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Study on Hardness Control of Ir-C-N System

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Abstract: In this paper, based on first-principles theoretical calculation and Vesta modeling, nitrogen atoms were doped in the Ir-C of Pnma phase and carbon atoms were doped in the Ir-N of Pnnm phase to obtain a new IR-C-N system.The structure optimization and static self-consistent cycle optimization of the doped structure were carried out. The elastic calculation of the optimized structure was carried out under the pressure of 0Gpa. Through the analysis of the calculation results, the compound has shown good brittleness under certain doping ratios.

Keywords: First principles, Ir-C-N system, Doping, Elastic properties, Hardness properties.

1. Introduction

As a transition metal suitable for the synthesis of superhard materials, iridium has a slightly lower elastic modulus than osmium, which is the second highest among all metals[1].Its high shear modulus and low Poisson's ratio make it very hard to process iridium.Though difficult and expensive to produce, Iridium has a number of applications, including strengthening machinery in extreme conditions.Iridium is highly resistant to corrosion and high temperature, so it is very suitable as an alloy additive[2-4].

The properties of materials are mainly affected by the crystal structure and chemical bond, so the properties of materials can be optimized by improving the chemical bond structure of materials[5].In the actual production and application of metal materials, alloying of materials by adding solute atoms is a conventional means to improve material properties.This is because the existence of solute (alloy) atoms will affect the chemical bond structure of its surrounding atoms, thus affecting the macroscopic properties of materials[6-8].

Therefore, we can study the superhard properties of Ir element by adding solute atoms to it, and Ir element belongs to transition metal. Currently, research on new superhard materials focuses on introducing light elements to form strong bonds (B,C,N,O) into transition metals with high elastic modulus[9-12].In addition, certain achievements have been made in the research on superhard materials NbB3, VB3, CrB4, MB2 and ReB2 under high pressure. Wang Peng, a master from Kunming University of Science and Technology, has made a series of analysis and discussion on the brittleness mechanism of iridium by using first-principles calculation (software package) as the research method.The basic properties of iridium (including cohesion energy, equilibrium lattice constant, elastic properties, chemical bond structure and the influence of solute atoms on bond structure), generalized stacking fault energy, properties of dislocation, nucleation and propagation of microcracks were calculated and analyzed[13].J.v.au., and A.Litini prepared IrB1.35 through experiments, and analyzed its maximum hardness of 49.8Gpa under 0.49N load by X-ray [14]. XiaofengLi and JunyiDu predicted IrB3 of three different space groups by CALYPOS.Moreover, its electrical and dynamic properties and mechanical properties were analyzed in combination with the first principles[15]. Zhi-jian Wu, Er-jun Zhao from the Chinese Academy of Sciences used VASP software to test and calculate the PAW pseudopotential of projection plus plane wave and the PBE functional under the generalized gradient approximation (GGA) according to the first principles.Relatively stable IrN2 and IrN3 compounds were obtained and their bulk modulus and shear modulus were calculated, and their superhard properties were analyzed[16]. S.K.R.Patila, S.V.Hare et al. calculated the elastic properties of IrN2 and compared them with other transition metal nitride compounds.The work on the synthesis and prediction of nitrides is analyzed[17].Reviewing the above literature, it can be seen that studies on the hardness properties of light elements introduced into the transition metal Ir focus on the introduction of a single element, and few literatures introduce two or more light elements into the transition metal iridium at the same time. Therefore, do hard IR-C-N systems exist, and if so, what hardness properties do they have?

Inspired by this background, this paper attempts to introduce carbon and nitrogen atoms into the transition metal Iridium to form a new compound, and calculates its properties through first principles, and studies the hardness characteristics of Ir-C-N system by referring to previous experience.

2. Computational Methods

In this paper, the projection and plane-wave method (PAW) of density functional theory (DFT) and the PBE functional[18,19] under the generalized gradient approximation (GGA)[18] are used to analyze the Ir-C structure of Pnma and the Ir-N structure of Pnnm, and the stability and elastic properties of the structure are measured.The selected space groups are doped by Veats modeling, and then the properties of Ir-C-N systems with different proportions are calculated.

The PNMa-structured Ir-C was doped with nitrogen atoms and optimized in the doping mode of $Ir_4C_{(12-x)}N_x$(x=0,2,4,6).

The PNNm-structured Ir-N was doped with carbon atoms and its structure was optimized. The doping mode was $Ir_2N_{(4-x)}C_x$(x=0,1,2,3)

In calculation, A square wave base with cutoff energy of 500ev was selected. To ensure the convergence of energy and structure of the system at the plane wave base level, its self-consistent accuracy was set at 10^{-5}eV/atom, and the convergence standard of interatomic force was set at 10^{-2}eV/A[20]

3. Results and Discussion

3.1. Calculation of $Ir_4C_{(12-x)}N_x$(x=0,2,4,6)

The ideal lattice structure of IRC in Pnma system was established.For Ir_4C_{12} system, lattice parameters are a=2.60698 Å， b=4.33881 Å， c=13.62879 Å, as shown in Table 1:

Table 1. Lattice constant of $Ir_4C_{(12-x)}N_x$(x=0,2,4,6).

	a/ Å	b(Å)	c/ Å	E(eV/atom)
Ir_4C_{12}	2.60698	4.33881	13.62879	-134.28-
$Ir_4C_{10}N_2$(1)	2.62982	4.29181	13.52184	-133.03
$Ir_4C_{10}N_2$(2)	2.63497	4.28638	13.15509	-133.00
$Ir_4C_{10}N_2$(3)	2.62173	4.33568	13.38052	-131.44
$Ir_4C_{10}N_2$(4)	2.64850	4.29205	13.04850	-131.94
Ir4C10N2(5)	2.62764	4.32759	13.68922	-133.04
$Ir_4C_{10}N_2$(6)	2.63470	4.24476	13.16027	-133.84
$Ir_4C_{10}N_2$(7)	2.63470	4.24476	13.16027	-133.84
$Ir_4C_{10}N_2$(8)	2.62764	4.32760	13.68923	-133.04
$Ir_4C_{10}N_2$(9)	2.64850	4.29205	13.04848	-131.94
$Ir_4C_8N_4$	2.68088	4.32095	13.07632	-130.08
$Ir_4C_6N_6$(1)	2.60606	4.33806	13.61061	-129.42
$Ir_4C_6N_6$(2)	2.73352	4.34367	12.74472	-128.61

On the basis of the ideal Ir_4C_{12}, the structure of $Ir_4C_{(12-x)}N_x$(x=0,2,4,6) is constructed, and the structure is optimized by the conjugate gradient algorithm. By replacing C atom, N atom is introduced.When doping the Ir-C system, it was found that different data results would be obtained by replacing different atoms with the same proportion of doping. In view of this situation, I marked each atom and calculated the data results of doping different atoms with the same proportion.As is shown in Figure 1

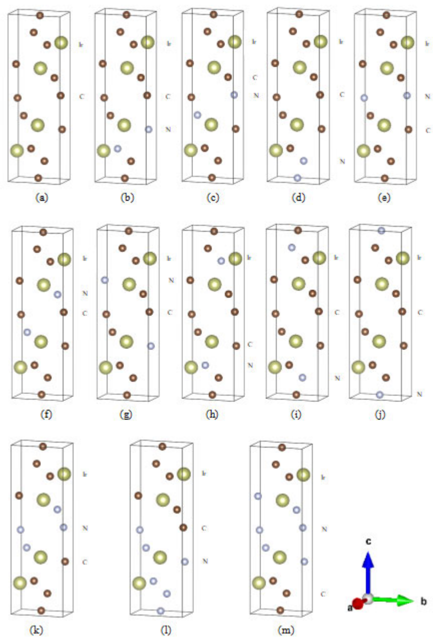

Figure 1. Crystal structure of $Ir_4C_{(12-x)}N_x$(x=0,2,4,6) (a)Ir_4C_{12};(b)$Ir_4C_{10}N_2$(1);(c)$Ir_4C_{10}N_2$(2);(d)$Ir_4C_{10}N_2$(3);(e)$Ir_4C_{10}N_2$(4)(f)Ir4C10N2(5);(g)$Ir_4C_{10}N_2$(6);(h)$Ir_4C_{10}N_2$(7);(i)$Ir_4C_{10}N_2$(8);(j)$Ir_4C_{10}N_2$(9);(l)$Ir_4C_8N_4$;(m)$Ir_4C_6N_6$(1);(n)$Ir_4C_6N_6$(2)

Through structural optimization and static self-consistent cycle optimization of the doped structure, the elastic constants, volume modulus B, shear modulus G, Young's modulus E and Poisson's ratio v of the optimized structure were calculated under the pressure of 0Gpa.Volume modulus is a physical quantity used to reflect the macroscopic characteristics of materials, that is, the relationship between the bulk strain and the average stress of an object[20].Shear modulus is the ratio of shear stress to shear strain of a material under shear stress and within the limit range of elastic deformation ratio, which represents the ability of a material to resist shear strain[21].Large modulus means strong rigidity of the material.Young's modulus is a physical quantity describing the resistance of solid materials to deformation.Poisson's ratio represents the volume change during elastic deformation of materials[22].The calculation results show the change of elastic modulus of the doped Ir-C-N system, as shown in Table 2.

Table 2. Elastic constants C_{ij}(GPa) and elastic moduli(GPa) of $Ir_4C_{(12-x)}N_x$(x=0,2,4,6).

Structure	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	B/G	v
Ir_4C_{12}	698	434	206	53	124	207	278	85	3.251	0.361
$Ir_4C_{10}N_2$(1)	678	414	156	22	125	206	142	102	1.386	0.209
$Ir_4C_{10}N_2$(2)	637	558	477	93	131	240	239	157	1.523	0.231
$Ir_4C_{10}N_2$(3)	640	144	-834	-126	125	221	93	95	0.985	0.121
$Ir_4C_{10}N_2$(4)	539	546	488	99	124	204	238	150	1.586	0.239
Ir4C10N2(5)	669	476	324	50	110	209	208	133	1.562	0.236
$Ir_4C_{10}N_2$(6)	658	577	474	108	131	266	244	167	1.458	0.221
$Ir_4C_{10}N_2$(7)	659	581	509	108	131	267	261	170	1.538	0.233
$Ir_4C_{10}N_2$(8)	668	476	300	54	110	210	199	134	1.488	0.225
$Ir_4C_{10}N_2$(9)	—	—	—	—	—	—	—	—	—	—
$Ir_4C_8N_4$	554	464	532	74	100	151	224	123	1.814	0.267
$Ir_4C_6N_6$(1)	567	629	755	231	149	232	321	213	1.498	0.227
$Ir_4C_6N_6$(2)	421	398	425	170	-29	120	187	357	0.524	-0.083

B/G is used to describe the smaller the brittleness and ductility ratio of a substance, the greater the hardness of a substance. 1.75 is the critical point. When B/G is greater than 1.75, the compound is malleable, while when B/ g is less than 1.75, it is brittle[23].The formation of new covalent bonds affects the hardness of the structure, causing the ductile material to become brittle.

3.2. Calculation of $Ir_2N_{(4-x)}C_x$(x=0,1,2,3)

Through the experience of Ir-C doping, I also doped the Ir-N system of Pnnm phase, as shown in Figure 2

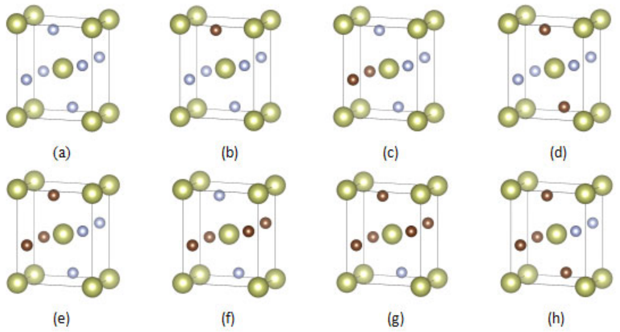

Figure 2. Crystal structure of $Ir_4N_{(4-x)}C_x$(x=0,1,2,3)

(a)Ir_2N_4;(b)$Ir_2N_3C_1$(1);(c)$Ir_2N_3C_1$(2);(d)$Ir_2N_2C_2$(1);(e)$Ir_2N_2C_2$(2);(f) $Ir_2N_2C_2$(3);(g)$Ir_2N_1C_3$(1);(h)$Ir_2N_2C_3$(2)

Lattice parameters are a=2.78011 Å, b=4.09548 Å, c=4.93031 Å, as shown in Table 3:

Table 3. Lattice constant of $Ir_4C_{(4-x)}N_x$(x=0,1,2,3).

	a/ Å	b(Å)	c/ Å	E(eV/atom)
Ir_2N_4	2.78011	4.09548	4.93031	-56.32
$Ir_2N_3C_1$(1)	2.70691	4.08405	4.88918	-56.16
$Ir_2N_3C_1$(2)	2.78011	4.09548	4.93031	-56.16
$Ir_2N_2C_2$(1)	2.70825	4.13976	4.88908	-55.72
$Ir_2N_2C_2$(2)	2.69965	4.12513	4.92141	-56.69
$Ir_2N_2C_2$(3)	2.70825	4.13978	4.88911	-55.72
$Ir_2N_1C_3$(1)	2.71782	4.13843	4.91779	-56.29
$Ir_2N_2C_3$(2)	2.71782	4.13845	4.91780	-56.29

On the basis of ideal Ir-N, the structure of $Ir_2N_{(4-x)}C_x$(x=0,1,2,3) was constructed, and the structure was optimized. C atom was introduced by replacing N atom, as shown in the figure.The same calculation was made for the optimized structure, as shown in Table 4.

Table 4. Elastic constants C_{ij}(GPa) and elastic moduli(GPa) of $Ir_4C_{(4-x)}N_x$(x=0,1,2,3).

Structure	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	B/G	v
Ir_2N_4	721	912	1151	203	118	378	466	248	1.878	0.274
$Ir_2N_3C_1$ (1)	599	757	943	185	118	320	375	221	1.699	0.254
$Ir_2N_3C_1$ (2)	599	756	943	185	118	321	375	221	1.699	0.254
$Ir_2N_2C_2$ (1)	588	702	840	162	109	297	366	199	1.833	0.269
$Ir_2N_2C_2$ (2)	556	699	886	152	107	309	356	199	1.785	0.264
$Ir_2N_2C_2$ (3)	588	703	841	163	109	297	366	199	1.832	0.269
$Ir_2N_1C_3$ (1)	578	601	722	86	67	284	322	146	2.202	0.303
$Ir_2N_2C_3$ (2)	577	606	731	87	67	286	328	147	2.233	0.305

The results showed that the hardness of the original Ir-N structure increased when the doped carbon atom ratio was less than 0.5, and the compound showed brittleness when $Ir_2N_{(4-x)}C_x$(x=1)

4. Conclusion

In this paper, the lattice constants, energy and elastic properties of $Ir_4C_{(12-x)}N_x$(x=0,2,4,6) and $Ir_2N_{(4-x)}C_x$(x=0,1,2,3) structures are calculated using the plane-wave projection method (PAW) of density functional theory (DFT) and the PBE functional under the generalized gradient approximation (GGA).All of these calculations were done at 0Gpa, and they showed that we could adjust the hardness of Ir-C-N compounds by changing the ratio of carbon and nitrogen atoms in different spatial systems,With the regulation B/G of the ratio changing continuously, the ratio is less than 1.75, which makes the compound gradually become brittle material from the original malleable material. It is hoped that the theoretical research in this paper can play a certain reference role for the subsequent regulation research of material hardness.

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