Applied Mechanics and Materials *Online: 2012-02-27*
ISSN: 1662-7482, Vols. 155-156, pp 926-930
doi:10.4028/www.scientific.net/AMM.155-156.926

Mechanical Properties of $Ti_{1-x-y}Al_xSi_yN$ Nanocomposite Studied by ab Initio

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Keywords: Ab initio calculation, Titanium Aluminum Silicon Nitride, Mechanical properties.

Abstract. Using first principles calculations based on the density functional theory, we have studied the structural and mechanical properties of $Ti_{1-x}Al_xN$ and $Ti_{1-x-y}Al_xSi_yN$ metastable phase. Focus on the calculation of the $Ti_{1-x-y}Al_xSi_yN$ the cohesive energy, mechanical constants, elastic modulus and shear modulus. These calculated values were analyzed, then we obtained that $Ti_{1-x}Al_xN$ lattice parameter decreased after adding Si, while the cohesive energy was rising, the mechanical properties decreased, indicating that in the case of the Al content determined, the structure of $Ti_{1-x-y}Al_xSi_yN$ is more stable than $Ti_{1-x}Al_xN$, but the mechanical performance ,stiffness and brittleness are reduced.

Introduction

Transition metal nitrides with NaCl-type (B1) transition are a class of unique chemical and physical properties of compounds. Their high hardness, good tribological properties, chemical inertness and stability, high elastic modulus, high melting point have been widely used in industrial cutting tools, auto parts, bio-medical equipment and aircraft engines protective coatings [1-5]. As one of cutting and forming tools, TiN hard coating has been widely used. In order to further improve the hardness and comprehensive performance of TiN, the researchers added Al and Si in the TiN film to form (Ti, Al) N [6] .In which NaCl-type (B1) TiAlN with its oxidation resistance and high hardness has attracted wide attention [7].TiAlSiN film formed by adding Si element to TiAlN is a film with good performance coating materials[8].C. W. Zou et al reported that TiAlSiN nanocomposite coatings prepared by middle frequency magnetron sputtering, and these coatings exhibited excellent performance with a low friction coefficient of 0.72 and a highhardness of 54 GPa. These properties made it possible for industrial applications[9]. Some authors reported when the Si content is increased to 6.0%, the coating exhibits a super hardness of 57 GPa as well as excellent fracture toughness and adhesion strength. And TiAlSiN nanocomposite coatings were prepared by multi-plasma immersion ion implantation and deposition (MPIIID) [10].

$Ti_{1-x}Al_xN$ films have different structures with different x. The films with $0 < x < 0.52$ show only a NaC1 structure, and with $x > 0.59$ show a wurtzite structure[11].In this paper, we have studied NaCl structure of $Ti_{1-x}Al_xN$ ($x = 0.25$, $x = 0.5$) in the case of Si atoms replaced with some Ti atoms, using ab-initio density functional theory calculations. Calculated with the VASP package $Ti_{1-x-y}Al_xSi_yN$ lattice parameter, cohesive energy, elastic constants, bulk modulus, etc., and other theoretical and experimental data obtained for comparison. Through the comparison we studied the influence of performance after the introduced Si element to $Ti_{1-x}Al_xN$.

Computational Details

Using first-principles package VASP (Vienna Ab-initio Simulation Package), we calculated the relevant single-atom (Ti, N, Si, Al) energy first, and then we optimized the lattice parameter of Ti1-x-yAlxSiyN to get the lowest-energy stable structure, access to the equilibrium state of the lattice parameter. Based on the geometry optimization, the cohesive energy, elastic constants, shear modulus, bulk modulus, etc. of Ti1-x-yAlxSiyN were calculated. The specific model for calculation was 4 × 4 × 4 structure, and the atomic number of the super cell was 64. A previous study [12] calculated the $Ti_{1-x}Al_xN$ (with x = 0.25 and x = 0.5) which models are shown in Figure 1 and 2. In this study a series of the Ti1-xAlxN models with x = 0.25 were calculated, through comparison the model was selected after adding Si atoms as shown in figure 3. A series of the $Ti_{1-x}Al_xN$ models with x = 0.5 were calculated, through comparison the models were selected after adding Si atoms as shown in figure 4 and 5. We calculated the lattice parameter, cohesive energy, elastic constants, and the values are shown in Table 1 and 2. To TiAlSiN crystal, for example, the formula for calculating the cohesive energy is given by (1). $E_{coh}^{TiAlSiN}$ is TiAlSiN crystal cohesive energy, E^{Ti} is the Ti single atomic energy, E^{Al} is a single atomic energy of Al, E^{N} is the atomic energy of Si , E^{N} is a N single atomic energy, $E_{tot}^{TiAlSiN}$ is the total energy of TiAlSiN, n is atomic number.

$$E_{coh}^{TiAlSiN} = -(E_{tot}^{TiAlSiN} - n_{Ti}E^{Ti} - n_{Al}E^{Al} - n_{Si}E^{Si} - n_{N}E^{N}) \tag{1}$$

The average atomic cohesive energy is needed in particular calculation of single atom energy, which can facilitate the comparison between the calculation results and the experimental values. The average atomic cohesive energy formula is given by (2).

$$E_{coh}^{TiAlSiN} = \frac{-(E_{tot}^{TiAlSiN} - n_{Ti}E^{Ti} - n_{Al}E^{Al} - n_{Si}E^{Si} - n_{N}E^{N})}{n_{Ti} + n_{Al} + n_{Si} + n_{N}} \tag{2}$$

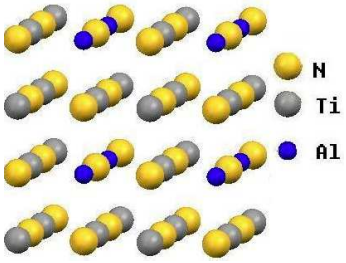

Fig. 1 $Ti_{0.75}Al_{0.25}N$ [14]

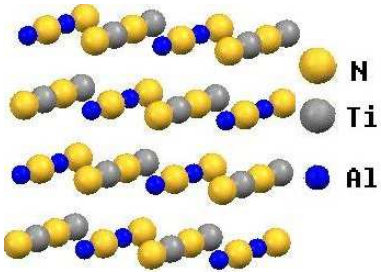

Fig 2 $Ti_{0.5}Al_{0.5}N$ [14]

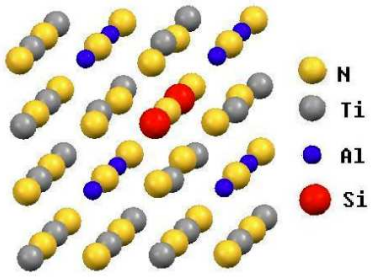

Fig 3. $Ti_{0.69}Al_{0.25}Si_{0.06}N$

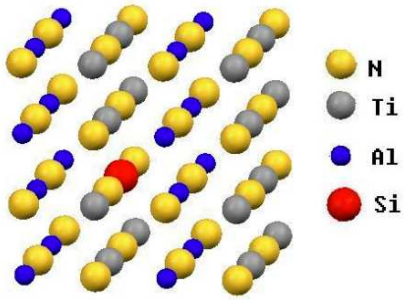

Fig 4. $Ti_{0.47}Al_{0.5}Si_{0.03}N$

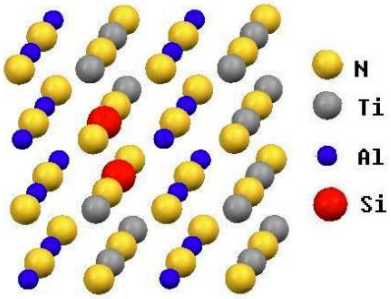

Fig 5. (a)$Ti_{0.44}Al_{0.5}Si_{0.06}N$

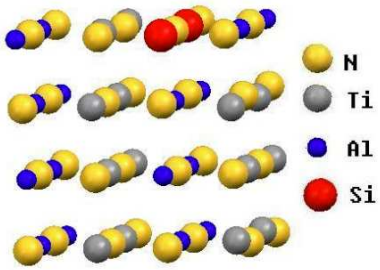

Fig 6. (b)$Ti_{0.44}Al_{0.5}Si_{0.06}N$

Results and Discussion

Table 1 shows the calculated lattice parameter, cohesive energy and other theoretical calculations and experimental values. Table 2 shows the calculated elastic constants, bulk modulus, shear modulus and other theoretical calculations and experimental values.

Confirmed in previous studies obtained $Ti_{1-x}Al_xN$ by introducing Al atoms to TiN, using Al atoms replaced Ti atoms, as the x increased, the lattice parameter showed decreasing trend, which due to the atomic radius of Al atom is smaller than Ti atom, and the number of valence electrons of Al atom is less than Ti atom [12, 13]. As the Si atomic radius smaller than Ti atom, we speculate if we add Si atoms to the $Ti_{1-x}Al_xN$ system, the lattice parameter will be further reduced. Table 1 we compared the $Ti_{0.75}Al_{0.25}N$ and $Ti_{0.69}Al_{0.25}Si_{0.06}N$ with the Al content x = 0.25; the $Ti_{0.5}Al_{0.5}N$, $Ti_{0.47}Al_{0.5}Si_{0.03}N$, $Ti_{0.44}Al_{0.5}Si_{0.06}N$ (a) and $Ti_{0.44}Al_{0.5}Si_{0.06}N$ (b) with x = 0.5, and we found the lattice constants are smaller after adding Si atoms , with the increasing of Si content this trend was more obvious. This is consistent with our speculation, and other theoretical calculations and experimental results also verify this results[13]. In Table 1, compared to the $Ti_{0.75}Al_{0.25}N$ and $Ti_{0.69}Al_{0.25}Si_{0.06}N$ with x = 0.25, the $Ti_{0.5}Al_{0.5}N$, $Ti_{0.47}Al_{0.5}Si_{0.03}N$, $Ti_{0.44}Al_{0.5}Si_{0.06}N$(a) and $Ti_{0.44}Al_{0.5}Si_{0.06}N$(b) with x = 0.5, the cohesive energy have different degrees, indicating that the structure of $Ti_{1-x-y}Al_xSi_yN$ obtained by adding Si to $Ti_{1-x}Al_xN$ is more stabilized. Simultaneous contrast $Ti_{0.44}Al_{0.5}Si_{0.06}N$(a) and $Ti_{0.44}Al_{0.5}Si_{0.06}N$(b), that (b) had the higher cohesive energy, and these two models are showed in Figure 5 and 6. Here the cohesive energy we calculated is the average cohesive energy, the higher the cohesive energy is, the stronger the crystal internal bond strength is, so the structure of (b) is relatively more stable.

Table 2 shows the elastic constants, bulk modulus, shear modulus and other mechanical properties values. It can be seen that the elastic constants of $Ti_{0.69}Al_{0.25}Si_{0.06}N$ and $Ti_{0.75}Al_{0.25}N$ with x = 0.25, the C11 decreased, while C12 and C44 are rising; when x = 0.5, which is similar to x = 0.25, and other studies are basically consistent with this trend. As the range of values of the bulk modulus (B) are shown in Table 2, which can be seen that $Ti_{0.69}Al_{0.25}Si_{0.06}N$ has been reduced than $Ti_{0.75}Al_{0.25}N$, while others [13] calculated values was increased, and the bulk modulus (B) with x = 0.5 is also not monotonic increase or reduction.

When the Al content is in certain circumstances, Shear modulus (G) and Young's modulus (E) are showed a declining trend, after adding Si atoms. As shown in Table 2, G/B values of all the $Ti_{1-x-y}Al_xSi_yN$ that obtained by adding Si atoms are decreased, and more close to 0.5, which indicate the brittleness of $Ti_{1-x-y}Al_xSi_yN$ is reduced and tend to ductility changes after adding Si atoms. Comprehensive analysis of the data in Table 2, the stiffness of $Ti_{1-x-y}Al_xSi_yN$ is reduced relative to the $Ti_{1-x}Al_xN$, and the mechanical properties showed a downward trend. According to the experimental study of Dong Yunshan et al. [7], with more than 3.5at% Si content, to further improve the Si content, the number of $TiSi_x$ phase would increase and gradually crystallization. And the hardness and elastic modulus of TiAlSiN would be decreased. Values shown in Table 2 consistent with this trend, indicating that our conclusions are reliable.

Table 1. Lattice parameter(a_0), cohesive energy(E_{coh})

Compound	Calculated value		Calculated value		Experimental value	
	a_0[nm]	E_{coh}[eV/atom]	a_0[nm]	E_{coh}[eV/atom]	a_0[nm]	E_{coh}[eV/atom]
TiN	a_0[nm]	6.956[12]	0.424[13]	9.44[13]	0.424[16]	6.9[18]
$Ti_{0.75}Al_{0.25}N$	0.4258[12]	6.513[12]	0.422[2]	8.83[13],8.66[13]	0.4233[17]	
$Ti_{0.5}Al_{0.5}N$	0.423[12]	6.131[12]	0.419[16]		0.419[14]	
$Ti_{0.69}Al_{0.25}Si_{0.06}N$	0.419[12]	6.556	0.418[13]	8.68[13]		
$Ti_{0.47}Al_{0.5}Si_{0.03}N$	0.421	6.212				
(a)$Ti_{0.44}Al_{0.5}Si_{0.06}N$	0.4186	6.137				
(b)$Ti_{0.44}Al_{0.5}Si_{0.06}N$	4.1798	6.157				

Table 2. Elastic constants(C_{11}, C_{12}, C_{44}), bulk modulus(B), shear modulus(G), young's modulus(E)

Compound	C_{11}[GPa]	C_{12}[GPa]	C_{44}[GPa]	B[GPa]	G[GPa]	E[GPa]	G/B
TiN	608[12]	118[12]	150[12]	281[12]	245[12]	569[12]	0.8719[12]
$Ti_{0.75}Al_{0.25}N$	529[12]	135[12]	174[12]	266[12]	197[12]	473[12]	0.7406[12]
$Ti_{0.75}Al_{0.25}N$	503[13]	154[13]	183[13]	270[13]	180[13]	441[13]	
$Ti_{0.5}Al_{0.5}N$	500[12]	136[12]	196[12]	257[12]	182[12]	442[12]	0.7082[12]
$Ti_{0.69}Al_{0.25}Si_{0.06}N$	495	172	179	256	179	435	0.6992
$Ti_{0.69}Si_{0.06}Al_{0.25}N$	496[13]	155[13]	227[13]	279[13]	201[13]	487[13]	0.7204
$Ti_{0.47}Al_{0.5}Si_{0.03}N$	446	166	212	260	140	355	0.5036
$Ti_{0.5}Si_{0.13}Al_{0.37}N$	525[17]	140[17]	193[17]	242[17]	174[17]	421[17]	0.7190
(a)$Ti_{0.44}Al_{0.5}Si_{0.06}N$	472	182	211	278	145	370	0.5216
(b)$Ti_{0.44}Al_{0.5}Si_{0.06}N$	441	175	218	264	133	341	0.5038

Conclusion

Using first-principles package VASP based on the density functional theory, we calculated the structural parameters and mechanical parameters of $Ti_{1-x-y}Al_xSi_yN$ obtained by adding Si atoms to $Ti_{1-x}Al_xN$ with different Al content. We found that (1) relative to the $Ti_{1-x}Al_xN$, the lattice parameter of $Ti_{1-x-y}Al_xSi_yN$ reduced; (2) the cohesive energy increases after adding Si atoms, indicating the structure of $Ti_{1-x-y}Al_xSi_yN$ is more stabilized; (3) mechanical properties of $Ti_{1-x-y}Al_xSi_yN$ shows a decline in the overall trend to $Ti_{1-}xAl_xN$. In short, $Ti_{1-x-y}Al_xSi_yN$ shows a lower stiffness and brittleness than $Ti_{1-x}Al_xN$.

Acknowledgments

The authors would like to thank the National Natural Science Foundation of China (Grant No. 50845065), Natural Science Foundation of Inner Mongolia (Grant No. 2009MS0812), Research Program at Universities of Inner Mongolia Autonomous Region (Grant No. NJ10103), and Innovation Foundation of Inner Mongolia University of Science & Technology (Grant No. 2009NC028) for financial supports.

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