Mechanical properties and spinodal decomposition of $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ coatings

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Abstract

A 64-atom special quasirandom structure (SQS) has been employed to model the $A_{0.5}B_{0.25}C_{0.25}D$, i.e., the $Ti_xAl_{1-x-y}Zr_yN$ with $x = 0.5$ and $y = 0.25$, coating alloys in rock salt structure. Elastic constants are calculated by an efficient stress-strain method. The presence of Zr in $Ti_xAl_{1-x-y}Zr_yN$ weakens the directional (covalent) nature of the nearest bonds and decreases the hardness of coatings. Additionally, the increase of Zr content changes Zener's elastic anisotropy ratio (A) from ($A > 1$) to ($A < 1$), resulting in the alteration of spinodal decomposition from $\langle 100 \rangle$ to $\langle 111 \rangle$ direction.

Keywords:

TiAlZrN

First-principles calculations

Mechanical properties

Spinodal decomposition

1. Introduction

Binary transition metal nitride such as TiN has been commercially available for many decades as protective hard coatings for cutting tool applications due to its relatively high hardness, good wear-resistance, and low friction [1]. To make the coatings more resistant against oxidation and thermal stability, ternary nitride $\text{Ti}_{1-x}\text{Al}_x\text{N}$ with cubic B1 structure has been developed as a typical coating material by alloying of TiN with Al, where the metastable solubility is limited around $x < 0.7$ [2-5], thus being widely used in industrial applications. In particular, the age-hardening abilities of Ti-Al-N coatings, which are due to the spinodal decomposition of c- $\text{Ti}_{1-x}\text{Al}_x\text{N}$ into nano-size cubic Ti-rich and Al-rich domains at elevated temperatures, have improved high temperature mechanical properties, and, therefore, attracted more attention [6]. With the increasing requirements on the high speed and dry cutting applications, a lot of efforts are made to increase further the properties of Ti-Al-N by adding alloying elements X (e.g., X = Cr, Nb, Ta, Si, Zr, and Y) to develop the quaternary Ti-Al-X-N coatings [7-13]. Recently, it was reported that the addition of Zr to Ti-Al-N has effective influence on the mechanical properties as well as thermal stability which relate to the spinodal decomposition [14]. Although several experiments have been performed on the Ti-Al-Zr-N coatings [15, 16], little is known on the aspect of theoretical work. Recent theoretical studies confirm that the spinodal decomposition of the ternary Ti-Al-N is influenced by elastic anisotropy [17]. Additionally, the hardness enhancement is also related to elastic modulus and bonding strength. Consequently, theoretical investigation of mechanical properties of Ti-Al-Zr-N alloys can play an important role in understanding the aforementioned experimental observation [14] regarding the effect of Zr addition on the Ti-Al-N coatings as well as the guidance for the further designation of multicomponent coatings with substantially improved properties.

The present work aims to investigate the mechanical properties and spinodal decomposition of the Ti-Al-Zr-N coatings via first-principles calculation. Concerning the treatment of quaternary disorder alloys, other works mainly use the conventional

supercell approach, e.g., the description for $\text{Ti}_{1-x-y}\text{Si}_x\text{Al}_y\text{N}$ [18], or use one or two metal atoms to arbitrarily replace the atoms on the metallic sublattice of the ternary special quasirandom structure (SQS) model, forming the quaternary alloys, such as the study for Ti-Al-Ta-N [8]. Here, we plan to develop the quaternary SQS model to describe the disordered Ti-Al-Zr-N alloy. The presently adopted SQS-64 (64 atoms, the same below) is developed based on the general SQS-32 for fcc based ternary alloys, where we put the 32 N atoms in the tetrahedral sites, forming the quaternary SQS for cubic B1 structure. Note that some fcc-based ternary SQS-32 models have been constructed previously [19], and these models will be used on the metallic sublattice for the Ti-Al-Zr-N system. The relative large SQS-64 employed herein can guarantee expected compositions of a quaternary alloy. The presented employed SQS-64 is shown in Figure 1 in their ideal and unrelaxed forms, which will be used to describe the mechanical properties and spinodal decomposition of the present $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ coating alloys.

2. Methodology

In the present work, a four-parameter Birch-Murnaghan equation of state (EOS) [20] is used to fit the first-principles energy (E) versus volume (V) data points to get the equilibrium properties of the $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ alloys,

$$E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-6/3} \quad (1)$$

where a , b , c , and d are the fitting parameters. Accordingly, the strain-stress method [21] is employed to calculate elastic stiffness constants. All the first-principles calculations in the present work are performed by the projector-augmented wave method (PAW) method as implemented in the Vienna ab initio simulation package (VASP) [22, 23]. The generalized gradient approximations (GGA) of Perdew–Burke–Ernzerhof (PBE) [24] is utilized to depict the exchange-correlation functional. Convergence tests indicated that a cutoff of 520 eV is sufficient to insure the total energy differences are less than 1 meV/atom for all the compounds of interest. The Monkhorst-Pack scheme [25] of k -points sampling is employed with at

least 10,000 points per reciprocal atom. The linear tetrahedron method including Blöchl corrections [26] is adopted for the integration in the Brillouin zone (BZ) and the energy convergence criterion of electronic self-consistency is chosen as 10^{-7} eV/atom for all calculations.

3. Results and discussion

Total energies of $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ calculated at 7 different volumes are fitted by the four parameters EOS of equation (1). The obtained equilibrium properties at 0 K, including lattice parameters (a_0), bulk modulus (B_0) as well as its pressure derivative (B_0'), are listed in Table I. For lattice parameters of the ternary Ti-Al-N, although no experimental data for comparison, the present calculations agree well with other theoretical results [18, 27, 28]. The maximum deviation between the present values and the theoretical ones available in the literature is 0.47%. Cubic crystals have three independent single-crystal elastic constants c_{ij} 's. Table I summarizes the calculated c_{ij} 's of $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ in comparison with other theoretical results [29]. The maximum errors between present c_{ij} 's and theoretical values [29] are within 9.7%, except for the C_{12} of $\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$, for which the errors are 21%. It is found that all the $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ alloys are mechanically stable since their elastic constants obey the elastic stability criteria [30]: $C_{44} > 0$, $C_{11} - |C_{12}| > 0$, $C_{11} + 2C_{12} > 0$. From the calculated c_{ij} 's, the polycrystalline bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio ν and anisotropy ratio A can be further estimated using the Voigt-Reuss-Hill approximation[31]. The present elastic properties are in consistent with the theoretical values [29]. The maximum difference between present results and other calculations [29] are 5.3%, 8.5%, 6.3% and 15.7% for bulk modulus B, shear modulus G, Young's modulus E and Poisson's ratio ν , respectively. To verify the accuracy of the present c_{ij} 's, we compare the bulk moduli from c_{ij} 's and from the EOS fittings of equation (1). Note that at each fixed volume, the cell shape and all internal atomic positions are fully relaxed. As shown in Table I, the bulk moduli from EOS agree well with the ones from c_{ij} 's, verifying further the accuracy of the present calculations. For facility

the analyses regarding the influence of Zr on the mechanical properties of Ti-Al-N alloys, we keep the Ti content constant. Thus, two groups of alloys with the first group of $\text{Ti}_{0.25}\text{Al}_{0.75}\text{N}$, $\text{Ti}_{0.25}\text{Al}_{0.5}\text{Zr}_{0.25}\text{N}$, and $\text{Ti}_{0.25}\text{Al}_{0.25}\text{Zr}_{0.5}\text{N}$ alloys and the second group of $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ and $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Zr}_{0.25}\text{N}$ alloys are used herein. Table I shows that with increasing Zr content the value of c_{11} increases, while the values of c_{12} and c_{44} decrease. Figure 2 shows the Blackman's diagram [32] of the Ti-Al-Zr-N alloys, which give the general characteristics of these alloys, such as elastic anisotropy ratio A and interatomic bonding type. The dashed line represents the $A = 1$, where A is Zener's elastic-shear anisotropy ratio, calculated by $A = 2c_{44}/(c_{11} - c_{12})$. Above or below the dashed line corresponds to the value of A larger or smaller than 1, respectively. The solid line represents the zero Cauchy pressure (PCauchy) which separates the positive and negative Cauchy pressure, where Cauchy pressure equals to $c_{12} - c_{44}$. According to Pettifor [32], Cauchy pressure is positive in case of fairly metallic bonds and negative for more directional or covalent like bonds. In consistent with the predictions from Tasnádi et al [17], the present ternary Ti-Al-N alloys are all in the covalent like region and the decreasing Cauchy pressure with increasing Al-content shows a tendency toward stronger covalent character. The strong covalent bonds indeed create a significant resistance to initialize the plastic flow to pin the dislocation, resulting in a quite high hardness. Therefore, the Ti-Al-N alloys with high Al-content are harder than the low Al-content ones due to the stronger covalent bonds for former, see Figure 2. However, with increasing Zr addition of the Ti-Al-N system, the hardness of $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ decreases because the bond character changes to metallic. To confirm this conclusion, we further estimate the Vickers hardness (H_v) by a simple and efficient model proposed by Chen et al. [33]:

$$H_v = 2(k^2 G)^{0.585} - 3 \quad (2)$$

where H_v (in GPa), k and G (in GPa) are the hardness, Pugh's modulus ratio (namely ratio of bulk to shear modulus), and shear modulus, respectively. Here the predicted H_v values are 21.9 GPa for TiN, 15.8 GPa for ZrN, and 35.7 GPa for AlN, comparing well with experimental results of 18-21 GPa for TiN [34] and 15 GPa for ZrN [34].

With regard to the ternary Ti-Al-N and the quaternary Ti-Al-Zr-N alloys (shown in Table I), the predicted change trends for hardness with different Al and Zr contents is inconsistent with the indications of Blackman's diagram (see Figure 2). However, experimental study suggests that the addition of Zr in Ti-Al-N has the ability to increase coating's hardness [14]. It should be note that the enhanced hardness observed from experiments, as a matter of fact, is mainly due to the solid solution strengthening [15, 16], which is beyond the scope of present work.

It is found that spinodal decomposition is influenced by elastic anisotropy [35]. For a cubic alloy with the Zener's elastic anisotropy ratio larger than unit 1, the $\langle 100 \rangle$ direction is the elastically soft direction. From the early stage decomposition at the film surface, the decomposed phases have a tendency to align along the $\langle 100 \rangle$ direction. Conversely, the spinodal decomposition will give rise to strong preferred orientations (the $\langle 111 \rangle$ direction) [35]. As shown in Figure 2, the computed elastic anisotropy of ternary Ti-Al-N agrees well with the previous predictions [17], indicating that the spinodal decomposition of TiAlN at higher Al content will begin along the $\langle 100 \rangle$ direction. However, with increasing Zr content in the quasi-ternary alloys, elastic anisotropy changes from the value larger than 1 to the value smaller than 1, suggesting that the early stage decomposition direction tends to prefer the $\langle 111 \rangle$ instead of the $\langle 100 \rangle$.

4. Conclusions

In summary, the 64-atom special quasirandom structure (SQS) has been developed to model the substitutionally quaternary random $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ ($x = 0.5$ and $y = 0.25$) alloys in rock salt structure. First-principles SQS calculations have been performed to investigate the structural and mechanical properties of $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$, and compared with the available data in the literature. It is found that the presence of the Zr in $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ weakens the directional (covalent) nature of the nearest bonds and decreases the hardness of coatings. Additionally, increasing Zr-content also changes Zener's elastic anisotropy ratio (A) from ($A > 1$) to ($A < 1$), thus result in the change

of directions of spinodal decomposition from $\langle 100 \rangle$ to $\langle 111 \rangle$. It is expected that the present calculations can provide new insight into the understanding of age hardening in the Ti-Al-Zr-N coatings.

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Table I Calculated structural and elastic properties of $\text{Ti}_x\text{Al}_{1-x-y}\text{Zr}_y\text{N}$ in rock salt structure, including the lattice parameters a_0 (Å), bulk modulus B_0 (GPa) and its pressure derivative B_0' by EOS fittings of Equation (1), single crystal elastic constants C_{ij} (GPa), polycrystal aggregate properties of bulk modulus B (GPa), Young's modulus E (GPa) and shear modulus G (GPa) in VRH approach, Zener's anisotropy ratio A , Poisson's ratio (ν), and Vickers hardness H_v (GPa).

		a_0	B_0	B_0'	C_{11}	C_{12}	C_{44}	B	G	E	A	ν	H_v
$\text{Ti}_{0.25}\text{Al}_{0.75}\text{N}$	PW	4.13	256	4.17	442	163	239	256	192	462	1.71	0.20	28.1
	Cal[29]				439	159	233	252	196	467		0.19	
$\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$	PW	4.18	267	4.30	465	163	205	264	181	443	1.35	0.22	24
	Cal[27]	4.19											
	Cal[29]				464	154	227	257	198	473		0.19	
$\text{Ti}_{0.75}\text{Al}_{0.25}\text{N}$	PW	4.22	279	4.41	535	150	176	278	183	450	0.91	0.23	22.7
	Cal[18]	4.20											
	Cal[28]	4.219											
	Cal[29]				544	124	187	264	196	472		0.20	
$\text{Ti}_{0.25}\text{Al}_{0.5}\text{Zr}_{0.25}\text{N}$	PW	4.29	254	4.32	455	147	178	250	168	412	1.16	0.22	22.2
$\text{Ti}_{0.25}\text{Al}_{0.25}\text{Zr}_{0.5}\text{N}$	PW	4.42	257	4.42	488	137	141	255	154	384	0.81	0.24	18.2
$\text{Ti}_{0.5}\text{Al}_{0.25}\text{Zr}_{0.25}\text{N}$	PW	4.33	266	4.76	493	146	152	262	160	399	0.87	0.24	19

Cal= other first-principles calculations

PW = the present work

Figure captions

Fig.1. Crystal structure of the quaternary SQS-64 with composition $A_{0.5}B_{0.25}C_{0.25}D$ in its ideal and unrelaxed form. Large spheres represent A (red color), B (blue color) and C (green color) atoms, respectively. The small spheres represents D atoms.

Fig. 2. Predicted Blackman's diagram of the $Ti_xAl_{1-x-y}Zr_yN$ alloys.

Figure 1

Figure 2