\max}/T_{\max}$ (Table I). The powder sample was loaded into a platinum capsule of 2 mm in diameter and 3.5 mm in height for the experiments performed at 11 GPa or lower and 1.6 mm in diameter and 2.8 mm in height for experiments performed at the higher pressures. The capsule was enclosed into the high-pressure cell assembly consisting of an MgO octahedron, which served as a pressure transmitting medium, a graphite (or lanthanum chromate LaCrO_3) heater, and thermo insulating tubes made of ZrO_2 and MgO. The experimental technique is described in detail elsewhere.^{18–20} The octahedron was compressed using eight tungsten carbide cubic anvils. $P_{\max}$ was obtained by a slow compression during 4 h followed by a rapid increase in temperature ($100^\circ\text{C min}^{-1}$) up to $T_{\max}$. The temperature was held constant during 10 min before the sample was quenched. After quenching, the sample was slowly decompressed during 18 h.

Additional HPHT experiments were conducted in a DAC with a diamond culet size of 300 μm . A Re gasket was pre-indented with the diamond anvils to a remaining gasket thickness of 30 μm upon which a hole of 125 μm in diameter was made with a MH20 Betsa spark erosion drill. Fine particles of $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ were loaded into this hole together with NaCl powder and ruby balls, the former as a pressure transmitting medium as well as thermal insulation and the latter for pressure calibration using the ruby fluorescence scale.²¹ Three cells were prepared; the quasihydrostatic pressure, as measured on ruby,²¹ was 3, 13, and 23 GPa in the sample chambers. The cells were annealed by laser heating (LH) to 2200 °C (± 200) during seven minutes using a double-side NIR laser system.^{22,23} After LH, the samples were carefully removed from the gasket and *ex-situ* x-ray diffraction (XRD) measurements were performed using a high brilliance in-house diffractometer²⁴ (Mo-K α radiation, $\lambda = 0.7108 \text{ \AA}$). *Ex-situ* XRD measurements were also performed on the samples HPHT treated in a MA press.

TABLE I. High pressure and high temperature conditions used for MA and DAC treatments.

Sample notation	Type	P (GPa)	T (°C)
8/1500	MA	8	1500 (± 50)
8/1900	MA	8	1900 (± 50)
11/1200	MA	11	1200 (± 50)
11/1500	MA	11	1500 (± 50)
10/1700	MA	10	1700 (± 50)
14/900	MA	14	900 (± 50)
14/1200	MA	14	1200 (± 50)
3/2200	DAC	3	2200 (± 200)
13/2200	DAC	13	2200 (± 200)
23/2200	DAC	23	2200 (± 200)

Transmission electron microscope (TEM) sample preparation of selected MA samples was performed using a Carl Zeiss CrossBeam 1540 EsB focused ion beam (FIB) according to the method described by Langford and Petford-Long.²⁵ A Fei Tecnai G² TF 20 UT analytical TEM (and scanning transmission electron microscope (STEM)) operated at an acceleration voltage of 200 kV and equipped with an EDS was used for structural characterization of the MA samples.

B. Theoretical calculations

Supporting first principles calculations to obtain the PT phase diagram were performed within the framework of density-functional theory as implemented in the QE package.¹⁶ We have considered pure AlN, because it is known to be the main source for detrimental transformation in coatings. It is also well established that solubility of Ti in AlN is very low,^{26,27} and it decreases with pressure.¹¹ Considering pure AlN allows us to reduce significantly computational costs for the simulations. We calculated phonon dispersions using linear response theory¹⁷ and we used quasi-harmonic approximation calculations²⁸ to obtain the temperature dependent phonon free energy. The k-mesh used was $16 \times 16 \times 16$ for the c-AlN and $16 \times 16 \times 12$ for the h-AlN structure. The q-mesh for the phonon calculation was $6 \times 6 \times 6$ for the c-AlN and $5 \times 5 \times 3$ for the h-AlN structures. Using these grids the transition pressure is found to be converged to within 0.01 GPa. The generalized gradient approximation according to Perdew-Burke-Ernzerhof was used for the exchange-correlational functional throughout all calculations.²⁹ In addition, we calculated the phase transition pressure at 0 K using the Vienna *ab-initio* simulation package (VASP) package^{30,31} for verification.

Calculations were performed on both cubic B1 structure and wurtzite B4 structure of AlN at a grid of volumes and temperatures using a temperature spacing of 50 °C and lattice parameter spacing of 0.1 $\text{\AA}$, corresponding to ~ 1 -2 GPa between each point depending on volume and temperature. Interpolation schemes based on the modified Morse potential³² was then used to obtain accurate equations of state and transition pressures. The PT phase diagram was constructed by comparing the total Gibbs free energies (Eq. (1)) of the two phases

$$G(P, T) = F(V, T) + P \times V. \quad (1)$$

Here $F(V, T)$ is the Helmholtz free energy, and P, T, V denote pressure, temperature, and volume, respectively. The temperature dependence of the free energy is derived solely from the phonon free energy and phonon entropy. Pressures were calculated from the free energy binding curves taking into consideration thermal expansion as well as optimizing the c/a ratio. The phase diagram was calculated for pressures up to 25 GPa and temperatures up to 2700 °C. This limit was chosen as the approximate melting point of AlN at high pressures. Though the adiabatic approximation of the phonon calculations is less reliable close to this limit, below 1700 °C and at high pressure up to even higher temperatures it gives

high accuracy. The equilibrium c/a ratio is found to vary only slightly within the region of the phase transition and remains at approximately 1.615 for all temperatures. In addition, using any value for c/a between 1.61 and 1.62 would not appreciatively affect the phase transition line.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffractograms from the $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ samples treated in a multi anvil press. The as-deposited coating shows three distinct lines, 111, 200, and 220, characteristic for the NaCl-type (B1) structure of the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ solid solution. The average lattice parameter as calculated from the lines is 4.21 Å. At HP/HT conditions of 8/1500 and 8/1900 additional peaks appear, where the two strongest correspond to 100 and 102 diffraction lines from the h-AIN phase. Similar behavior is seen for the 11/1200-sample as well. However, the relative intensity of the 100 and 102 lines of the 11/1200-sample is considerably lower (only visible at higher magnification, see inset in Figure 1) indicating a smaller amount of the h-AIN phase. An equivalent heat treatment at ambient pressure would lead to a much larger amount of h-AIN,³³ hence the applied pressure of 11 GPa has indeed decreased the tendency of forming the hexagonal phase.

Broad x-ray diffraction lines indicate the presence of small crystallites and/or micro strain. The relative broadness of the h-AIN seen here has its origin in the nucleation of small strained h-AIN crystallites in the grain boundaries similar to what is reported by Rachbauer *et al.*³³ Furthermore, the intensities of the h-AIN peaks increase at the higher temperature, suggesting a promoted transformation of c-AIN into hexagonal phase with temperature at constant pressure. The reduction of peak intensity of h-AIN in the 11/1200 sample can however not be explained solely by the lower temperature compared to the 8/1500 and 8/1900 sample. This is even more clearly seen for the 11/1500 sample, which was treated at the same pressure but at higher temperature and shows no signs of h-AIN. Instead the reason for the

decreased intensity of the diffraction peaks of hexagonal AIN phase is a result of the increased pressure.

The samples 11/1500, 10/1700, and 14/1200 show no signs of hexagonal phase. For the 14/1200-sample, there is instead a tendency of formation of a shoulder at the three cubic peaks towards smaller d-spacings. This shoulder is best seen at the 200 and 220-peaks at the approximate d-spacings of 2.06 and 1.49 Å and indicates the presence of c-AIN. This is also seen for sample 11/1500 and 10/1700 with shoulders on the 111-peak and pronounced 200 and 220 peaks at 2.06 and 1.47 Å. Hence, the XRD results from these samples suggest a more developed spinodal decomposition compared to 14/1200 which seems logical at the higher temperatures.

The discrepancies between the measured and marked positions are results from chemical shifts of the diffraction lines since the domains formed during the spinodal decomposition are not pure compounds. In addition, the exact lattice parameter of c-AIN is uncertain as it is not a stable compound at ambient conditions. The effect of the progression of the spinodal decomposition is seen in the uppermost diffractogram in Figure 1 from the 14/900-sample, which shows broadening of the diffraction lines of the main phase and no traces of h-AIN. At this lower temperature (900 °C), a less developed chemical modulation is present compared to 1200 °C resulting in less pronounced c-AIN peaks. The XRD results after DAC are not shown but for the 3/2200 there are clear diffraction peaks corresponding to h-AIN. For the 13/2200 and 23/2200, however, there is no h-AIN present and instead peaks indicating the presence of c-AIN, which again shows the suppression of h-AIN with pressure at isotherms.

As the XRD results show a very low amount of h-AIN in the 11/1200 sample, a more detailed TEM characterization was performed of this sample. Figure 2(a) shows a bright field micrograph over an area from the 11/1200 sample containing h-AIN as determined with selected area electron diffraction. The same area is seen in dark field mode in Figure 2(b) with intensity primarily from the 100-reflection shown in the selected area diffractogram in Figure 2(c) revealing a distribution of h-AIN primarily at the grain boundaries. The presence of h-AIN mainly in the grain boundaries may suggest that h-AIN forms earlier than what could be expected from a single crystal. One reason for this is probably an increased diffusivity along the boundaries compared to within the grains. Also, there may be a compositional variation across the grain boundaries, which promotes an earlier start of the cubic to hexagonal transformation.³⁴

Figures 2(c) and 2(d) show STEM from two multi anvil samples treated at 1200 °C at a compression of 11 and 14 GPa. Diffuse domains of TiN- (bright) and AlN-rich (dark) domains are seen, consistent with previous studies.⁹ The revealed nanostructured TiN- and AlN-rich domains have been reported in several studies after heat treatments at atmospheric pressures^{35,36} which supports the results from XRD that the 11/1200 indeed has undergone spinodal decomposition followed by the c-AIN to h-AIN transformation for some AlN-rich regions along the grain boundaries. The high resolution transmission electron micrograph (HRTEM) in Figure 2(f) from the interior of a grain in the

FIG. 1. X-ray diffractograms of $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ samples treated in the multi anvil press in comparison with the untreated material (ambient).

FIG. 2. Transmission electron micrographs of two samples showing (a) the 11/1200 sample in bright field mode over a region containing h-AlN and in (b) in dark field mode with intensity from the (100) plane spacings marked with the arrow in (c). Scanning transmission electron micrographs of (d) the 11/1200 sample and (e) the 14/1200 showing TiN- and AlN-rich domains and (f) a high resolution transmission electron micrograph from the 11/1200 sample with resolved lattice fringes viewed along [011] showing coherency between decomposed domains seen in (d).

11/1200-sample shows a coherent cubic coherent lattice with no grain boundaries, thus, implying an isostructural spinodal decomposition. The combined mixture of mainly c-TiN and c-AlN with small crystallites of h-AlN agrees well with the XRD results in Figure 1.

An average domain size can be measured from the intensity variations in the STEM using a procedure described elsewhere³⁷ and is 5.2 ± 0.5 nm at 11/1200 and 5.1 ± 0.4 nm at 14/1200. Hence, the size of the domains are the same as for samples heat treated at 1000 °C and ambient pressure conditions³⁷ despite the higher temperature of 1200 °C. According to Knutsson,³⁸ the coarsening step during spinodal decomposition of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ is diffusion limited and at these pressures the effect of a reduced diffusivity with an increased pressure cannot be neglected. A rough estimate of the pressure effect is shown in the following equations:³⁹

$$D = D_0 \cdot \exp(-H/kT), \quad (2)$$

$$H = U + PV, \quad (3)$$

where D is the diffusion coefficient, H is the enthalpy, k is Boltzmann's constant, T is the temperature, U is the internal energy, V is the activation volume, and P is the pressure. If the activation volume is assumed to be of the same magnitude as the atomic volume, the diffusion coefficient is decreased with one order of magnitude when increasing the pressure with 1 GPa. This effect competes with the fact that spinodal decomposition is promoted by an external pressure.^{11,37} Hence, the coarsening stage is most likely reached earlier due to the applied pressure but the pressure effect of the diffusivity dominates during the coarsening stage and lowers the domain size growth.

Figure 3 shows the calculated PT phase diagram of pure AlN where the thermodynamically stable phases of AlN are separated by the theoretically constructed phase boundary. At room temperature, the phase transition from h-AlN to c-AlN occurs at 13.9 GPa in QE and the 0 K transition at 12.9 GPa in VASP. This is in accord with previous theoretical studies^{11,13,14} and experimental values.¹² From the curvature

FIG. 3. PT phase diagram of AlN. The solid line separates the regions of stable hexagonal (wurtzite-type, B4) and cubic (rocksalt-type, B1) phases of AlN according to first-principles calculations. The squares in the phase diagram indicate the PT conditions of the $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ treatment after which the evidence of spinodal decomposition (i.e., the presence of c-TiN and c-AlN) was observed. The hexagons indicate the experimental conditions where the presence of h-AlN phase was observed in the samples after HPHT treatment.

of the equilibrium line, it is apparent that the cubic phase is stabilized not only by an increased pressure but also by an increased temperature. The phase diagram in Figure 3 has similar topology, but deviates somewhat from the one calculated by Siegel *et al.*,¹⁵ especially in the temperature range 0–1800 °C. In comparison to Siegel *et al.*,¹⁵ our transition curve in Figure 3 is shifted with 2–3 GPa to lower pressure, which is in agreement with the literature value of the theoretical 0 K transition pressure^{11,40} calculated with various approximations. Performing 0 K calculations on bulk $\text{Ti}_{1-x}\text{Al}_x\text{N}$ in VASP also shows that introduction of Ti stabilizes the cubic phase with respect to the hexagonal and pushes the phase transition to lower pressures. Doing single impurity calculations with a ratio of 1 Ti atom to 31 Al (equivalent to $x=0.96875$) the transition at 0 K drops from 12.9 GPa to 9.63 GPa and with 1 Ti to 7 Al ($x=0.875$) the transition is as low as 8.29 GPa.

The results we obtained due to the XRD investigation of the HPHT treated samples are also plotted in Figure 3. The squares in the phase diagram indicate the PT conditions of the $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ treatment after which the evidence of spinodal decomposition (i.e., the presence of c-AIN was observed). The hexagons indicate the experimental points where the presence of h-AIN phase was detected after HPHT treatment. The isotherms at 1200, 1500, and 2200 °C and the isobar at 11 GPa confirm the trend of the increased stability of c-AIN with increasing temperature or pressure. Hence, the experimental trends, i.e., the increased stability of c-AIN with both pressure and temperature, are in excellent agreement with the calculated.

It should be noted that the experimental values are achieved for the ternary solid solution of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ and not for AlN as in the calculated phase diagram. A direct comparison between experimental $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ results, i.e., the 11/1500 and 10/1700, and theoretical AlN results suggests that the addition of Ti further stabilizes the cubic phase of AlN. Calculations on TiAlN also show this, though note that the calculated values for the phase transition of TiAlN is for 0 K only and also not for the phase separated structure. One reason for this behavior in the phase separated alloy could be a template effect since the nanostructured domains of c-AIN are coherently surrounded by c-TiN which stabilizes the structure. Also, the onset of h-AIN is likely to generate an increase in elastic energy due to the ~20% larger molar volume⁴ associated with this phase, which further stabilize the cubic phase.

IV. CONCLUSIONS

In this work, we have studied the decomposition behavior of c- $\text{Ti}_{0.60}\text{Al}_{0.40}\text{N}$ solid solution coatings at elevated temperatures and pressures. We find excellent agreement between experimental and theoretical data showing a stabilization effect of c-AIN over h-AIN promoted by an increased pressure at elevated temperatures and by an increased temperature at elevated pressure. Also, by TEM, we confirm that the early stage transformation of cubic to hexagonal AlN preferentially occurs in column boundaries. In addition, this work furthermore demonstrates that the presence of Ti in

$\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings broadens the PT region where c-AIN is stable. $\text{Ti}_{1-x}\text{Al}_x\text{N}$ is commonly used as a protective coating on cutting inserts and the c-AIN to h-AIN transformation is known to contribute to the deterioration of the cutting properties. These results hence imply that the external stress acting on the coating during cutting suppresses the transformation into h-AIN. Also, the broadening of the PT region for c-AIN with the presence of Ti opens up the possibility for even further stabilization with additional alloying elements.

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- ¹O. Knotek, M. Bohmer, and T. Leyendecker, *J. Vac. Sci. Technol. A* **4**, 2695 (1986).
- ²H. A. Jehn, S. Hofmann, V. E. Ruckborn, and W. D. Munz, *J. Vac. Sci. Technol. A* **4**, 2701 (1986).
- ³M. Odén, J. Almer, G. Håkansson, and M. Olsson, *Thin Solid Films* **377–378**, 407 (2000).
- ⁴P. H. Mayrhofer, A. Hörling, L. Karlsson, J. Sjöln, T. Larsson, C. Mitterer, and L. Hultman, *Appl. Phys. Lett.* **83**, 2049 (2003).
- ⁵A. Hörling, L. Hultman, M. Odén, J. Sjöln, and L. Karlsson, *Surf. Coat. Technol.* **191**, 384 (2005).
- ⁶F. Tasnádi, I. A. Abrikosov, L. Rogström, J. Almer, M. P. Johansson, and M. Odén, *Appl. Phys. Lett.* **97**, 231902 (2010).
- ⁷L. Rogström, J. Ullbrand, J. Almer, L. Hultman, B. Jansson, and M. Odén, *Thin Solid Films* **520**, 5542 (2012).
- ⁸M. Odén, L. Rogström, A. Knutsson, M. R. Ternér, P. Hedström, J. Almer, and J. Ilavsky, *Appl. Phys. Lett.* **94**, 053114 (2009).
- ⁹A. Knutsson, M. P. Johansson, L. Karlsson, and M. Odén, *J. Appl. Phys.* **108**, 044312 (2010).
- ¹⁰D. Holec, F. Rovere, P. H. Mayrhofer, and P. B. Barna, *Scr. Mater.* **62**, 349 (2010).
- ¹¹B. Alling, M. Odén, L. Hultman, and I. A. Abrikosov, *Appl. Phys. Lett.* **95**, 181906 (2009).
- ¹²L. Bayarjargal and B. Winkler, *Appl. Phys. Lett.* **100**, 021909 (2012).
- ¹³F. Peng, D. Chen, H. Fu, and X. Cheng, *Physica B* **403**, 4259 (2008).
- ¹⁴W. Feng, S. Cui, H. Hu, W. Zhao, and Z. Gong, *Physica B* **405**, 555 (2010).
- ¹⁵A. Siegel, K. Parlinski, and U. D. Wdowik, *Phys. Rev. B* **74**, 104116 (2006).
- ¹⁶P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys. Condens. Matter* **21**, 395502 (2009).
- ¹⁷S. Baroni, S. De Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- ¹⁸N. Dubrovinskaia, L. Dubrovinsky, N. Miyajima, F. Langenhorst, W. A. Crichton, and H. F. Braun, *Z. Naturforsch. B* **61**, 1561 (2006).
- ¹⁹E. Y. Zarechnaya, L. Dubrovinsky, N. Dubrovinskaia, N. Miyajima, Y. Filinchuk, D. Chernyshov, and V. Dmitriev, *Sci. Technol. Adv. Mater.* **9**, 044209 (2008).
- ²⁰G. Parakhonskiy, N. Dubrovinskaia, L. Dubrovinsky, S. Mondal, and S. Van Smaalen, *J. Cryst. Growth* **321**, 162 (2011).
- ²¹J. D. Barnett, S. Block, and G. J. Piermarini, *Rev. Sci. Instrum.* **44**, 1 (1973).
- ²²L. Dubrovinsky, K. Glazyrin, C. McCammon, O. Narygina, E. Greenberg, S. Uebelhack, A. I. Chumakov, S. Pascarelli, V. Prakapenka, J. Bock, and N. Dubrovinskaia, *J. Synchrotron. Radiat.* **16**, 737 (2009).

- ²³L. Dubrovinsky, T. Boffa-Ballaran, K. Glazyrin, A. Kurnosov, D. Frost, M. Merlini, M. Hanfland, V. B. Prakapenka, P. Schouwink, T. Pippinger, and N. Dubrovinskaia, *High Press. Res.* **30**, 620 (2010).
- ²⁴L. Dubrovinsky, N. Dubrovinskaia, I. Kantor, F. Nestola, and D. Gatta, *High Press. Res.* **26**, 137 (2006).
- ²⁵R. M. Langford and A. K. Petford-Long, *J. Vac. Sci. Technol. A* **19**, 2186 (2001).
- ²⁶B. Alling, A. V. Ruban, A. Karimi, O. E. Peil, S. I. Simak, L. Hultman, and I. A. Abrikosov, *Phys. Rev. B* **75**, 045123 (2007).
- ²⁷B. Alling, A. V. Ruban, A. Karimi, L. Hultman, and I. A. Abrikosov, *Phys. Rev. B* **83**, 104203 (2011).
- ²⁸S. Baroni, P. Giannozzi, and E. Isaev, *Rev. Mineral. Geochem.* **71**, 39 (2010).
- ²⁹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ³⁰G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- ³¹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ³²V. L. Moruzzi, J. F. Janak, and K. Schwarz, *Phys. Rev. B* **37**, 790 (1988).
- ³³R. Rachbauer, S. Massl, E. Stergar, D. Holec, D. Kiener, J. Keckes, J. Patscheider, M. Stiefel, H. Leitner, and P. H. Mayrhofer, *J. Appl. Phys.* **110**, 023515 (2011).
- ³⁴A. Knutsson, M. P. Johansson, L. Karlsson, and M. Odén, *Surf. Coat. Technol.* **205**, 4005 (2011).
- ³⁵L. J. S. Johnson, M. Thuvander, K. Stiller, M. Odén, and L. Hultman, *Thin Solid Films* **520**, 4362 (2012).
- ³⁶R. Rachbauer, E. Stergar, S. Massl, M. Moser, and P. H. Mayrhofer, *Scr. Mater.* **61**, 725 (2009).
- ³⁷N. Norrby, M. P. Johansson, R. M'Saoubi, and M. Odén, *Surf. Coat. Technol.* **209**, 203 (2012).
- ³⁸A. Knutsson, Ph.D. dissertation, Linköping University, 2012.
- ³⁹American Society for Metals, *Diffusion: Papers Presented at a Seminar of the American Society for Metals, October 14 and 15, 1972* (American Society for Metals, Metals Park, Ohio, 1973), pp. 14–15.
- ⁴⁰N. E. Christensen and I. Gorczyca, *Phys. Rev. B* **47**, 4307 (1993)