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COMPUTER MODELLING OF A VERY HEAT RESISTANT Hf₆C₃N₂ FOR COVER OF HYPERSONIC FLIGHT VEHICLES

Abstract. The creation of a very heat resistant cover for returnable orbiters and for hypersonic flying aircrafts is an actual problem in modern science and technics. Therefore, computer modelling and investigations molecular structure of various multicomponent compounds are important tasks. In the paper, based on the computer model the molecular structure and a very heat resistant of carbonitride hafnium Hf₆C₃N₂ have been investigated by using of the semiempirical quantum mechanical method PM3. Some mechanical, electrical, optical and thermodynamic parameters of this material have been researched. Debye temperature and melting temperature have been calculated. The found theoretical value of melting temperature of carbonitride hafnium Hf₆C₃N₂ is approximated to obtained experimental results. The block diagram of carried out investigations has been presented. The results of investigations indicate that these materials can be applied as a very heat resistant cover for hypersonic flight vehicles and returnable orbiter.

Keywords: very heat resistant cover; molecular structure; carbonitride hafnium; melting temperature; quantum mechanical method.

Introduction

It is known, that a growth of airspace industry imposes strict technical demands to flight vehicles: they must to possess a high-speed quality, abrasion-proof and oxidation-resistant, pass a high temperature test and withstand temperature up to 4000K when penetration of atmosphere and can be used many times. During penetration of atmosphere the temperature on the surface of aircraft's wings can be reach up to 2000°C and on the end of parts of wings can be reach up to 4000°C and higher. Therefore, when creation such flight vehicles it should be to solve problems to make very heat resistant materials possessing high strength properties. Possessing the melting temperature higher 4000°C such materials can be used in forebodes of aircrafts, in jet engines, in end parts of wings of aircrafts and space vehicles.

At present, in many counties there have been carried out intensive experimental and theoretical investigations solid compounds based on niobium, tantalum and carbonitride hafnium [1,2]. In particular, the much progress had been reached for the triple system of (HfC_xN_y). In accordance with recent publication [2], the scientists could obtain the HfC_{0.5}N_{0.35} compound. This compound is a very closed to theoretical calculated one and has a melting temperature of ~4200°C and hardness of 21,3 GPa.

The goal of this paper is a construction of the computer model of molecular structure of carbonitride hafnium Hf₆C₃N₂ and by applied semiempirical method PM3 (Parametrical Model 3) to calculate the values of some mechanical, optical and thermodynamic parameters of this material.

The algorithm of carbonitride hafnium research

Let us consider the algorithm of research of the properties of carbonitride hafnium Hf₆C₃N₂. In the first stage, by using the free evaluate version HyperChem Professional v7.5 program the computer model of molecular structure of the carbonitride hafnium

HfC_{0.5}N_{0.35} triple compound is constructed. The chemical structure of the material having HfC_{0.5}N_{0.35} composition is expressed formula of Hf₆C₃N₂.

In the second stage, as result of construction of computer model of the carbonitride hafnium Hf₆C₃N₂ the Cartesian coordinates of each atom are determined (see table 1). Then, based on Cartesian coordinates of the carbonitride hafnium Hf₆C₃N₂ by using of quantum mechanical method PM3 the energy parameters of this material are determined.

In the next stage, some mechanical and thermodynamic parameters including melting temperature of carbonitride hafnium are calculated. At last, the criterion of $T_m > 4000K$ is checked. If this criterion is not satisfied then the composition (chemical formula) of carbonitride hafnium is corrected and then calculation process is started again.

Table 1 – Cartesian coordinates of carbonitride hafnium Hf₆C₃N₂.

Atom	Cartesian coordinates, in angstroms, Å		
	x	y	z
Hf	0.91582	-1.19132	0.88673
Hf	-1.28284	0.50067	1.03908
Hf	-0.94183	-1.13788	-1.17881
Hf	1.24649	1.87595	-3.06892
Hf	3.10415	1.82251	-1.00338
Hf	0.90548	3.51450	-0.85102
N	2.72778	3.74814	-2.48388
N	-1.41203	-1.95333	1.09177
C	0.37996	0.60694	-1.48097
C	0.19250	1.50771	-0.26172
C	1.40118	0.57756	-0.34548

Molecular structure model of Hf₆C₃N₂. Calculation methodology

Fig. 1 shows calculated visual model of carbonitride hafnium Hf₆C₃N₂ having similar chemical structure as theoretical calculated HfC_{0.5}N_{0.35}.

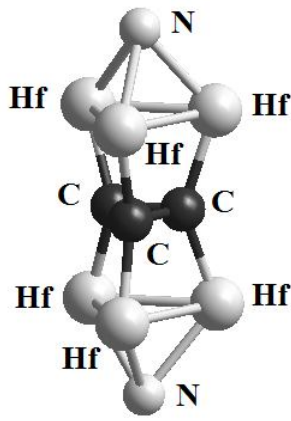


Fig. 1. Visual model of carbonitride hafnium $\text{Hf}_6\text{C}_3\text{N}_2$.

Based on the quantum mechanical method PM3, the properties of carbonitride hafnium with chemical structure $\text{Hf}_6\text{C}_3\text{N}_2$ were investigated. The state of an electron in a molecule is described by a one-electron wave function termed molecular orbital [3]. These functions are multicentered.

Thus, their description includes the electron distances from atomic nuclei. There are various options to find molecular orbitals. One of them, the method of finding molecular orbital wave function U_i , as a linear combination of atomic orbitals χ_q of the atoms composing the molecule:

$$U_i = \sum_{q=1}^n c_{qi} \cdot \chi_q \quad (1)$$

Here: c_{qi} are the coefficients, χ_q are atomic orbitals chosen as basic functions, n is a number of orbitals. In this study, the Gaussian functions were used as atomic orbitals [3]:

$$\chi_{nlm}(\mu, r, \theta, \phi) = r^{n-1} e^{-\mu r^2} Y_{lm}(\theta, \phi) \times \sqrt{\frac{2^{2n} (n-1)!}{(2n-1)!}} \cdot \sqrt{(2\mu)^{2n+1} / \pi} \quad (2)$$

Here: μ is a parameter of variation, r , θ , ϕ are spherical coordinates of electron, $Y_{lm}(\theta, \phi)$ are complex spherical functions, m is a number of atom orbitals chosen as a basic functions, c_{qi} are values of unknown coefficients which are determined by solving of the below equations of molecular orbitals

$$\sum_q (H_{pq} - \varepsilon_i S_{pq}) c_{qi} = 0 \quad (3)$$

or

$$\begin{cases} (H_{11} - \varepsilon S_{11})c_1 + \dots + (H_{1m} - \varepsilon S_{1m})c_m = 0; \\ (H_{21} - \varepsilon S_{21})c_1 + \dots + (H_{2m} - \varepsilon S_{2m})c_m = 0; \\ \dots \\ (H_{m1} - \varepsilon S_{m1})c_1 + \dots + (H_{mm} - \varepsilon S_{mm})c_m = 0. \end{cases}$$

Here: H_{pq} are the matrix elements of Hamiltonian for an electron moving in a certain effective field of the molecule irrespective of other electrons, they are

calculated in the Wolfsberg-Helmholtz approximation [3], S_{pq} are overlapping integrals of atomic orbitals χ_p and χ_q , they are calculated based on the Gaussian functions.

(3) equations are linear homogeneous equations concerning c_{qi} . In order that these equations have non-zero solutions, based on the coefficients of unknown quantities the constructed determinant must equal 0. That is,

$$\begin{vmatrix} H_{11} - \varepsilon S_{11} & H_{12} - \varepsilon S_{12} \dots H_{1m} - \varepsilon S_{1m} \\ H_{21} - \varepsilon S_{21} & H_{22} - \varepsilon S_{22} \dots H_{2m} - \varepsilon S_{2m} \\ \dots & \dots \\ H_{m1} - \varepsilon S_{m1} & H_{m2} - \varepsilon S_{m2} \dots H_{mm} - \varepsilon S_{mm} \end{vmatrix} = 0.$$

When this determinant is opened then m degree of equation has been obtained relatively ε quantity:

$$\varepsilon^m + a_1 \varepsilon^{m-1} + a_2 \varepsilon^{m-2} + \dots + a_0 = 0 \quad (4)$$

In (4) a_0 , a_1 , etc. quantities are determined by using S_{pq} and H_{pq} matrix elements. By solving (4) equation, m number $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_m$ roots are obtained. These roots are molecule orbital energies.

By including each ε_m in (3) equations' system, unknown c_{qi} coefficients are determined. By using ε_1 root determined the coefficients define I-st molecular orbital, by using ε_2 root determined the coefficients define II-nd molecular orbital, etc.

Calculation of energy, mechanic and thermodynamic parameters

For each object, electrons are adjusted by two on energy levels starting from lowest level.

ε_{HOMO} and ε_{LUMO} have been determined as top-most molecular orbit's energy and lowest empty molecular orbit's energy, respectively, trapped by electrons.

Ionization potential $I_p = -\varepsilon_{LUMO}$ has been calculated by using band gap $E_g = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ and strength $\eta = E_g / 2$.

The wavelength of radiated photon of this material is calculated by formula

$$\lambda = \left(c \cdot h / (1,6 \cdot E_g) \right) \cdot 10^{28} \text{ nm}.$$

Here: h is Planck constant; c is the speed of light in vacuum. When λ is calculated then the values of E_g in eV are used. It is considered that when $\eta < 1$ eV the material is soft and when $\eta > 1$ eV one is solid.

The stability of material is calculated by next formula

$$\Delta E = E - \sum_A E_A.$$

Here: E is the total energy of the system, E_A is total energy of A atom in the system and ΔE is a parameter characterizing the stability of system. It is considered that when $\Delta E > 0$ the material is unstable and when $\Delta E < 0$ one is stable.

Table 1 shows calculated energy parameters of carbonitride hafnium $\text{Hf}_6\text{C}_3\text{N}_2$ based on the semiempirical quantum mechanical method PM3.

Table 1 – Energy parameters of carbonitride hafnium Hf₆C₃N₂

ϵ_{HOMO} , eV	ϵ_{LUMO} , eV	Total energy, E (amu.)	Stability parameter ΔE (amu.)	Ionization potential, I_p (eV)	Band gap, E_g (eV)	Strength parameter η (eV)	Wave length of emitted photon, λ (nm)
-6,89	-2,30	-48,42	-4,48	6,89	4,59	2,30	271

Based on these calculated parameters, some properties of carbonitride hafnium Hf₆C₃N₂ can be analyzed.

If binding energy E_b of carbonitride hafnium Hf₆C₃N₂, cross-section area S and inter atoms bonding r are known the Young modulus can be calculated:

$$Y = F/S = E_b/(r \cdot S), \quad F \approx E_b/r \quad (4)$$

If the Young modulus is known, then a rigidity parameter k , a modulus of deformation σ , a shear modulus G , a bulk elasticity modulus K , and a hardness modulus HN [3] can be calculated [3]:

$$k \approx Y \cdot S/D, \quad \sigma = Y \cdot r/D, \quad G = Y/(2(1+\nu)), \quad K = Y/(3(1-2\nu)), \quad HN = G \cdot A \cdot e^{-B \cdot T} \quad (5)$$

Here: ν is the Poisson ratio, $A = 0.83699$, $B = 2.204 \cdot 10^{-3} \text{ K}^{-1}$, $T = 300 \text{ K}$. Based on data presented in tables 1 and 2, some mechanical parameters of carbonitride hafnium Hf₆C₃N₂ have been calculated (table 3). The calculation of Debye temperature is important stage because if the values of mechanical parameters and Debye temperature are known then the melting temperature of material can be determined.

Table 2 – Some data of sample of carbonitride hafnium Hf₆C₃N₂

The sample size, D (nm)	Inter atoms bonding, r (nm)	Cross-section area, S (m ²)	binding energy, E_b (amu)	Material breaking force, F (N)	Poisson ratio
0.79	0.22	$5 \cdot 10^{-19}$	3.37	$6.546 \cdot 10^{-8}$	0.348

Table 3 – Calculated mechanical parameters of carbonitride hafnium Hf₆C₃N₂

Rigidity parameter, N/m	Modulus of deformation, (GPa)	Shear modulus, (GPa)	Bulk elasticity modulus, (GPa)	Young modulus, (GPa)	Hardness modulus, (GPa)
82.651415	37.63	49.3	145.3	132.9	21.3

Let us use below formula for calculation of Debye temperature [5]:

$$\theta_D = \frac{h}{k_B} \cdot \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} V_m \quad (6)$$

Here: h is the Planck constant, k_B is the Boltzmann constant, n is a number of atoms, ρ is a mass density, M is a molar mass, V_m is an average velocity of sound in given material. An average velocity of sound can be determined from formula [6]:

$$V_m = \left[\left(2/V_t^3 + 1/V_l^3 \right) / 3 \right]^{-1/3} \quad (7)$$

Here: V_t and V_l are transverse and longitudinal velocities of elastic wave in the material, respectively:

$$V_t = \sqrt{G/\rho}, \quad V_l = \sqrt{(3K + 4G)/(3\rho)} \quad (8)$$

If the Debye temperature is known then a temperature of melting is determined by below formula [6]:

$$T_m = 2\pi M C a^2 \theta_D^2 k_B / h^2 \quad (9)$$

Here: $C = 0.050$ is the constant found from experiment [2]. By using of (6)-(9) the Debye temperature and melting temperature are calculated for carbonitride hafnium Hf₆C₃N₂, respectively: $\theta_D = 304\text{K}$ и $T_m = 4414\text{K}$ (4141°C).

Fig. 2 shows the block diagram of the above-described algorithm of computer modelling and investigation of properties of the carbonitride hafnium Hf₆C₃N₂. More detailed this algorithm is described in above part.

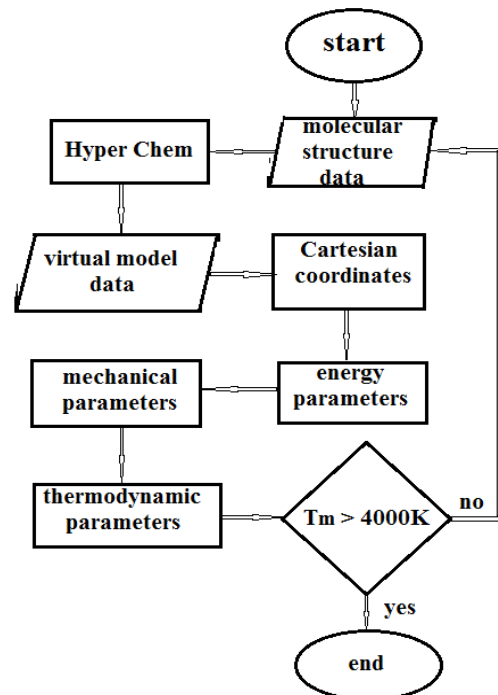


Fig. 2. The block diagram of the investigation algorithm of carbonitride hafnium Hf₆C₃N₂.

Conclusion

By using of the semiempirical quantum mechanical method PM3 the electronic structure of carbonitride hafnium Hf₆C₃N₂ have been investigated. Based on the constructed visual computer model, orbital energy, ionization potential, total energy of electrons, also, some mechanical, electrical, optical and

thermodynamic parameters have been calculated. Obtained results shows that given material is stable and possess super high melting temperature $T_m = 4141^\circ\text{C}$. This material can be applied for very heat resistant

cover for hypersonic flight vehicles and returnable orbiter. The found theoretical value of melting temperature of carbonitride hafnium $\text{Hf}_6\text{C}_3\text{N}_2$ is approximated to obtained experimental results.

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Комп'ютерне моделювання понаджароміцних властивостей $\text{Hf}_6\text{C}_3\text{N}_2$ для захисних покриттів гіперзвукових літальних апаратів

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Анотація. Створення понаджароміцних покриттів для космічних кораблів, які повернуться на Землю, а також для літальних апаратів, що рухаються в атмосфері з гіперзвуковими швидкостями, є актуальною проблемою сучасної науки і техніки. Тому для створення таких матеріалів важливим завданням є дослідження і комп'ютерне моделювання молекулярної структури різних багатоконпонентних сполук. У даній статті, на основі побудованої комп'ютерної моделі молекулярної структури матеріалу карбонітриду гафнію з хімічною формулою $\text{Hf}_6\text{C}_3\text{N}_2$, застосувавши напівемпіричний квантовомеханічний метод РМЗ, обчислений ряд значень механічних, електричних, оптичних і термодинамічних параметрів цього матеріалу. Обчислені температура Дебая і температура плавлення матеріалу. Знайдені теоретичні значення температури плавлення збігаються з раніше визначеними з експериментів. Результати досліджень показують, що ці матеріали можна використовувати в якості жароміцного покриття при створенні гіперзвукових літальних апаратів, а також космічних апаратів, що повертаються на Землю.

Ключові слова: понаджароміцне покриття; молекулярна структура; карбонітрид гафнію; температура плавлення; квантово-механічний метод.

Компьютерное моделирование сверхжаропрочных свойств $\text{Hf}_6\text{C}_3\text{N}_2$ для защитных покрытий гиперзвуковых летательных аппаратов

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Аннотация. Создание сверхжаропрочных покрытий для космических кораблей, возвращаемых на Землю, а также для летательных аппаратов, движущихся в атмосфере с гиперзвуковыми скоростями, является актуальной проблемой современной науки и техники. Поэтому, для создания таких материалов важной задачей является исследование и компьютерное моделирование молекулярной структуры различных многокомпонентных соединений. В данной статье, на основе построенной компьютерной модели молекулярной структуры материала карбонитрида гафния с химической формулой $\text{Hf}_6\text{C}_3\text{N}_2$, применив полумпирический квантовомеханический метод РМЗ, вычислен ряд значений механических, электрических, оптических и термодинамических параметров этого материала. Вычислены температура Дебая и температура плавления материала. Найденные теоретические значения температуры плавления совпадают с ранее определенными из экспериментов. Результаты исследований показывают, что эти материалы можно использовать в качестве жаропрочного покрытия при создании гиперзвуковых летательных аппаратов, а также космических аппаратов, возвращаемых на Землю.

Ключевые слова: сверхжаропрочное покрытие; молекулярная структура; карбонитрид гафния; температура плавления; квантовомеханический метод.