Compounds with different chemical ratios in Hf-N system First principles of physical properties

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Abstract: The first-principles method based on density functional theory was used to study the compound with different chemical ratios in Hf-N system, and the seven most stable compounds were selected, and their elastic constants Cij and phantoms were calculated. Parameters such as quantity B and shear modulus G. By comparing the elastic modulus, B/G value and Vickers hardness Hv of these seven compounds, it is concluded that HfN-NiAs and Hf_3N_4-Zr_3N_4 are potential superhard materials. The calculated enthalpy results show that Hf_3N_4-Zr_3N_4 has the best thermodynamic stability.

1. Introduction

With the continuous development of modern technology and industrial technology, super-hard materials are widely used in industry, the demand is gradually increasing and diamonds are widely used but they are less in nature and difficult to synthesize as well as difficult to meet demand, so design and the synthesis of new hard materials is an important research topic at present.

Transition metal compounds are widely used in cutting tools, grinding and wear-resistant coatings, etc. Because of their unique physical and chemical properties, such as high hardness, high melting point, good chemical inertness and thermal stability. Among them, HfN is a new type of superhard material with high hardness, high melting point, wear resistance, oxidation resistance and corrosion resistance. In recent years, many scholars at home and abroad have begun to study the nitrides of transition metal ruthenium and found that it has good elastic properties and thermodynamic stability. Therefore, this paper uses the first-principles method based on density functional theory to study the physical properties of compounds with different chemical ratios in Hf-N system.

2. Structure of compounds with different chemical ratios in Hf-N system

For different chemical ratios of niobium nitrides, there are no possible parameters relcated to the experimental structure, and a total of 28 possible structures are selected in this paper. For HfN, we choose NiAs and WC structures as their initial structures; in addition we choose HfN_2、CaF_2、OsN_2、WN_2 as the initial structure of HfN_2; for HfN_3, in addition to MnB_3, we also selected IrB_3 and ReB_3 as their possible structures. Research; we have studied Ta_2N_3 as the initial structure of Hf_2N_3; for HfN_4, in addition to CrB_4 structure, we also studied it with MnB_4 structure; for Hf_3N_4, in addition to Zr_3N_4 structure, we also chose Th_3P_4 and Ta_3B_4 structures; For Hf_3N_5, we choose Ta_3N_5 structure

Analyzed and studied its initial structure. The principle of substitution is to replace other metal atoms with Hf atoms (eg: Hf).

The atoms replace Ni, W, Ca, Os, Mn, Ir, Re, Ta, Cr, Th, and Zr), respectively, and replace the

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non-metal atoms in the corresponding structure with N atoms (for example, N atoms replace As, C, F, respectively). B and P).

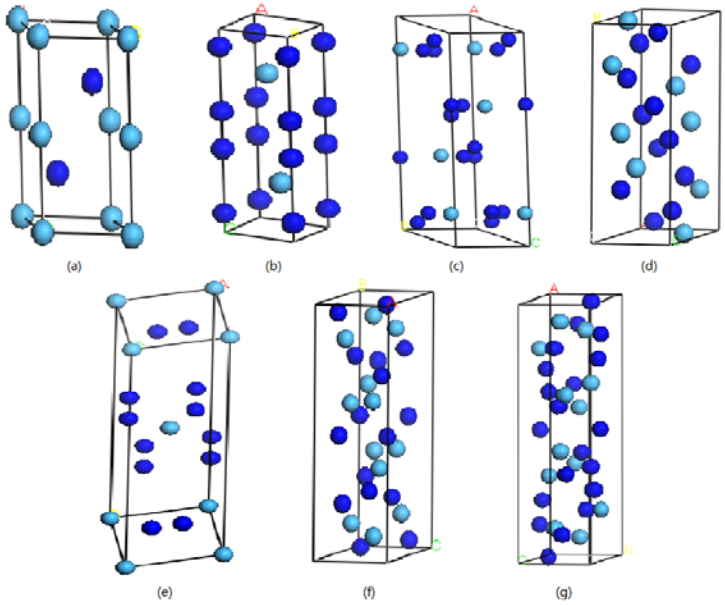

Figure 1. Crystal structure of Hf-N system：(a) HfN-NiAs (b) HfN_2 (c) HfN_3-MnB_3 (d) Hf_2N_3-Ta_2N_3 (e) HfN_4-CrB_4 (f) Hf_3N_4-Zr_3N_4 (g) Hf_3N_5-Ta_3N_5

3. Phase stability and elastic properties of niobium nitrides with different structures

3.1 Thermodynamic stability analysis

In order to better study the nitrides of these different structures, we draw their energy convex hull diagrams, as shown in Figure 2. The abscissa in the figure represents the content of N in each proportion of compounds, and the ordinate represents the unit. The formation of crystals is flawed. The energy convex hull map is a graph used to indicate that the formation enthalpy of the compound changes with the change of the ground state compound of different ratios. On the energy convex hull diagram, connect any two phases with a line. If the generation enthalpy of the third phase is below the line, the phase can be generated by the first two phases. If, in one configuration, the third phase is below the adjacent two phases, it indicates that the phase is difficult to decompose into adjacent phases. The formation of any structure, if it is on the energy convex hull curve, proves that this compound is the most stable, and is the easiest to synthesize experimentally[1][2].

It can be seen from Figure 2 that our energy convex hull is composed of the ground state structures of the two phases of HfN-NiAs and Hf_2N_3-Ta_2N_3, which are on the energy convex hull curve, indicating that they have been experimentally synthesized. Among the 7 phases, we can see that the energy convex hull map reaches the lowest point when Hf:N is 3:4, that is, the formation H of Hf_3N_4 of Zr_3N_4 structure is the lowest, indicating that Hf_3N_4-Zr_3N_4 is compared. Easy to synthesize.

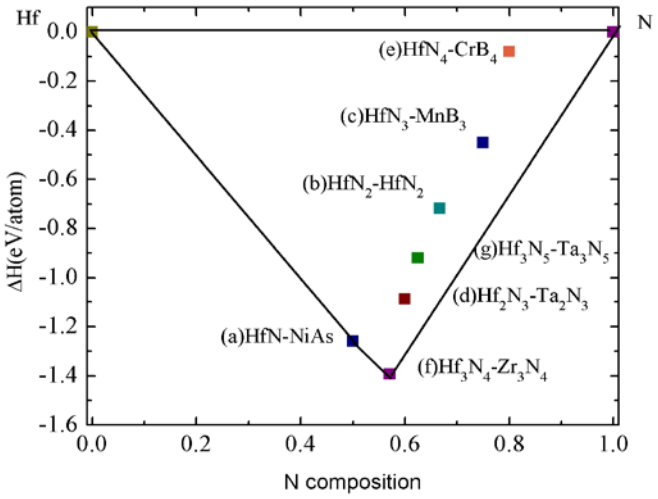

Figure 2. Energy convex hull diagram of Hf-N system

3.2 Mechanical stability analysis

It is well known that elastic properties are necessary for the existence of matter, so studying the elastic properties of matter is necessary to help us determine the physical properties of matter. Among them, the elastic constant can be obtained by the stress-strain method listed in Table 1.

Table 1. The calculated the elastic constantsCij (GPa)of Hf-N system of compound under the GGA approximation.

	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{15}	C_{23}	C_{25}	C_{35}	C_{46}
HfN-NiAs	433		513	104			113	166					
HfN_2-HfN_2	352		641	30			176	107					
HfN_3-MnB_3	93	183	176	15	41	17	49	55	16	65	15	14	-1
Hf_2N_3-Ta_2N_3	317	443	486	105	124	101	216	134		142			
HfN_4-CrB_4	115	-3	95	8	34	4	-3	53		-2			
Hf_3N_4-Zr_3N_4	252	410	424	57	95	115	130	151		130			
Hf_3N_5-Ta_3N_5	104	96	54	63	88	103	113	98		78			

We conducted further studies on the seven most stable compounds selected. The seven compounds studied belong to three crystal systems: Hf_2N_3-Ta_2N_3, HfN_4-CrB_4, Hf_3N_4-Zr_3N_4, Hf_3N_5-Ta_3N_5 are orthorhombic systems; HfN-NiAs, HfN_2-HfN_2 are hexagonal systems; HfN_3-MnB_3 is Monoclinic system. We used the mechanical stability judgment method to judge the mechanical stability of these seven compounds in turn. The mechanical stability criteria and independent elastic tensor of orthorhombic, hexagonal and monoclinic systems are given below [3].

(1) Orthogonal system:

The independent elastic constants of the elastic tensors are C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13} and C_{23}. The criterion for mechanical stability is:

$C_{11}>0, C_{22}>0, C_{33}>0, C_{44}>0, C_{55}>0, C_{66}>0,$

$C_{11}+C_{12}+C_{33}+2(C_{11}+C_{13}+C_{23})>0,$

$C_{11}+C_{22}-2C_{12}>0,$

$C_{11}+C_{33}-2C_{13}>0, C_{22}+C_{33}-2C_{23}>0$

In the orthorhombic system, the $C_{22}<0$ of HfN_4-CrB_4 does not satisfy the mechanical stability criterion, indicating that it is unstable in mechanical properties. Hf_2N3-Ta_2N_3, Hf_3N_4-Zr_3N_4 and Hf_3N_5-Ta_3N_5 satisfy the mechanical stability criterion, indicating that their mechanical properties are stable.

(2) Hexagonal system:

The independent elastic constant of the elastic tensor is $C_{11}, C_{33}, C_{44}, C_{12}$ andC_{13} , $C_{11}=C_{22}, C_{44}=C_{55}, C_{66}=1/2(C_{11}-C_{22})$ and $C_{13}=C_{23}$。

The criterion for mechanical stability is: $C_{44}>0, C_{11}>|C_{12}|, (C_{11}+C_{12})C_{33}>2C_{132}$

In the crystal system, both of HfN-NiAs and HfN_2-HfN_2 satisfy the conditions, indicating that their mechanical properties are stable.

(3) Monoclinic system: The independent elastic constants of the elastic tensors are $C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, C_{23}, C_{15}, C_{25}, C_{35}$ and C_{46}.

The criterion for mechanical stability is：

$C_{11}>0, C_{22}>0, C_{33}>0, C_{44}>0, C_{55}>0, C_{66}>0,$

$C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})>0,$

$C_{33}C_55-C_{352}>0, C_{44}C_{66}-C_{462}>0,$

$C_{22}(C_{33}C_{55}-C_{352})+2C_{23}C_{25}C_{35}-C_{232}C_{55}-C_{252}C_{33}>0,$

$2[C_{15}C_{25}(C_{33}C_{12}-C_{13}C_{23})+C_{15}C_{35}(C_{22}C_{13}-C_{12}C_{23})+C_{25}C_{35}(C_{11}C_{23}-C_{12}C_{13})]-[C_{152}-(C_{22}C_{33}-C_{232})+C_{252}(C_{11}C_{33}-C_{132})+C_{352}(C_{11}C_{22}-C_{122})]+C_{55}g>0$,

among them, $g=C_{11}C_{22}C_{33}-C_{11}C_{232}-C_{22}C_{132}-C_{33}C_{122}+2C_{12}C_{13}C_{23}$

In the monoclinic system, HfN3-MnB3 conforms to the mechanical stability criterion, indicating that it is mechanically stable.

According to the mechanical stability criterion, HfN-NiAs, HfN_2-HfN_2, HfN_3-MnB_3, Hf_2N_3-Ta_2N_3, Hf_3N_4-Zr_3N_4, Hf_3N_5-Ta_3N_5 are all stable in mechanical properties. Among them, C_{22} of HfN_4-CrB_4 is negative (-3GPa), indicating that it is mechanically unstable. The elastic constant reflects the ability of a substance to resist elastic deformation. From Table 1, we can see that most of the niobium nitrides have larger C_{11}, C_{22}, and C_{33} than HfN_3-MnB_3, which proves that these compounds are harder to compress than HfN_3-MnB_3. Among them, C_{44} is a physical quantity that can directly judge the hardness of the material indentation. Among all the compounds studied, the elastic constant C_{44} (104GPa) of NiAs of HfN structure and the elastic constant C_{44} (105GPa) of Hf_2N_3 of Ta_2N_3 structure are larger, indicating The HfN-NiAs and Hf_2N_3-Ta_2N_3 compounds have relatively strong shearing power.

Table 2 Space group , bulk modulus B (GPa), shear modulus G (GPa), hardness Hv in Hf - N system.

	Space group	B	G	B/G	Hv
HfN-NiAs	194 P_{63}/MMC	250	133	1.880	13.7
HfN_2-HfN_2	194 P_{63}/MMC	232	73	3.178	3.4
HfN_3-MnB_3	12 C_2/M	80	29	2.759	1.4
$Hf2N_3$-$Ta2N_3$	62 PBNM	244	112	2.179	9.7
HfN_4-CrB_4	71 IMMM	15	54	0.278	89.3
Hf_3N_4-Zr_3N_4	62 PNMA	207	93	2.226	8.2
Hf_3N_5-Ta_3N_5	62 PNMA	226	96	2.679	7.6

Calculating Young's modulus, Poisson's ratio and hardness can be obtained by the following formulas:

$$Y = 9BG/(3B+G) \tag{2-1}$$

$$\upsilon = (3B-2G)/(6B+2G)\ Y = 9BG/(3B+G) \tag{2-2}$$

$$H\nu = 2\left(K^2G\right)^{0.585} - 3 \tag{2-3}$$

In the calculation of hardness, we mainly refer to the formula used by Chen et al. [4] in calculating the hardness of the material, where K=G/B.

For the convenience of observation, the phantom volume B (GPa) and the shear modulus G (GPa) of the Hf-N system compound are shown in Fig. 3.

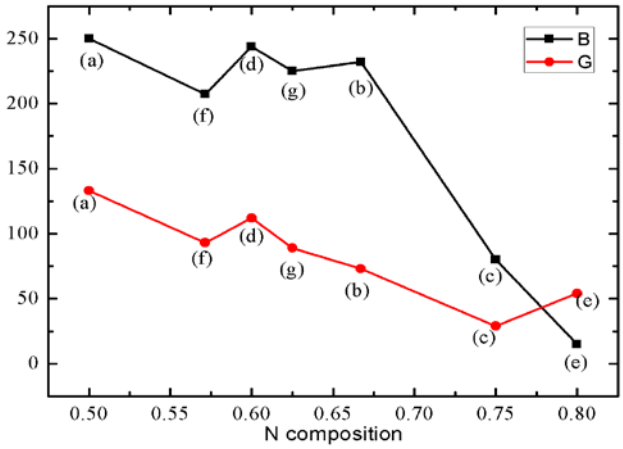

Fig. 3 Bulk modulus B (GPa), shear modulus G(GPa) of Hf-N system compound: (a) HfN-NiAs (b) HfN_2-HfN_2 (c) HfN_3-MnB_3 (d) Hf_2N_3-Ta_2N_3 (e) HfN_4-CrB_4 (f) Hf_3N_4-Zr_3N_4 (g) Hf_3N_5-Ta_3N_5

The moduli of the material reflects the ability of the material to resist volume changes. As can be seen from Fig. 3, HfN-NiAs, HfN_2-HfN_2, Hf_2N_3-Ta_2N_3, Hf_3N_4-Zr_3N_4 relatively stable, it has the lowest modulus of 15 GPa, indicating that it is a compound that is easily compressed. Shear modulus is a physical quantity used to indicate the material's ability to resist deformation. It is more predictive of the hardness of the material. In Figure 3, the HfN of the NiAs structure has the highest shear modulus of 133 GPa, indicating that it is resistant to the largest shear deformation. The large (small) B/G value is related to the toughness (brittleness) of the material, and their critical value is 1.75[5]. By calculation, the B/G values of the six compounds HfN-NiAs, HfN_2-HfN_2, HfN_3-MnB_3, Hf_2N_3-Ta_2N_3, Hf_3N_4-Zr_3N_4 and Hf_3N_5-Ta_3N_5 are: 1.880, 3.178, 2.759, 2.179, 2.226 and 2.679, respectively. Their values are all greater than 1.75, so they are tough materials, and HfN_4-CrB_4 has a B/G value of 0.278, which is less than the critical value and is a brittle material. Through the hardness formula given by Chen et al. above, it is found that the singular modulus and shear modulus of the only brittle material HfN_4-CrB_4 are small, but have the highest hardness. It is worth mentioning that HfN-NiAs, Hf_2N_3-Ta_2N_3 and Hf_3N_4-Zr_3N_4 not only have higher bulk modulus and shear modulus, smaller B/G ratio, but also higher hardness, indicating that they are transitions. A potentially superhard material in the nitride of metal ruthenium.

4. Conclusion

In this paper, a first-principles method based on density functional theory is used. According to the correlation of compounds, 28 structures are selected as the initial structure, and the parameters such as the formation enthalpy and elastic constant of all compounds considered in the Hf-N system are studied. Calculate and reuse the principle of energy minimization to screen out the seven most stable compounds. The mechanical stability of these seven compounds was judged by mechanical stability judgment method. The bulk modulus, shear modulus and hardness were analyzed. Through systematic research and analysis, among the seven compounds considered. HfN-NiAs, Hf_2N_3-Ta_2N_3 and Hf_3N_4-Zr_3N_4 have relatively high bulk modulus, shear modulus and hardness, indicating that they are potentially superhard materials. Among them, HfN-NiAs (B: 250GPa, G: 133GPa, Hv: 13.7) and Hf_2N_3-Ta_2N_3 (B: 244GPa, G=112GPa, Hv: 9.7) have relatively high moduli, shear modulus and Vickers. Hardness is the most stable material in the structure we are considering. It is worthy of further theoretical and experimental research by researchers.

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