Electronic and elastic properties of $Ti_xZr_{1-x}N$

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Abstract. The lattice parameter, elastic modulus, elastic constants and electronic structure of $Ti_xZr_{1-x}N$(x=0, 0.25, 0.5, 0.75, 1) were studied with first-principle pseudopotential plane-waves method. The lattice parameters of $Ti_xZr_{1-x}N$ increase with Zr atoms increasing. Bulk modulus B, shear modulus G and Young's Modulus E express a monotonously decreasing with Zr concentration. For the shear modulus is proportional to the hardness, the hardness is supposed to be decreasing with Zr concentration. By analyzing the density of states, N p and Ti(Zr) d states hybridized strongly, which form the strong p-d covalent bonds, having positive impact on the hardness.

Introduction

The TiN-ZrN system has gained much attention due to its various charactieristics, such as high melting point, high hardness, corrosion resistance and god-like color of the constitutive binary nitrides[1]. Thus TiN-ZrN are widely used as hard coatings, grain refiners and strengthening phases.

There already are some reports on the structural and mechanical properties of (Ti,Zr)N alloys. Single-phase $Ti_{1-x}Zr_xN$ thin films could be stable up to 1200℃ and the lattice parameters increase with Zr content, almost obeying vegard-like behavior.[2] It is found that the Ti-Zr bonds are weaker than Ti-N bonds from the results of band structure calculations.[3] The calculated single-crystal stiffnesses, namely C_{11}, C_{12} and C_{44}, gradually decrease with the Zr concentration.[4]

After all, the relationship between elastic properies and electronic structures which is important to explain the change of mechnical properties of $Ti_{1-x}Zr_xN$, is still not studied. Thus, the theoretical investigations of $Ti_xZr_{1-x}N$(x=0, 0.25, 0.5, 0.75, 1) with the DFT (Density Functional Theory) method were carried out. The lattice parameter, elastic constants, elastic modulus and density of states (DOS) are studied. The relationship between the elastic properties and DOS is reported here firstly.

Method of calculation

The whole calculations were carried out with the DFT[5] based on the Cambridge Serial Total Energy Package (CASTEP) plane wave code[6]. The interaction of ionic core and valence electrons were described with ultrasoft pseudopotentials. Valence states were corresponding to N $2s^2$ $2p^3$, Ti $3s^2$ $3p^6$ $3d^2$ $4s^2$ and Zr $4s^2$ $4p^6$ $4d^2$ $5s^2$. The exchange and correlation terms adopted the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerh (PBE) parameterized by Perdew[7] method. With Monkhorst and Pack k-point meshes, brillouin-zone integrations were calculated[8]. The cutoff energies and the numbers of k-point were set as 600 eV and 14×14×14.

During the calculation，the unit cell with periodic structure was adopted. The space group of TiN is FM-3M (shown in Fig.1) and there are 4 carbon atoms and 4 titanium atoms in one unit cell. Then, the titanium atoms are gradually substituted with 1, 2, 3 and 4 Zr atoms.
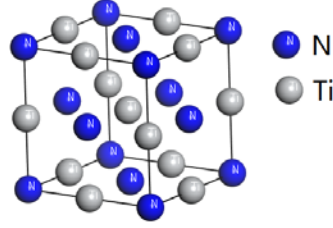
Fig.1 Unit cell of TiN.

Results and discussion

Crystal lattice parameter. The present lattice parameters after geometry for TiN and ZrN compared with other experimental and theoretical data are shown in Table 1. It is can be found that our results agree well with other experimental and theoretical data.

Table 1. Present lattice parameters after geometry for TiN and ZrN compared with other theoretical and experimental data.

	$a(\text{Å})$		
	present	experiment	theory
TiN	4.25	4.24[9], 4.24[10]	4.24[11], 4.30[12]
ZrN	4.59	4.54[11], 4.61[13]	4.59[14], 4.57[12]
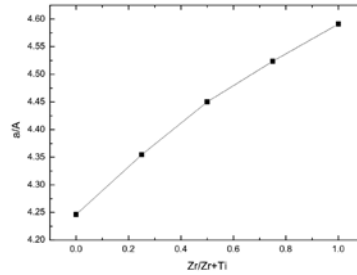
Fig. 2 The equilibrium lattice parameters of $Ti_xZr_{1-x}N$(x=0, 0.25, 0.5, 0.75, 1).

From Fig.2 it can be found that the lattice parameters a increase almost linearly with Zr concentration. That's due to the atom radius and the covalent radius of Zr are bigger than the ones of Ti atom.

**Elastic properties of $Ti_xZr_{1-x}N$.** The elastic constants C_{ijkl} are calculated with the equation[15]

$$C_{ijkl} = (\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}})_X ,$$

where e_{kl}, σ_{ij}, X, x are Eulerian strain tensor, applied stress tensor and the coordinates before and after deformation respectively. Only three independent elastic constants are for cubic symmetry, C_{11}, C_{12} and C_{44}. The bulk modulus B can be deduced from the elastic constants:

$$B = \frac{c_{11} + 2c_{12}}{3} .$$

The isotropic shear modulus G and Young's modulus E are usually used to evaluate the elasticity properties of materials. They are also can be deduced from elastic constants: (G is regarded as the average of the Voigt and Reuss bounds)[16]:

$$G = \frac{1}{2}[\frac{c_{11} - c_{12} + 3c_{44}}{5} + \frac{5c_{44}(c_{11} - c_{12})}{4c_{44} + 3(c_{11} - c_{12})}], \quad E = \frac{9BG}{3B + G} .$$
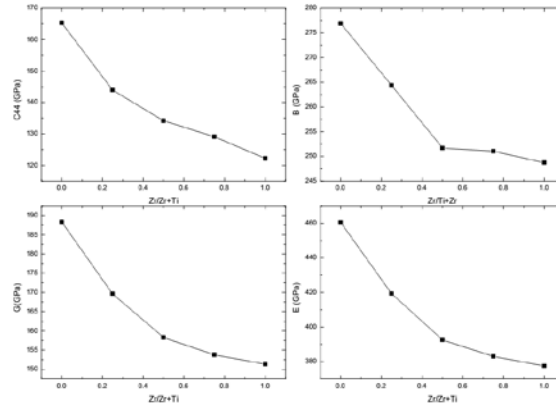
Fig.3 Variations of elastic constant C_{44}, shear modulus G, Young's modulus E and bulk modulus B with the concentration Zr of $Ti_xZr_{1-x}N$. (the units in GPa)

B decreases monotonously with the Zr atoms increasing, which means the ability of resistance to uniform compression drops with the decreasing Zr atoms. Moreover, the values of C_{44} and *G* of $Ti_xZr_{1-x}N$ also present a monotonously decreasing order with Zr atoms increasing, which suggests the ability of resistance to shear strain declined with Zr atoms increasing. Large value of shear modulus is according to the pronounced directional bonding between atoms[17]. Thus with the Zr concentration increasing, less directional for $Ti_xZr_{1-x}N$ the bonding behavior is. Furthermore, shear modulus is directly proportional to the hardness[18]. Therefore, the hardness is supposed to be decreasing with the increasing Zr concentration. In addition, *E* express a monotonously decreasing order with the Zr atom increasing, which is according to the decreasing resistance ability of stretching.

Electronic structure of $Ti_xZr_{1-x}N$. To find out the electronic origin of the composition dependence of elastic properties of $Ti_xZr_{1-x}N$, the density of states (DOS) are calculated. As the DOS located near the Fermi level are crucial to the bonding, the total density of states (TDOS) and partial density of states (PDOS) near Fermi level for $Ti_xZr_{1-x}N$ are listed in **Fig.4**.
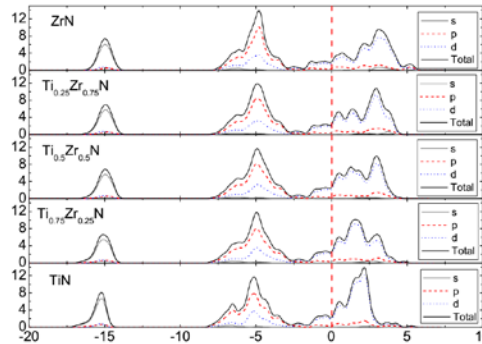
Fig.4 TDOS and PDOS for $Ti_xZr_{1-x}N$(x=0, 0.25, 0.5, 0.75, 1). Fermi level is expressed in dash line at 0eV.

The TDOS and PDOS of $Ti_xZr_{1-x}N$(x=0, 0.25, 0.5, 0.75, 1) are similar. They can be divided into three parts. The first part located below -13eV contains predominantly nonmetal N 2s states, which expressed the electronic core structure. The second part from -8.4eV to Fermi level (0 eV), strongly hybridized Np and Ti(Zr)d states presents the covalent bonding between Ti(Zr) and N. The third part, from Fermi level to 6.0eV, is mainly derived from metal d orbitals with little nitride p orbitals, which describes metal-metal bonds.

From Fig.4 it is found that the peaks located near -15eV in the first part transfer to the higher energy with the Zr concentration increasing. The reason is that the electronegativity of zirconium is lower than that of titanium. Based on reference [19], the highly directional coupling between metal d and non-metal 2p electrons results in a shear-resistive covalent bonding and such bonding gives a positive contribution to the hardness. Therefore, the second part forms the strong p-d covalent bonds, which gives a positive contribution to the hardness. While the third part has a negative impact on the hardness. From Fig.4, the DOSs at the Fermi level increase with the Zr concentration

also can be found.

Conclusion

With the DFT and ultrasoft pseudopotentials, the crystal structure, elastic properties, and electronic structure of $Ti_xZr_{1-x}N$(x=0, 0.25, 0.5, 0.75, 1) are calculated and analyzed. The lattice parameters of $Ti_xZr_{1-x}N$ increase with the Zr concentration. B, G and E show a monotonously decreasing order with increasing Zr concentration, which can be deduced to be that Zr-dopping can decrease the atomic bond strength of TiN. By analyzing the DOS, N p and Ti(Zr) d states hybridized strongly, forming the strong p-d covalent bonds, has a positive impact on the hardness.

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