The structural, elastic, and electronic properties of $Zr_xNb_{1-x}C$ alloys from first principle calculations*

Sun Xiao-Wei(孙晓玮), Zhang Xin-Yu(张新宇)†, Zhang Su-Hong(张素红), Zhu Yan(朱 岩), Wang Li-Min(王利民), Zhang Shi-Liang(张世良), Ma Ming-Zhen(马明臻), and Liu Ri-Ping(刘日平)‡

State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, *China*

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The structural, elastic, electronic, and thermodynamic properties of $Zr_xNb_{1-x}C$ alloys are investigated using the first principles method based on the density functional theory. The results show that the structural properties of $Zr_xNb_{1-x}C$ alloys vary continuously with the increase of Zr composition. The alloy possesses both the highest shear modulus (215 GPa) and a higher bulk modulus (294 GPa), with a Zr composition of 0.21. Meanwhile, the $Zr_{0.21}Nb_{0.79}C$ alloy shows metallic conductivity based on the analysis of the density of states. In addition, the thermodynamic stability of the designed alloys is estimated using the calculated enthalpy of mixing.

Keywords: $Zr_xNb_{1-x}C$ alloys, elastic constant, shear modulus, first principles

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1. Introduction

Transition metal carbide (TMC) alloys are of great technological interest because of their unique electronic, mechanical, physical, and chemical properties. They have high melting points and excellent electronic conductivities and hardness values among all known compounds.[1–4] These prominent characteristics make them important materials in industrial applications such as coatings and diffusion barriers. Among the well-known TMC alloys, the carbides of group IV and V elements, ZrC and NbC, have drawn considerable attention in the research for unique combination of extreme hardness as well as metallic, electrical, and thermal conductivities.

Both ZrC and NbC crystallize into the NaCl (B_1-type) structure,[5] used in the high temperature nuclear reactors and alloys, and also as the main constituent in cutting tools. Many theoretical and experimental investigations have focused on these two binary alloys. For example, their elastic constants were studied using the density functional perturbation theory by Wu *et al.*,[6] and the accuracy of the metric tensor method was proven.[7] The phonon dispersion relations were studied using a phenomenological model theory by Weber,[8] whose results indicated that the extreme physical properties of ZrC and NbC are attributed to the strong covalent metal–non-metal bonding. The elastic constants of ZrC at high pressure were calculated by Fu *et al.*[9] and the remarkable anisotropy and brittleness of ZrC in the applied pressure range were reported. According to the computed elastic constants, shear modulus, and related quantities, Rathod *et al.*[10] suggested that NbC is highly anisotropic, stiffer, and ductile in nature.

It has been reported that the ternary systems with intermediate compositions could demonstrate better performances. The ternary systems formed with 3d metals (TiC, TiN) and 5d metals (HfC, HfN) were found to be harder than the corresponding binary compounds.[11] $Re_xW_{1-x}C$, exhibits the higher shear modulus and stability than ReC and WC at $x = 0.23$.[12] $ZnSe_xTe_{1-x}$, with a tuned fundamental band gaps by changing the compositions of the concerned element, is more potential in the application of optoelectronic devices than ZnSe and ZnTe.[13] It is believable to obtain a material with preferable properties by alloying ZrC and NbC which are in the same structure, with close lattice parameters[14] and similar physical properties.[6,8] Holleck[11] and Jhi[15] have evaluated that the microhardness of mixed ZrC and NbC was larger than that of each of the compositions. Several investigations have been conducted on $Zr_xNb_{1-x}C$ alloys. Zaoui *et al.*[16,17] and Feng *et al.*[18] explored the structural, elastic, and electronic properties of $Zr_xNb_{1-x}C$ alloys from first principle calculations, showing that the equilibrium lattice constants, elastic constants, and the bulk modulus vary with the addition of some special compositions. However, it is noteworthy that supercell models were used in their work, which means the ordered site occupations of the ternary alloys are considered, contrary to the actual situation of disordered site occupations. Moreover, instead of systematical study of the $Zr_xNb_{1-x}C$ alloys at different compositions, only three special compositions of 25%, 50%, and 75% were modeled. It fol-

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†Corresponding author. E-mail: xyzhang@ysu.edu.cn

‡Corresponding author. E-mail: riping@ysu.edu.cn

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lows that some special performances, based on the procedure, occurred at general compositions may be omitted.

In the work presented here, in order to avoid the two deficiencies mentioned above we adopt the virtual crystal approximation (VCA) method,[19] which is proved to describe effectively the disordered structures (see Refs. [20]–[22], for example), to model the $Zr_xNb_{1-x}C$ alloys, and systematically study their properties by modulating valence electron concentration with the value of composition x varying in a range of 0.1–0.9. To obtain a composition with which a particular performance appears, the structural, elastic, and electronic properties are reinvestigated and compared carefully with previous results. Additionally, the enthalpy of mixing is evaluated to assess the thermodynamic stability of the designed alloy, which is a key factor that needs to be considered by experimentalists.

2. Computational method

The structural, elastic, electronic, and thermodynamic properties of $Zr_xNb_{1-x}C$ alloys are calculated by using the Cambridge Serial Total Energy Package (CASTEP), which is based on the first-principle method within the frame of density functional theory (DFT).[23] The electron–ion interaction is modeled by Vanderbilt-type ultrasoft pseudopotentials.[24] The exchange and correlation are calculated by utilizing the generalized gradient approximation (GGA)[25] in the scheme of Perdew–Burke–Eruzerhof (PBE). Pseudo atomic calculations are performed for C-$2s^2$ $2p^2$, Zr-$4s^2$ $4p^6$ $4d^2$ $5s^2$, and Nb-$4s^2$ $4p^6$ $4d^4$ $5s^1$, respectively, because of their relatively high energies. The plane wave cutoff energy is chosen to be 500 eV. In the self-consistent field calculations, the tolerance is below 5×10^{-7} eV/atom and the maximum atomic force is converged to less than 0.01 eV/Å. The Brillouin-zone integrations are performed using k-point generated with $25\times25\times25$ Monkhorst–Pack meshes.[26] These parameters have been tested to be sufficient for convergence. The $Zr_xNb_{1-x}C$ alloy which crystallizes into an NaCl structure is modeled using the VCA method, in which the alloy pseudo-potential that consists of two or more element types is constructed within a first-principles VCA scheme. More details about the VCA method can be found in Ref. [19].

3. Results and discussion

3.1. Structural properties

In the present work, the structural parameters of $Zr_xNb_{1-x}C$ alloys are obtained through structural optimization, in which the different values of doping ratio x of the $Zr_xNb_{1-x}C$ alloys are set to be in a range from 0 to 1.0, by using the VCA method in the NaCl structure. The variation of lattice constant a with x is illustrated in Fig. 1, together with the experimental data[27] and the other calculated results,[17,18,28] where the points $x = 0$, 1 represent NbC and ZrC compounds, respectively. As shown in Fig. 1, the calculated lattice constant a increases monotonically with x increasing. The lattice constant 4.48 Å (4.70 Å) of NbC (ZrC) is in excellent agreement with the experimental value 4.47 Å (4.698 Å),[27] which illustrates the validity of the method used in the present study and ensures the reliable calculating of the further elastic constants, electronic structure, and thermodynamic properties. It can be clearly seen from Fig. 1 that the results of Zaoiu *et al.*[17] accord well with the tendency of Vegard's law, while the results of Feng *et al.*[18] display a large deviation from Vegard's law. Our presented results are in reasonable agreement with the theoretical data, which are between the results from Zaoiu *et al.* and Feng *et al.*, and show a similar changing trend to Feng *et al.*'s results, but with a more prominent downward bowing.

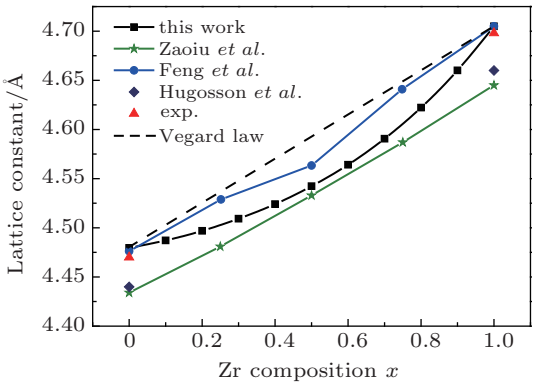


Fig. 1. (color online) Lattice constants each as a function of x, together with the experimental data[27] and the calculated results of Hugosson *et al.*,[28] Zaoiu *et al.*,[17] and Feng *et al.*[18]

3.2. Elastic properties

The three independent elastic constants C_{11}, C_{12}, and C_{44} of cubic crystals $Zr_xNb_{1-x}C$ are calculated through the stress-strain method, in which the elastic stiffness coefficients can be determined by computing the stress generated by a small strain applied to an optimized unit cell.[29] Then the polycrystalline bulk modulus B and shear modulus G can be obtained based on C_{ij} according to the relations $B = (C_{11}+2C_{12})/3$ and $G = (C_{11}-C_{12}+3C_{44})/5$, and hence the Young's modulus E, and Poisson's ratio υ, which are important for technological and engineering applications, are expressed as $E = 9BG/(3B+G)$ and $\upsilon = (3B-2G)/(6B+2G)$. All these calculated elastic parameters are listed in Table 1, together with the available experimental and theoretical results. Different calculations and experimental methods have diverse levels of accuracy. Thus, the values we calculated are approximately in agreement with other theoretical calculations and experimental data for $x = 0$, 0.5, 1.

Table 1. Calculated values of elastic constant C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), and Poisson's ratio υ.

x		C_{11}/GPa	C_{12}/GPa	C_{44}/GPa	B/GPa	G/GPa	E/GPa	υ
0		667	117	168	300	205	632	0.15
	Exp	620[a]	200[a]	150[a]	302[h]			
	other cal.	627[b], 640[c], 596.82[d], 656[j]	135[b], 160[c], 152.46[d], 169[j]	164[b], 140[c], 166.91[d], 163[j]	299[b], 332[c], 301[d]			
0.1		646	124	179	298	209	606	0.16
0.2		661	111	181	294	214	629	0.14
0.3		627	122	179	290	205	587	0.16
0.4		616	118	187	284	210	578	0.16
0.5		601	116	186	277	207	563	0.16
	other cal.			184[i], 172[j]	284[i], 293[j]			
0.6		570	119	187	269	202	529	0.17
0.7		550	115	190	260	200	510	0.17
0.8		531	109	185	249	195	494	0.17
0.9		496	107	172	236	181	459	0.18
1.0		458	104	152	222	162	420	0.19
	Exp	470[a]	100[a]	160[a]	223[g]	170[g]		
	other cal.	446[d], 480[e], 445.94[d], 631[j]	103[d], 102[e], 103.28[d], 120[j]	153[d], 170[e], 152.70[d], 131[j]	225[f], 217[d],	185[f]		

Exp: [a]Ref. [8], [g]Ref. [30], [h]Ref. [2],

Other cal.: [b]Ref. [10], [c]Ref. [31], [d]Ref. [18], [e]Ref. [32], [f]Ref. [9], [i]Ref. [16], [j]Ref. [17]

From the calculated elastic stiffness constants shown in Table 1, it is seen that all the $Zr_xNb_{1-x}C$ alloys are mechanically stable because they satisfy the mechanical stability criteria of cubic crystal, $C_{11} > 0$, $C_{44} > 0$, $C_s = (C_{11} - C_{12})/2 > 0$, $C_{11} + 2C_{12} > 0$.

The variation trends of tetragonal shear modulus $C_s = (C_{11} - C_{12})/2$ and C_{44} with x are shown in Fig. 2, together with the results of the supercell method.[17,18] It is clearly seen that a discrepancy exists. The tetragonal shear modulus C_s monotonically decreases with x increasing, contrary to the case of Feng *et al.*[18] with a maximum at $x = 0.25$. In terms of C_{44}, though the curves bow upward, the bending levels are different from each other, and the maxima of the curves lie at entirely different positions.

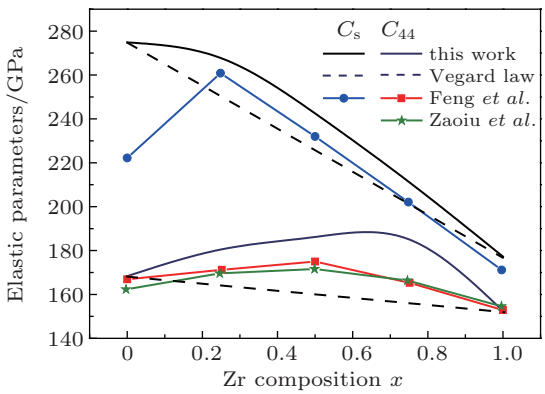


Fig. 2. (color online) Plots of C_{44} and C_s versus Zr composition x. The results of Zaoiu *et al.*,[17] Feng *et al.*[18] and Vegard's law are also shown here for comparison.

The dependences of bulk modulus B and shear modulus G on x are plotted in Fig. 3. The bulk modulus decreases monotonically with the variation of x from 300 GPa at $x = 0$ (NbC) in our calculation with a different shape from that of Zaoiu *et al.*[17] or Feng *et al.*[18] Generally, the shear modulus is a measure of resistance to reversible deformations under shear stress, whereas bulk modulus is a measure of resistance to volume change by applied pressure.[33] Material with high hardness usually has a higher bulk modulus, which is a momentous factor, whereas hard material has a high shear modulus,[15] which is also an essential factor. The $Zr_xNb_{1-x}C$ alloys display a maximum shear modulus value of 215 GPa at $x = 0.21$, and the bulk modulus of the alloy with this composition is 294 GPa, which is relatively higher than that with other compositions. Thus, the $Zr_{0.21}Nb_{0.79}C$ alloy may possess the highest hardness and can be considered to be potentially the hardest of the ternary $Zr_xNb_{1-x}C$ alloys. Pugh[34] proposed that the G/B ratio reflects the brittleness or ductility of a material. The criterion value that distinguishes between a brittle material and a ductile material is approximately 0.5. If $G/B > 0.5$, the material is brittle; otherwise, it is ductile. In this paper, the calculated value of G/B is 0.73 at $x = 0.21$. Therefore, $Zr_{0.21}Nb_{0.79}C$ should be brittle.

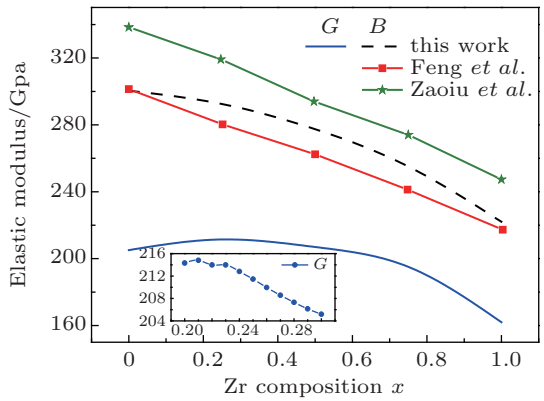


Fig. 3. (color online) Variations of B and G with Zr composition x. The inset shows a magnified section with a maximum of G.

A material which shows a superior capability to resist tension and pressure in the range of elastic deformation usually possesses a larger Young's modulus E. In other words, the larger the Young's modulus of a material, the harder the deformation is.[35,36] The ability to resist the shear strain of material is revealed through its Poisson's ratio υ. The variation tendencies of E and υ can be seen in Table 1. The Young's modulus reaches a maximum value of 629 GPa at $x = 0.2$, and the alloy possesses the smallest Poisson ratio 0.14 at the same point. This result also supports the conclusion that $Zr_{0.21}Nb_{0.79}C$ alloy, with a closely related composition to $Zr_{0.2}Nb_{0.8}C$, can have excellent hardness. The electronic and thermodynamic properties of the alloy are discussed below to shed light on its physical mechanism.

3.3. Electronic properties

In order to gain further insight into the mechanical properties, the site-decomposed partial and total density of states (DOS) of $Zr_{0.21}Nb_{0.79}C$ are calculated as shown Fig. 4. The alloy of $Zr_{0.21}Nb_{0.79}C$ represents metallic features because of the nonzero density of state at E_F, which primarily comes from the 4p and 4d states of metal atoms. The 2p orbital of carbon atoms also contributes to the Fermi energy vicinity to some extent but they are less significant than that of metal atoms. Moreover, there is a strong hybridization between the carbon

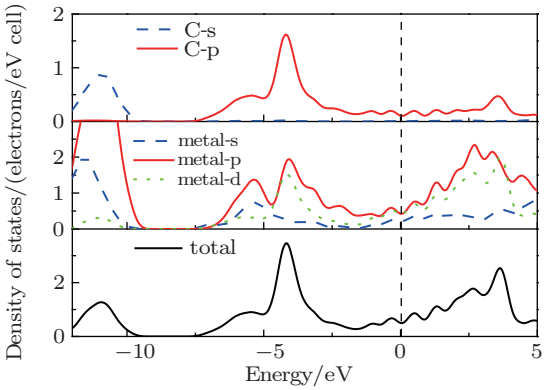


Fig. 4. (color online) Total and site-decomposed partial density of state of the $Zr_{0.21}Nb_{0.79}C$ alloy.

2p and metal 4d orbitals around −4 eV, which indicates covalent bonding in the alloy and leads to a separation of the bonding states. Furthermore, the charge transfer between carbon and metal atoms can be found through the population analysis. It follows that the bonds in the $Zr_{0.21}Nb_{0.79}C$ alloy are a mixture of metallic, covalent, and ionic bonding.

3.4. Thermodynamic properties

The enthalpy of mixing (ΔH_{mix}) is calculated using the supercell method to investigate the thermodynamic stability of $Zr_{0.21}Nb_{0.79}C$. In this calculation, the crystal cell is modeled with a 2×2×1 structure, and five values of x, namely, 0, 0.125, 0.25, 0.375, and 0.5, are selected. At zero temperature, without the contribution of the entropy to the free energy, the enthalpy of mixing is written in the form of

$$\Delta H_{mix} = E_{Zr_xNb_{1-x}C} - xE_{ZrC} - (1-x)E_{NbC},$$

where $E_{Zr_xNb_{1-x}C}$, E_{ZrC}, and E_{NbC} represent the enthalpy of the $Zr_xNb_{1-x}C$ ternary alloys, ZrC, and NbC compounds, respectively. The negative enthalpy value indicates the thermodynamic stability of the ternary $Zr_xNb_{1-x}C$ alloy at 0 K and 0 GPa; otherwise, they are unstable. The calculated results are plotted in Fig. 5. As seen from the figure, the $Zr_{0.21}Nb_{0.79}C$ alloy shows the characteristic of stability because of the negative mixing enthalpy.

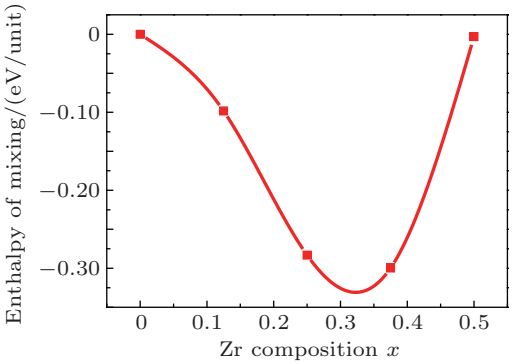


Fig. 5. (color online) Enthalpy of mixing as a function of Zr composition x.

4. Conclusions

The structural and elastic properties of $Zr_xNb_{1-x}C$ alloys are systematically investigated using the virtual crystal approximation, and the results are compared carefully with those obtained with the supercell method. Our calculated lattice constants of binary compounds (ZrC and NbC) are in good agreement with the experimental data. The variations of lattice constant a, tetragonal shear modulus C_s and C_{44}, and bulk modulus B, display appreciable difference between previous results and ours, which demonstrates the effect of order or disorder in the site occupation of atoms in alloys, also confirm the necessity of considering the disorder arrangement. With the Zr composition x increasing, the variations of the lattice constant and

elastic constants deviate from the Vegard's law. From the bulk modulus and shear modulus curves of $Zr_xNb_{1-x}C$ alloys, we find that bulk modulus decreases monotonically, and a maximum shear modulus of 215 GPa occurs at $x = 0.21$, implying that $Zr_{0.21}Nb_{0.79}C$ is the potentially hardest in the ternary $Zr_xNb_{1-x}C$ alloys, which is also supported by the results of Young's modulus and Poisson's ratio. The analysis of the DOS indicates the metallic nature and a mixture of metallic, covalent, and ionic bonding in $Zr_{0.21}Nb_{0.79}C$ alloy. The remarkable thermodynamic stability is also addressed by the calculation of enthalpy of mixing. So $Zr_{0.21}Nb_{0.79}C$ could serve as an engineering hard material in applications. Relevant experiments are expected.

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