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# Phase stabilities and thermal decomposition in the $Zr_{1-x}Al_xN$ system studied by ab initio calculation and thermodynamic modeling

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## Abstract

The ab initio density functional theory is used to calculate the lattice constants, total energy and bulk modulus of binary hexagonal close packed (hcp) and face-centered cubic (fcc) ZrN, AlN and ternary $Zr_{1-x}Al_xN$ phases. The calculated results are supported by previously reported experimental and theoretical data. The lattice stabilities of binary phases and demixing energies of ternary phases calculated by the ab initio method are then used in thermodynamic modeling to construct the Gibbs free energy diagram of the immiscible quasi-binary ZrN–AlN system at different temperatures. The results show that, for the composition $x \leqslant 0.472$, $Zr_{1-x}Al_xN$ solid solutions are more stable in fcc than in hcp structure, which is in a good agreement with the experimentally reported value of $x < 0.43$. The constructed chemically binodal and spinodal decomposition curves show that fcc $Zr_{1-x}Al_xN$ solution coatings should undergo phase decomposition into fcc ZrN and fcc AlN. However, considering the relatively large lattice mismatch between the fcc ZrN and the fcc AlN, the coherent spinodal decomposition may probably be hindered due to rapid phase transformation from fcc AlN to the stable hcp AlN. This is supported experimentally in that no intermediate fcc AlN has so far been observed in the Zr–Al–N system.

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*Keywords:* ZrN; Zr–Al–N; Spinodal decomposition; Ab initio calculation; Thermodynamic modeling

## 1. Introduction

Much effort has recently been focused on the development of new super- and ultrahard materials (e.g. [1–7] and references therein), because of their fundamental scientific interest and their industrial applications [8,9]. Transition metal nitride coatings have been commercially available for many decades, and offer a combination of high hardness, high thermal stability, reasonably good high temperature strength and oxidation resistance [10–12]. Among the ternary Me–Al–N (Me = transition metal) systems, Ti–Al–N and Cr–Al–N coatings have been the most widely investigated, whereas very few studies have been devoted to the Zr–Al–N system. It is known that ZrN has a lower coefficient of friction than TiN and other transition metal nitrides, and is relatively hard [13,14]. However, its poor oxidation resistance hampers a broader range of applications. Therefore, alloying ZrN with Al was suggested in order to improve the oxidation resistance and possibly also the mechanical properties [15]. Recent experimental studies have shown that only the face-centered cubic (fcc, NaCl-type) $Zr_{1-x}Al_xN$ solid solution exists for $0 < x < 0.43$, and the hardness increases from 21 to 28 GPa when the Al content increase from $x = 0$ to 0.43 [16]. With further addition of Al, hexagonal close packed (hcp, ZnS-type) AlN appears and the hardness of the coatings decreases. Based on these relatively limited experimental data, it is of interest to study the phase stability as well as the thermal decomposition mechanism of this ternary system by means of combined ab initio density functional theory (DFT) and thermodynamic calculations in order to predict and compare its properties with other systems.

In recent decades, theoretical investigations of hard transition metal nitrides have attracted much interest.

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These studies can be categorized as either (i) first-principles ab initio calculations [17,18] or (ii) thermodynamic modeling [19,20]. It is well known that the advantage of ab initio calculation is the fact that no experimental input data are needed and a much deeper physical insight can be obtained. However, its applications are limited to the ground state properties at 0 K (unless dynamics computations such as the Car–Parrinello method, which are several orders of magnitude more time consuming, can be afforded), and to a given structure (which in turns limits the composition range), because the theoretical modeling is based on reciprocal space methods. Conversely, thermodynamic modeling is much simpler and faster, and it can cover the whole composition range and account for variety of chemical activities at different temperatures. However, such calculations require the knowledge of the relative stability of different structures and of the interaction parameters between the constituent components. Such data are experimentally unavailable for strongly immiscible systems. Recently, Zhang et al. developed a combined method that uses ab initio calculations to determine the lattice stabilities and interaction parameters of the phases involved, which are then used in thermodynamic modeling. This method has been successfully applied to the $Ti_{1-x}Si_xN_y$ [21,22], $Ti_{1-x}Al_xN$ [23] and $Cr_{1-x}Al_xN$ [24] systems. It will be used here for the mixed ternary $Zr_{1-x}Al_xN$ and quasi-binary ZrN–AlN systems in order to investigate the conditions of the relative stability of the different phases, and of the decomposition of fcc $Zr_{1-x}Al_xN$ solid solution over the whole composition range.

The paper is organized as follows. In Section 2, the theory and computational methods are described. In Section 3, the results regarding lattice parameters, bulk moduli and their first derivative (pressure dependence), phase stabilities, thermodynamic properties and possible phase decomposition are presented and discussed. The paper concludes with a brief summary in Section 4.

## 2. Theoretical methods used in the present work

### 2.1. The method of ab initio calculation

The ab initio DFT calculations were done using the Vienna Ab initio Simulation Package (VASP) developed at the Institute of Materials Physics of the University of Vienna [25–27]. The calculations were conducted in a plane-wave basis, using fully non-local Vanderbilt-type ultra-soft pseudopotentials to describe the electron–ion interaction [28], which allows one to use moderate cutoff for the construction of the plane-wave basis. The exchange and correlation terms were described by the generalized-gradient approximation proposed by Perdew and Wang [29]. The integration in the Brillouin zone has been done on special $k$ points ($8 \times 8 \times 8$ Monkhorst–Pack grid) determined according to the Monkhorst–Pack scheme [30] with energy cutoff of 600 eV, and using the tetrahedron method with Blöchl corrections for the energy calculation.

The fcc (NaCl-type) structure (space group $Fm\text{–}3m$, No. 225) was described by a simple fcc Bravais lattice with atoms placed in the $(0,0,0)$ and $(1/2,1/2,1/2)$ positions. It has been allowed to relax in volume, i.e. lattice parameter $a$, keeping the relative position of atoms and the cell shape constant. The hcp (ZnS-type) structure (space group $P63mc$, No. 186) was described by a hexagonal Bravais lattice with two metal atoms placed in the $(1/3,2/3,0)$ and $(2/3,1/3,1/2)$, and two non-metal atoms in the $(1/3, 2/3, u)$ and $(2/3,1/3,u+0.5)$ positions, where $u$ is the internal structure parameter which determines the vertical position of the non-metal atoms. Here, we used the initial ideal value of $u = 0.375$ for further, full relaxation. The lattice parameters, internal structural parameters and cell shape were all subject to the lattice relaxation. Both fcc and hcp structures were studied using a supercell setup containing four metal and four non-metal atoms. For ternary $Zr_{1-x}Al_xN$ phases in fcc and hcp structure, Zr and Al atoms were randomly distributed over the whole metal sublattice. The choice of the position of metal sublattice in substitution was found to have no significant effect on the results of the present calculations. This is in agreement with the finding of Hugosson et al. who systematically studied several $Me_{1-x}Al_xN$ systems [18]. The total energies and the lattice constants of metastable hcp ZrN and fcc AlN, stable fcc ZrN and hcp AlN, and the ternary fcc and hcp $Zr_{1-x}Al_xN$ ($x = 0.25, 0.5, 0.75$) phases were calculated and optimized. The optimized values were used for the determination of the lattice stabilities of metastable hcp ZrN and fcc AlN phases with respect to the corresponding stable fcc ZrN and hcp AlN phases, as well as for the determination of the interaction parameters of the ternary fcc and hcp $Zr_{1-x}Al_xN$ solid solution phases.

In order to determine the molar volume, the bulk modulus and its pressure derivative of the relevant phases, the total energy ($E$) was calculated as a function of the cell volume ($V$) by means of the ab initio DFT method. Afterwards, the Murnaghan equation of state (EOS, Eq. (1)) [31] has been applied to fit the calculated $E-V$ curves close to the equilibrium.

$$E_{\mathrm{Murn}}(V) = -E_0 + \frac{B_0 V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0'-1}+1\right] - \frac{B_0 V_0}{B_0'-1}. \tag{1}$$

From this fit, the bulk modulus $B_0$, its pressure derivatives $B_0'$, cell volume $V_0$ and total energy $E_0$ were obtained. The cohesive energies $E_c$ were calculated from the total energy of compounds at equilibrium by subtracting the total energies of spin-polarized free atoms. In order to study the relative stabilities of the ternary compounds with reference to the terminal phases, we define in Eq. (2) the formation energy of the ternary phase with reference to the terminal phases, i.e. demixing energy $\Delta E_{\mathrm{demixing}}$, as the difference between the total energy of the ternary $Zr_{1-x}Al_xN$ phase $E_{Zr_{1-x}Al_xN}$, and of the reference states of fcc ZrN, $E^{\mathrm{fcc}}_{\mathrm{ZrN}}$, and hcp AlN, $E^{\mathrm{hcp}}_{\mathrm{AlN}}$.

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