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Fabrication and oxidation resistance of the non-stoichiometric tantalum-hafnium carbonitride

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Abstract: This research was conducted to obtain non-stoichiometric tantalum-hafnium carbonitride powder of the *Fm*3*m* (225) structural type using a combination of mechanical activation (MA) and self-propagating high-temperature synthesis (SHS) methods. Mechanical activation for 60 min in a low-energy mode (347 rpm) forms Ta/Hf/C composite particles 1 to 20 μm in size with a layered structure and contributes to a uniform distribution of elements. SHS of a mechanically activated Ta + Hf + C mixture in a nitrogen atmosphere (0.8 MPa) leads to the formation of a single-phase tantalum-hafnium carbonitride powder with the $Ta_{0.25}Hf_{0.75}C_{0.5}N_{0.3}$ composition where particles feature by a «spongy» morphology with pores and caverns and consist of submicron grains. Spark plasma sintering (SPS) was used to obtain a bulk sample of tantalum-hafnium carbonitride with a grain size of 3 to 5 μm, relative density of 98.2 ± 0.3 %, hardness of 19.8 ± 0.2 GPa, and crack resistance of 5.4 ± 0.4 MPa·$m^{1/2}$. The kinetics of (Ta,Hf)CN oxidation at 1200 °C in air is described by a parabolic law suggesting the formation of an $Hf_6Ta_2O_{17}$ + *m*HfO_2 oxide layer with a low oxygen diffusion rate where the oxidation rate is 0.006 mg/(cm^2·s). A (Ta,Hf)CN oxidation mechanism is proposed, which states that Ta_2O_5 and HfO_2 are formed on the surface of grains at the first stage that react with each other at the second stage to form a $Hf_6Ta_2O_{17}$ homologous superstructure and monoclinic HfO_2. CO, CO_2, NO and NO_2 gaseous oxidation products are released with the formation of pores and cracks.

Keywords: carbonitride, mechanical activation, self-propagating high-temperature synthesis (SHS), ceramics, spark plasma sintering (SPS), oxidation resistance.

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Получение нестехиометрического тантал-гафниевого карбонитрида и исследование его окислительной стойкости

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Аннотация: В данной работе комбинацией методов механического активирования (МА) и самораспространяющегося высокотемпературного синтеза (СВС) получен порошок нестехиометрического тантал-гафниевого карбонитри-

да структурного типа *Fm*3*m* (225). Механическое активирование в течение 60 мин в низкоэнергетическом режиме (347 об/мин) приводит к формированию композиционных частиц Ta/Hf/C слоистой структуры, размер которых варьируется от 1 до 20 мкм, и способствует равномерному распределению элементов. Продуктом СВС механоактивированной смеси Ta + Hf + C в среде азота (0,8 МПа) является однофазный порошок тантал-гафниевого карбонитрида состава $Ta_{0,25}Hf_{0,75}C_{0,5}N_{0,3}$, частицы которого характеризуются губчатой морфологией с порами и кавернами и состоят из субмикронных зерен. Посредством искрового плазменного спекания (ИПС) получен объемный образец тантал-гафниевого карбонитрида, размер зерен которого варьируется от 3 до 5 мкм, с относительной плотностью 98,2 ± 0,3 %, твердостью 19,8 ± 0,2 ГПа и трещиностойкостью 5,4 ± 0,4 МПа·$м^{1/2}$. Кинетика окисления (Ta,Hf)CN при температуре 1200 °C на воздухе описывается параболическим законом, что свидетельствует о формировании оксидного слоя $Hf_6Ta_2O_{17}$ + *m*HfO_2 с низкой скоростью диффузии кислорода, скорость окисления при этом составляет 0,006 мг/($см^2$·с). Предложен механизм окисления (Ta,Hf)CN, заключающийся в том, что на первой стадии на поверхности зерен формируются Ta_2O_5 и HfO_2, которые на второй стадии вступают в реакцию друг с другом с образованием гомологичной сверхструктуры $Hf_6Ta_2O_{17}$ и моноклинного HfO_2. Высвобождение газообразных продуктов окисления CO, CO_2, NO и NO_2 сопровождается образованием пор и трещин.

Ключевые слова: карбонитрид, механическое активирование, самораспространяющийся высокотемпературный синтез (СВС), керамика, искровое плазменное спекание (ИПС), окислительная стойкость.

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Introduction

Few of the most advanced materials can withstand intensive mechanical and thermal loads above 2000 °C. The only choice is group IVB and VB transition metal compounds: borides, carbides, and nitrides. Due to the presence of strong covalent and ionic bonds, these materials have high melting temperatures (>2,500 °C), excellent mechanical and thermophysical properties, and chemical and phase stability [1, 2]. Tantalum and hafnium carbides are of special interest among other refractory compounds. They have the highest melting points (3,880 and 3,890 °C, respectively), a higher hardness (~25 GPa), elastic modulus (~450 GPa), and strength (~250 MPa) while thermal conductivity ranges from 20 to 30 W/(m·K) [3—5].

A significant disadvantage of refractory compounds is their relatively low oxidation resistance. Most of them work well in protective atmospheres, while in the air they oxidize intensively at 400—800 °C, forming porous and cracking oxide films, which cannot protect the base material from further oxidation [6].

There are several approaches to increasing their heat resistance. For example, the addition of SiC to refractory ceramics initiates the formation of a dense $MeSiO_4$ oxide layer, thus preventing oxygen diffusion to the material [7, 8]. Another approach is to create more complex compounds from refractory transition metal carbides and nitrides. Such solid solutions tend to have enhanced physical, mechanical, and thermophysical properties, and higher oxidation resistance, since refractory oxide films with low oxygen diffusion rates are formed [9]. Savvatimskiy A. et al. [10] showed that the $Ta_{0.80}Hf_{0.20}C$ melting temperature is 4030 °C. It significantly exceeds the melting temperatures of tantalum and hafnium carbides, the current «record-breakers». Kurbatkina V. et al. [11] demonstrated

that double carbides (Ta, Hf)C and (Ta, Zr)C have a higher hardness and Young's modulus compared to binary compounds.

Among the complex compounds, transition metal carbonitrides are no less interesting in terms of high-temperature applications. Hong Q.J. et al. [12] performed a theoretical analysis and showed that the introduction of nitrogen atoms into the lattice of refractory (Ta, Hf)C increases not only the melting point but also the oxidation resistance. As they reported, for the Ta—Hf—C—N system the tantalum-hafnium carbonitride ($Hf_{0.75}Ta_{0.25}C_{0.5}N_{0.25}$) has the highest properties. We thus decided to manufacture this compound and analyze its properties.

However, the synthesis of non-stoichiometric compounds is challenging. Conventional technologies produce only MeC_xN_{1-x} stoichiometric phases, since it is not possible to adjust the nitrogen content in the final product. An alternative method for producing a wide range of multicomponent compounds is self-propagating high-temperature synthesis (SHS) [13], as developed by A.G. Merzhanov and I.P. Borovinskaya in 1972. This is a simple, single-stage, and highly efficient process.

This study aims to manufacture (Ta, Hf)CN dense ceramics by means of spark plasma sintering. The raw material is the powder produced by SHS of mechanically agitated activated Ta + Hf + C mixture in a nitrogen environment. Ceramics oxidation resistance was also studied.

Materials and methods

Hafnium powder HFM-1 (TU 48-4-176-85 (97) specification, particle size $d \leq 50$ μm, 98.8 % purity), tantalum powder TaP-1 (TU 1870-258-00196109-01 95.136-69 specification, particle size $d = 40 \div 60$ μm, 99.9 % purity) and carbon black P804T (TU 38-1154-88 specification, particle size $d \leq 0.2$ μm, 99.5 % purity) were used as precursors. The mechanical milling was performed in an argon environment using a 4.8 Grade argon (GOST 10157-79, 99.993 % purity). The SHS process involved filtration combustion in grade 1 nitrogen (GOST 9293-74, 99.999 % purity).

Before synthesis, the Ta + Hf + C powder mixture (24.3 Ta + 72.1 Hf + 3.6 C wt.%) was mechanically activated in an Activator-2S high-performance planetary ball mill (Activator, Russia). The powder mixture and steel balls (1 : 20 weight mass ratio) were loaded into steel jars filled with argon at 0.6 MPa. Mechanical activation lasted for 60 min at a 347 rpm speed of the jars.

A constant-pressure lab reactor was used for the SHS process. The activated Ta + Hf + C powder mixture was placed loosely on a removable reactor rack. The reactor chamber was evacuated with a fore vacuum pump. Then nitrogen was pumped through a dedicated pipe to a pressure of 0.8 MPa. A self-sustaining exothermic reaction was initiated by briefly applying a voltage to the tungsten coil connected to the power supply.

The SHS powder was consolidated with a Labox 650 spark plasma sintering machine (SinterLand, Japan) in an argon environment at 2000 °C, 50 MPa press pressure, and 20 min. holding time. The heating rate was 100 °C/min.

The microstructure and elemental composition were analyzed with a JSM-7600F scanning electron microscope (JEOL Ltd., Japan) equipped with an INCA SDD 61 X-MAX *X*-ray microanalysis system (Oxford Instruments, UK) in backscattered electron mode, 15 kV accelerating voltage and 3 nm resolution.

The phase composition of the powders after mechanical activation and SHS and of the sintered samples was studied using a Diffray-401 *X*-ray diffractometer (Research Instruments, Russia), CuK_α radiation, step scanning mode (scanning step: 0.1°) 20° to 100°angle range, 2 s exposure. The ICDD PDF databases were used to analyze the resulting spectra.

The nitrogen and carbon contents in the synthesized powders and sintered samples were determined by carrier gas hot extraction. A TC-600 (Leco, USA) instrument estimated the amount of nitrogen and oxygen in the compounds by IR adsorption (for oxygen) and thermal conductivity (for nitrogen) analysis during the reduction melting of the samples in a resistance furnace in a helium flow. A CS-600 (Leco) instrument was used to measure the carbon content. For this purpose, the samples were subjected to oxidative melting in an induction furnace and the amount of CO_2 released was measured by IR absorption.

The density of compacted ceramic materials was determined by hydrostatic weighing under GOST 20018-74 [14]. At least 10 measurements were taken in air and distilled water ($\rho_w = 0.9978$ g/cm^3). A layer of vaseline

(ρ_v = 0.870 g/cm^3) was applied to cover the open pores. We applied an ES 220A analytical balance (Precisa, Switzerland), ±0.0001 g accuracy.

A Micro-Hardness Tester (CSM Instruments, Switzerland) was used to measure Young's modulus (*E*) at a 100 mN applied load.

We used a Durascan 70 hardness testing machine (Struers ApS, Denmark) to estimate the hardness and crack resistance of the consolidated materials by the Vickers method, GOST 2999-75 [15]. A max load of 9.8 kg was applied for 20 s. After the load was removed, the diagonals of the imprint on the sample surface and the crack lengths were measured. At least 10 measurements were taken with each sample. The software evaluated the hardness automatically. We used the Anstis equation to assess the fracture toughness:

$$K_{1c} = 0{,}016\left(\frac{E}{HV}\right)^{1/2}\frac{P}{c^{3/2}}, \quad (1)$$

wherein *E* is Young's modulus, GPa; *HV* is the hardness, GPa; *P* is the applied load, N; *c* is the crack length from the center of the imprint to the crack end, m.

We used an SSHOL 1.1,6/12-M3 electric furnace (Tula-Therm, Russia) at 1200 °C for 180 min to study the chemical kinetics and oxidation of a box-shaped (Ta, Hf)CN shape. The samples were measured using a micrometer. Before the analysis, the samples were polished on a Tegramin grinding and polishing system (Struers, Denmark). The sample was placed on a platform in the furnace in an alundum crucible. The degree of oxidation was assessed after 5, 10. 15, 20, 30, 60, 120, and 180 min using the gravimetric method. We measured the weight gain using a GR-202 analytical balance (AND, Japan), 10^{-4} g accuracy. Before weighing, the samples and with crucibles were cooled to room temperature.

Results and discussion

Mechanical activation (MA) is an important step before SHS. It enhances reactivity and helps control the microstructure of the combustion products [16]. Fig. 1 shows that the MA of tantalum, hafnium, and carbon powders (Ta + Hf + C) for 60 min resulted in formation of composite Ta/Hf/C particles ranging from 1 to 20 μm. A detailed examination of their cross sections identified the layers (Fig. 1, *b* and *c*) corresponding to heavy (Ta and Hf: light areas) and light (C: dark areas) elements.

Fig. 2 shows the (Ta, Hf)CN microstructure after SHS of a mechanically activated Ta + Hf + C mixture in a nitrogen environment. The morphology of SHS powder particles (Fig. 2, *a*) is identical to that of the composite Ta/Hf/C particles after MA (see Fig. 1, *a*). Cross-sectional analysis of (Ta, Hf)CN particles discovered pores and caverns. A more detailed examination revealed melted grains from 1 to 3 μm (Fig. 2, *b*). This can be explained by hafnium and tantalum melting during combustion (adiabatic combustion temperature t_{ad} = 3073 °C) and the formation of (Ta, Hf)CN through the liquid phase. As Fig. 2, *c* shows, Ta, Hf, C, and N are evenly distributed after SHS.

Chemical analysis indicated that the SHS powder contains 3.7 wt.% C and 2.2 wt.% N, which corresponds to $Hf_{0.75}Ta_{0.25}C_{0.5}N_{0.25}$. It should be noted that the oxygen content does not exceed 0.8 wt. %.

Fig. 3 shows the sample XRD patterns after SHS and spark plasma sintering (SPS). The crystal structure of the sintered (Ta, Hf)CN substance is identical to that of the synthesized powder. Its space group is *Fm*3*m* (225). However, after sintering, the main phase peaks became more symmetrical, indicating a homogenization of the chemical composition across the sample during SPS. The (Ta, Hf)CN lattice parameter after SHS and SPS is 0.455 nm. This is between HfC (0.464 nm) and HfN (0.453 nm). The value we obtained is higher than that for TaC (0.446 nm) and TaN (0.434 nm). In both cases, the XRD patterns show HfO_2 peaks of the *P*42/*nmc* (14) space group.

Fig. 4 shows a typical microstructure of the sample after sintering. The grain size of the main (Ta, Hf)CN phase (light areas) varies from 3 to 5 μm, with small HfO_2 inclusions (dark gray areas) at their boundaries. The sintered (Ta, Hf)CN powder has a 98.2 ± 0.3 % relative density and high mechanical properties (hardness *H* = 19.8 ± 0.2 GPa, Young's modulus *E* = 570 ± ± 20 GPa, fracture toughness K_{1c} = 5.4 ± 0.4 MPa·m$^{1/2}$). This is comparable to the properties of similar materials [11, 17—19].

We studied the kinetics and oxidation mechanism of the $Hf_{0.75}Ta_{0.25}C_{0.5}N_{0.25}$ using a muffle electric furnace at 1200 °C for 180 min. Fig. 5 shows the kinetic curve of the sample mass change. The oxidation of tantalum-hafnium carbonitride follows a parabo-

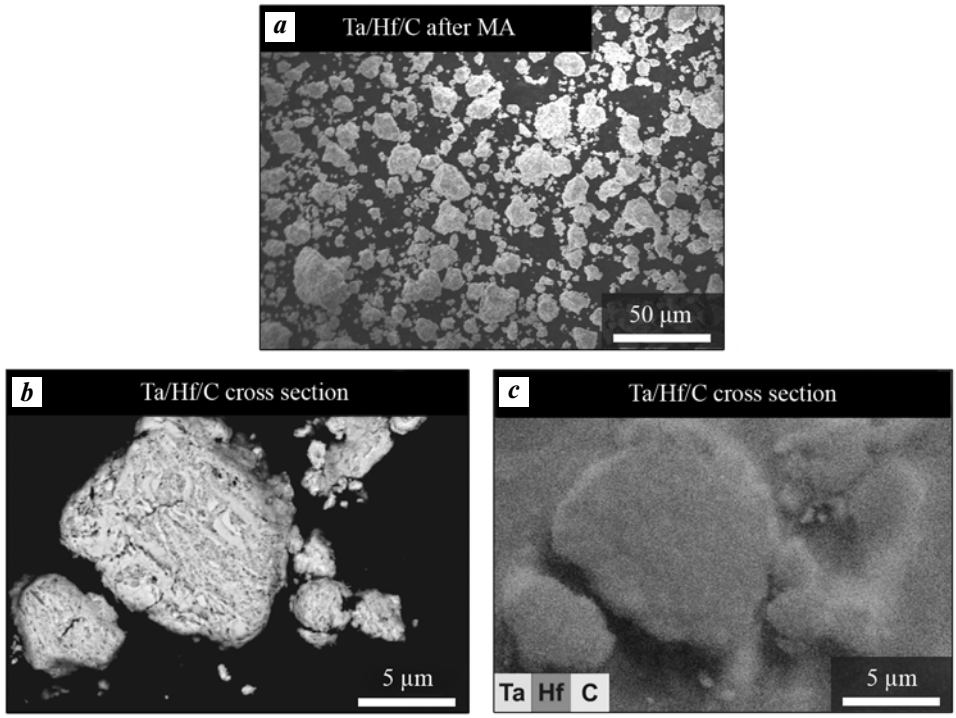

Fig. 1. Micrograph (***a***), cross section (***b***) of Ta/Hf/C composite particles and map of element distribution after mechanical activation (***c***)

Рис. 1. Микрофотография (***a***), поперечное сечение (***b***) композиционных частиц Ta/Hf/C и карта распределения элементов после механического активирования (***c***)

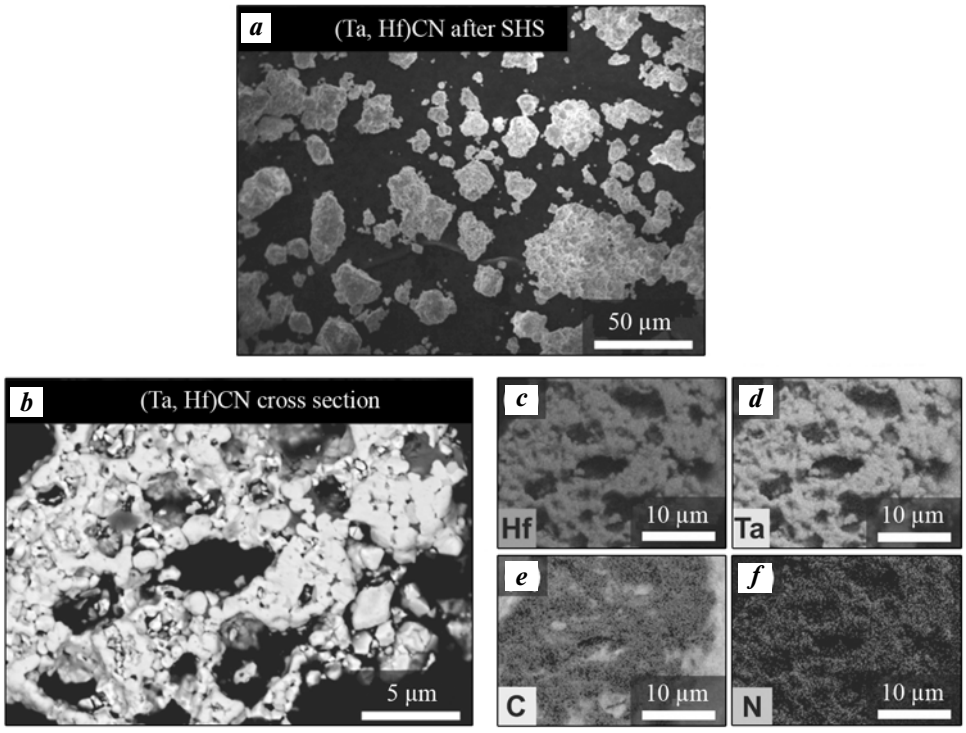

Fig. 2. Micrograph (***a***), cross section (***b***) of (Ta,Hf)CN particles and distribution of elements after SHS (***c***–***f***)

Рис. 2. Микрофотография (***a***), поперечное сечение (***b***) частиц (Ta,Hf)CN и распределение элементов после СВС (***c***–***f***)

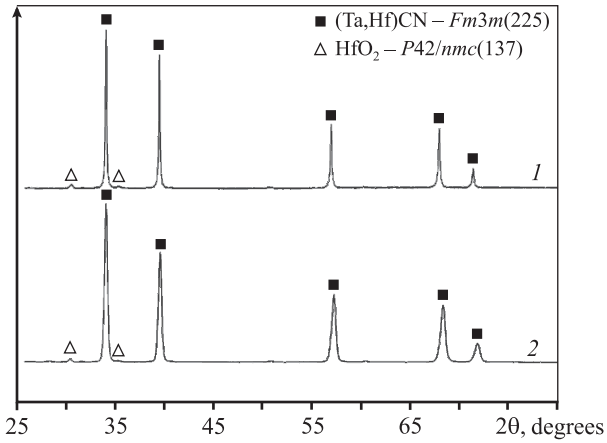

Fig. 3. XRD patterns of (Ta,Hf)CN samples after SPS (***1***) and SHS (***2***)

Рис. 3. Дифрактограммы образцов (Ta,Hf)CN после ИПС (***1***) и СВС (***2***)

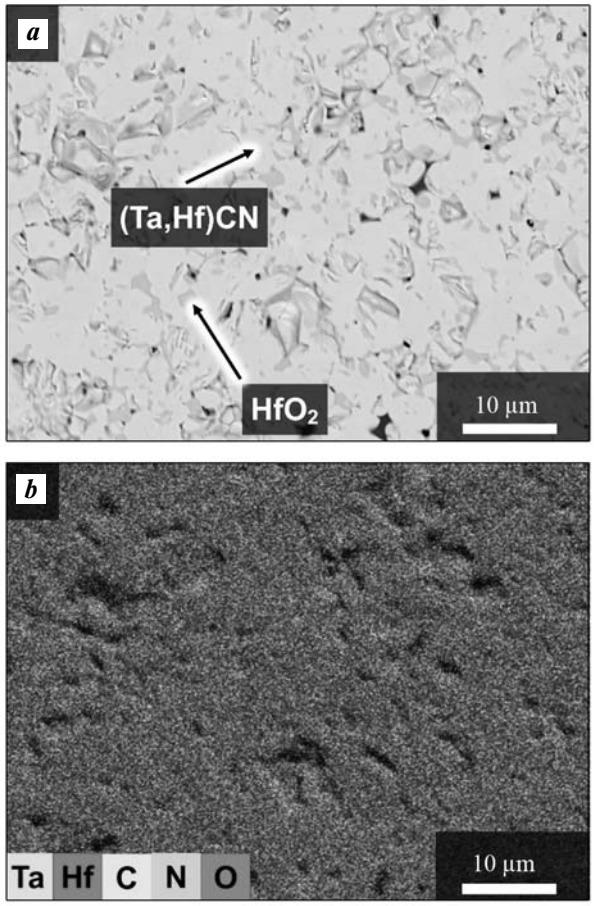

Fig. 4. Microstructure of sample (Ta,Hf)CN (***a***) and map of element distribution after SPS (***b***)

Рис. 4. Микроструктура образца (Ta,Hf)CN (***a***) и карта распределения элементов после ИПС (***b***)

lic law. Between 0 and 30 minutes, the max oxidation rate was 0.012 mg/(cm^2·s); as the oxide layer grew, it decreased to 0.004 mg/(cm^2·s). The average oxidation rate was ~0.006 mg/(cm^2·s) and the weight gain was 62 mg/cm^2.

As Fig. 6 shows, a dense oxide layer is formed on the surface of the $Hf_{0.75}Ta_{0.25}C_{0.5}N_{0.25}$ sample after oxidation. XRD indicated (Fig. 7) that it consists of two phases: monoclinic HfO_2, $P21/c(14)$ space group; and the $Hf_6Ta_2O_{17}$ orthorhombic superstructure ($Ima2(46)$). The intensity of the complex oxide peaks is much greater than that of hafnium oxide. It indicates the predominance of $Hf_6Ta_2O_{17}$ in the oxide layer.

Based on the results presented in this work and the literature [24], we may assume the following oxidation process (Fig. 8). Initially, Ta_2O_5 and HfO_2 are formed on the surface of (Ta, Hf)CN grains as result of the reaction

$$8Hf_{0,75}Ta_{0,25}C_{0,5}N_{0,25} + 14{,}5O_2 =$$

$$= Ta_2O_5 + 6HfO_2 + 4CO_2 + 2NO_2. \qquad (2)$$

The $Hf_{0.75}Ta_{0.25}C_{0.5}N_{0.25}$ compound has a high Hf content, so mainly HfO_2 is formed on the surface of the particles. Since the Gibbs energy for the Ta_2O_5 formation (ΔG = –72 kJ/mol [20]) is more negative when compared to that for HfO_2 (ΔG = –1088 kJ/mol [21]), Ta_2O_5 is most probably located at the surface of

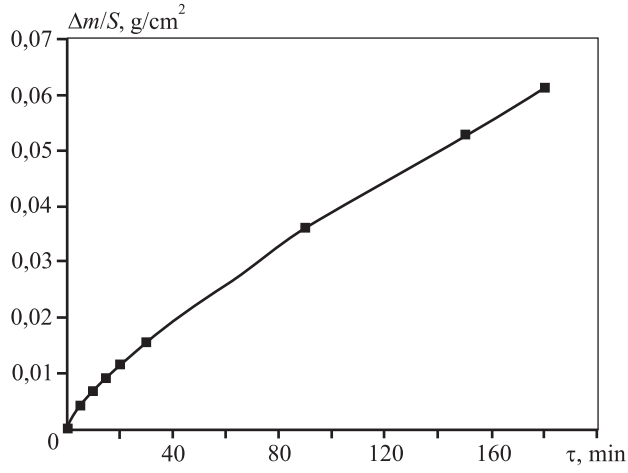

Fig. 5. Kinetic curve of (Ta,Hf)CN sintered sample oxidation

Рис. 5. Кинетическая кривая окисления спеченного образца (Ta,Hf)CN

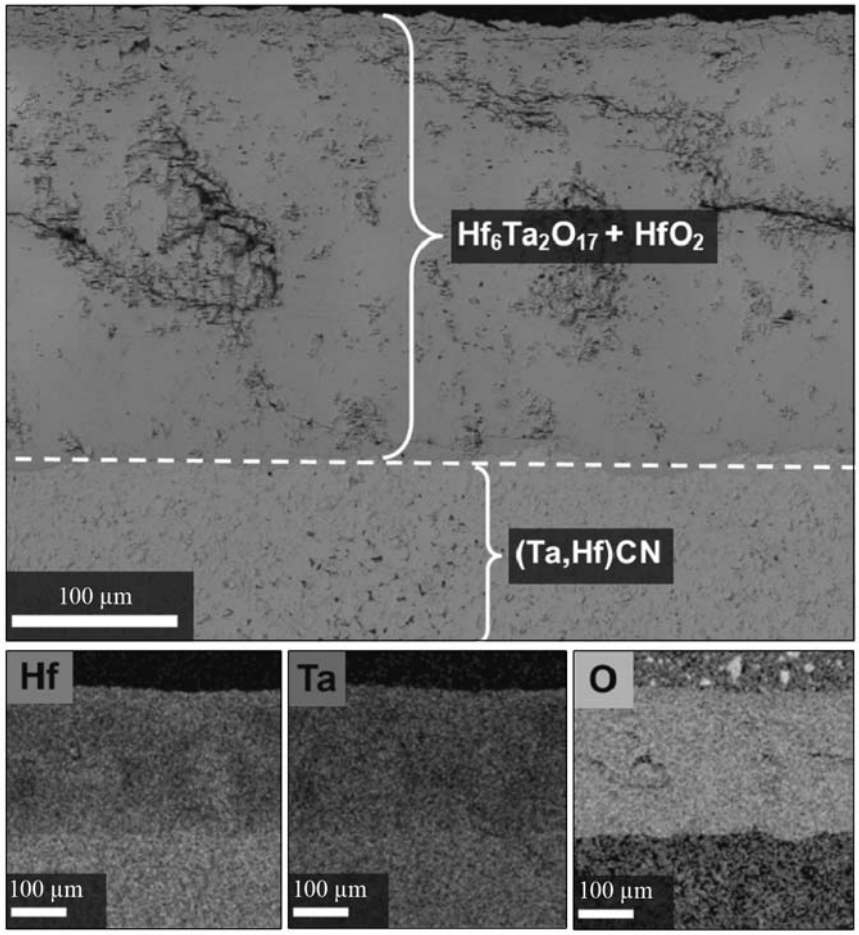

Fig. 6. Micrograph of (Ta,Hf)CN cross section after oxidation at t = 1200 °C and distribution of elements in oxide layer

Рис. 6. Микрофотография поперечного сечения образца (Ta,Hf)CN после окисления при t = 1200 °C и распределение элементов в оксидном слое

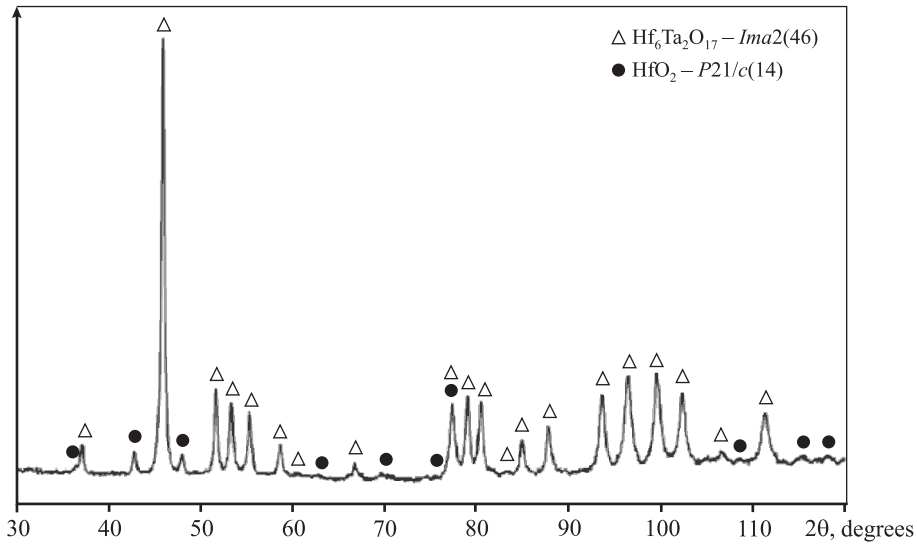

Fig. 7. XRD pattern of (Ta,Hf)CN oxide layer

Рис. 7. Дифрактограмма оксидного слоя (Ta,Hf)CN

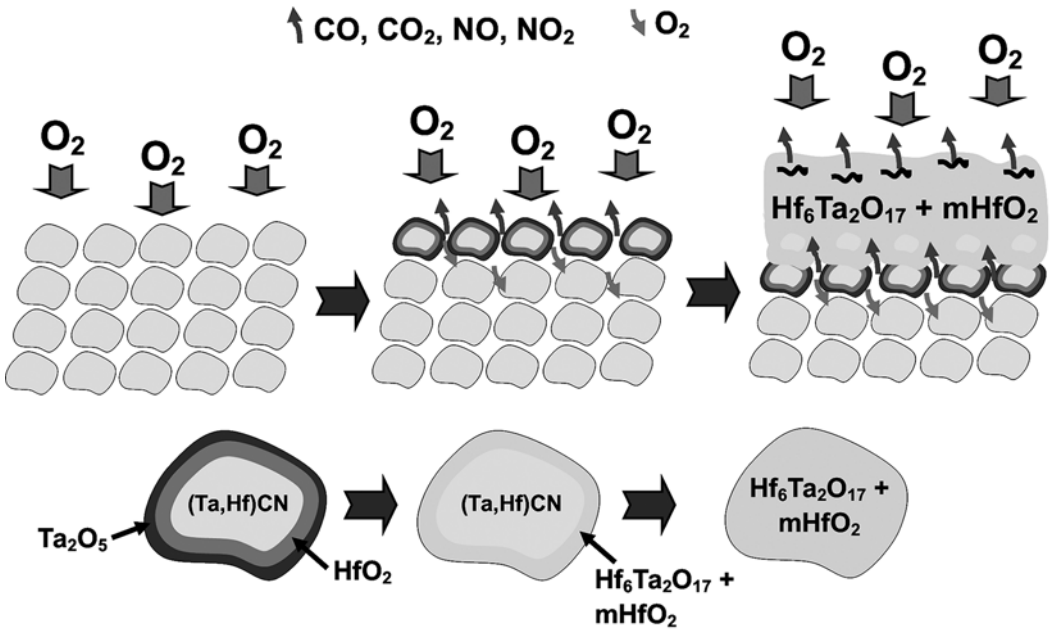

Fig. 8. (Ta,Hf)CN oxidation mechanism

Рис. 8. Механизм окисления (Ta,Hf)CN

HfO_2, as shown in Fig. 8. The phase diagram [22] indicates that HfO_2 and Ta_2O_5 oxides mutually react at t = 1200 °C to form $Hf_6Ta_2O_{17}$ and a monoclinic HfO_2 substance:

$$7HfO_2 + Ta_2O_5 = Hf_6Ta_2O_{17} + HfO_2. \quad (3)$$

Gaseous CO_2 and NO_2 are generated during the (Ta, Hf)CN oxidation (reaction (2)). The gases pass through the oxide layer, forming pores and cracks.

From studies [23, 24] we can conclude that $Hf_6Ta_2O_{17}$ as an oxide layer has a lower oxygen diffusion rate compared to HfO_2, high density, and adhesion to the substrate. It explains the relatively low oxidation rate of (Ta, Hf)CN.

Conclusion

An SHS process applied to a mechanically activated Ta + Hf + C mixture produces a $Hf_{0.75}Ta_{0.25}C_{0.5}N_{0.25}$ single-phase non-stoichiometric tantalum-hafnium carbonitride powder. Mechanical activation contributed to the uniform distribution of elements and the formation of composite Ta/Hf/C particles. SHS produces spongy particles consisting of submicron grains.

The SPS process at t = 2000 °C, 50 MPa and 20 min holding time produces bulk tantalum-hafnium carbonitride with 98.2 ± 0.3 % relative density, 19.8 ± 0.2 GPa hardness, 570 ± 20 GPa Young's modulus, and 5.4 ± ± 0.4 MPa·$m^{1/2}$ fracture toughness. The mechanical properties of the resulting ceramics are higher than those of binary compounds. They are comparable to double carbides.

The tantalum-hafnium carbonitride demonstrated high oxidation resistance (0.006 mg/(cm^2·s)) at t = 1,200 °C in the air. The oxidation kinetics follows the parabolic law. This can be explained by the formation of an oxide film with a low oxygen diffusion rate. The film consists of the $Hf_6Ta_2O_{17}$ homologous superstructure and the HfO_2 monoclinic substance.

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