Phase stabilities and decomposition mechanism in the Zr–Si–N system studied by combined ab initio DFT and thermodynamic calculation

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Abstract

The total energy, lattice constant, bulk modulus and its first derivative of stable binary face-centered cubic (fcc)-ZrN, hexagonal close-packed (hcp)(β)-Si$_3$N$_4$, and unstable hcp-Zr$_3$N$_4$ and fcc-SiN, as well as the total energy and lattice constant of the ternary fcc(NaCl)- and hcp(β)-Zr$_{1-x}$Si$_x$N$_y$ solid solution phases were calculated by ab initio density functional theory (DFT) at 0 K. A combination of ab initio DFT and thermodynamic calculations was then used to study the phase stabilities and possible mechanisms of the decomposition of the Zr$_{1-x}$Si$_x$N$_y$ solid solution at elevated temperatures accounting for the mixing entropy and for the temperature dependence of the interaction parameter that describes the mixing enthalpy. It is shown that the exponential dependence of the interaction parameter on temperature yields more reliable results than the conventionally used linear one. The fcc- to hcp-phase transition points obtained by the exponential dependence in the range of $x \cong 0.10$–0.15, are in a better agreement with the experimental results than the results obtained from linear dependence. We have also calculated the temperature–composition diagrams and found that spinodal phase segregation mechanism may be possible only for a relatively high Si content, whereas for the low Si content, where a hardness enhancement has been reported, the most probable mechanism of the phase segregation is nucleation and growth.
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1. Introduction

High hardness enhancement has been reported for a variety of nanocrystalline nc-TmN/a-Si$_3$N$_4$ nanocomposites (Tm = Ti, W, V, ...), with nc-TiN/a-Si$_3$N$_4$ being the most studied system [1–3]. The nanostructure consists of a few nanometers of a transition metal nitride size with a Si$_3$N$_4$-like interfacial layer about one monolayer (ML) thick, which is strengthened by valence charge transfer from the TiN [4–6]. A similar conclusion has been drawn from experimental results for several other nc-TmN/a-Si$_3$N$_4$ systems (Tm = W, V, (Ti$_{1-x}$Al$_x$) [3]). It has been shown that the formation of such nanostructure occurs by self-organization upon the spinodal segregation of the

TiN and SiN$_x$ phases [7–9]. A similar conclusion has been obtained also for the Ti$_{1-x}$B$_x$N system [10]. In the present paper we shall show that spinodal phase segregation appears unlikely in the Zr–Si–N system where the phase segregation occurs most probably by nucleation and growth. It should be pointed out that pure, stoichiometric Si$_3$N$_4$ and ZrN are, like many other transition metal nitrides in combination with Si$_3$N$_4$ and BN, immiscible [11].

The Zr–Si–N system has been experimentally studied by several groups who used reactive sputtering. In the majority of the papers the deposition conditions used did not enable the formation of fully segregated nanostructure. For example, Nose et al. [12] used a low deposition temperature of $\leqslant 100\ ^\circ$C at which the diffusion, which controls kinetically the segregation, is too slow. The only crystalline phase identified in these films was the cubic B1 NaCl

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structure of ZrN, whose lattice constant slightly increased with the initial increase of the Si content to about 4 at.% followed by an about 4% decrease for Si content of 12.8 at.%, which is probably due to the formation of substitutional $Zr_{1-x}Si_xN_y$ solid solution (the atomic diameter of Si is 0.132 nm, smaller than that of Zr of 0.160 nm). These researchers reported a hardness maximum of about 35 GPa for a Si content of about 3 at.%. The morphology changed from columnar to equiaxial at about 5 at.% Si. Films containing 12.8 at.% Si showed the lowest hardness of 18 GPa and a crystallite size of 2–2.5 nm. In a subsequent investigation [13], these authors reported that higher deposition temperatures up to 400 °C had only a little effect on the hardness. Although such a temperature is still too low to enable a complete segregation of the immiscible stoichiometric face-centered cubic (fcc)(NaCl)–ZrN and hexagonal close-packed (hcp)(β)-Si_3N_4 phases [14], one would expect some noticeable improvement of the hardness. Therefore one has to consider a possible effect of impurities which, in the Ti–Si–N nanocomposites, limits the maximum achievable hardness to about 35 GPa [3]. However, impurities are not reported in these papers. Song et al. studied the microstructure and properties of Zr–Si–N diffusion barrier films [15], and showed that with increasing substrate bias from −50 to −200 V, the Zr/Si ratio and the surface roughness increased, but the resistivity of the film decreased. With the decrease of the bias, the microstructure of Zr–Si–N film changed from composites consisting of ZrN nanocrystals in amorphous SiN_x to fully amorphous films. The reason for this change was not been clarified in that paper; it may be associated with oxygen impurities [8]. In a series of studies [16–18], Sandu et al. also found a hardness maximum of about 32 GPa for a Si content of about 3 at.% in coatings deposited at temperatures of 240 and 440 °C. Coatings deposited at room temperature showed a maximum hardness of only 20 GPa for Si content of about 6 at.%. In this work as well as in that of Nose et al., the maximum hardness correlated with a maximum biaxial compressive stress, which was enhanced by energetic ion bombardment of the growing films. In all these papers, the coatings had a pronounced columnar morphology instead of a fully isotropic one, as reported by Veprek et al. for fully segregated nanocomposites on the basis of scanning electron microscopy [19,20] and high-resolution transmission electron microscopy [21].

The relatively low hardness of about 32–35 GPa reported in all these papers may be due to oxygen impurities, which, however, have not been reported in majority of the papers. Only in the paper by Sandu is an oxygen and carbon impurity content "below 2 at.% for each" (i.e. ≤4 at.% total) mentioned, i.e. the total impurity content is slightly higher than the Si content of about 3 at.% at which the hardness maximum is found [16]. The hardness of such coating is determined by the strength of the oxygen-related defects within the SiN_x interface [3,20,21]. The above-quoted papers contain also some suggestions regarding the formation of the nanostructure. ZrN/SiN_x nanomultilayers with different thicknesses of Si_3N_4 were investigated by Dong et al. [22]. By analogy with the TiN/SiN_x heterostructures [23,24], the maximum hardness of about 32 GPa was achieved in ZrN/SiN_x heterostrutres for pseudomorphic fcc(NaCl)–SiN about 1–2 ML thick. When the SiN_x thickness was larger than about 1.1 nm, amorphous SiN_x formed and the hardness strongly decreased [22].

In this paper, we shall study the phase stabilities of the Zr–Si–N system and possible mechanism of the segregation of the Zr- and Si-nitrides by means of combined ab initio calculation and thermodynamic modeling, as used in the recent papers for other systems [9,25–27]. Special attention will be given to the importance of the dependence of the interaction parameter on temperature, because many authors have considered only the Redlich–Kister polynomial [28] in linear approximation or even as a temperature-independent parameter, which yielded physically unreasonably high spinodal temperatures. Therefore, we consider also the exponential T-dependence which has been recently recommended by Kaptay [29] and successfully used for the thermodynamic modeling of the Zn–Zr system [30]. In Section 2 we describe the details of the computational methods followed by results and discussion in Section 3, and a brief summary in Section 4.

2. Theoretical methods used in the present work

2.1. Ab initio density functional theory (DFT) 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 [31–33]. The calculations were conducted using the projector augmented wave (PAW) method to describe the electron–ion interaction [34,35]. The exchange and correlation terms were described by the generalized-gradient approximation (GGA) proposed by Perdew and Wang [36]. 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 [37] with an energy cutoff of 600 eV, and the tetrahedron method with Blöchl corrections for the energy calculation.

In the calculations we considered the fcc(NaCl-type), space group Fm-3m, No. 225 with a supercell containing 16 atoms, and hcp (β-type), space group P6₃/m, No. 176 with a supercell of 14 atoms. First we conducted the relaxation of the cells of the binary stable phases to a minimum total energy. In the case of the fcc(NaCl) cell with high symmetry, only the relaxation of the lattice constant is necessary. In the case of the hcp(β) cell we performed a geometry optimization for hcp(β)-Si_3N_4 with a full relaxation of the ion positions, cell shape and cell volume. The optimum geometries were then used to determine the lattice stabilities of the unstable hcp(β)-Zr_3N_4 and fcc-SiN with respect to the corresponding stable fcc-ZrN and hcp(β)-Si_3N_4