

Production of coating based on high-entropy carbide in the arc discharge plasma

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A coating based on high-entropy carbide was synthesized by using a coaxial magnetoplasma accelerator for generating a high-speed arc discharge plasma. The plasma was used to deposit the coating on a copper substrate under appropriate conditions. In the process of the plasma-dynamic synthesis, a stable high-entropy impurity-free compound TiZrNbHfTaC_5 with the cubic $Fm\bar{3}m$ structure was formed. This compound has a sufficiently dense and uniform structure (with the porosity of $\sim 7\%$) $\sim 20\ \mu\text{m}$ thick. The resulting coating exhibits increased physical and mechanical characteristics including nanohardness of $\sim 32\ \text{GPa}$ and Young's modulus of $\sim 303\ \text{GPa}$. These values make the material promising for producing hardened, wear-resistant and heat-protective products.

Keywords: plasma, arc discharge, high-entropy carbide, coating.

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A variety of ultra-high-temperature ceramic (UHTC) materials, including coatings, attract close attention in view of creating new-generation constructional materials. They are able to combine improved mechanical properties with excellent thermal stability, which is a key to developing ceramic and composite components and items to be applied in high-temperature environments. Hafnium carbide (HfC) and tantalum carbide (TaC) which belong to the family of transition-metal carbides are among the most promising UHTC materials due to their ultra-high melting points ($T_m(\text{HfC}) = 3893\ \text{°C}$, $T_m(\text{TaC}) = 3983\ \text{°C}$) and improved mechanical characteristics [1].

The idea of using in UHTC hafnium and tantalum carbides is consistently evolving in the direction of creating based on them multicomponent compounds, which is possible because of the similarity of their crystal structures [2]. Finally, hafnium and tantalum carbides are mutually soluble and can form continuous single-phase solid solutions, including a number of high-entropy compounds among which there may be distinguished a carbide system with other IV- and V-group transition metals: Ti, Zr, Nb, Hf and Ta [3]. TiZrNbHfTaC_5 is considered to be significantly more resistant to oxidation than any of its constituent simple carbide forms [4]; it is able to maintain high flexural strength up to $2000\ \text{°C}$ [5] and exhibit a steady-state creep rate 10 times lower than that of the corresponding simple carbides [6].

Synthesis of high-entropy carbide TiZrNbHfTaC_5 is a challenging task. To solve it, it is necessary to ensure extreme conditions, e.g. temperatures above $2300\ \text{°C}$, which severely limits capabilities of the most common chemical and physical methods for obtaining such a material [7]. Thereat, of decisive importance in forming single-phase structure are, in addition to high temperature, such factors

as high dispersion and purity of raw materials and well-homogeneous mixing of components [8]. An even more labor-consuming task is the synthesis of TiZrNbHfTaC_5 in the form of a coating; therefore, so far there are no reliable information on producing such a material.

High-entropy carbide may be synthesized in the form of a coating by methods providing extreme conditions for the material formation with combining dissimilar substances. These features are to the full extent inherent to the plasmadynamic synthesis method in which a high-speed jet of the arc discharge plasma is used as a medium for high-energy plasma-chemical synthesis reactions. In this study, the arc discharge and, subsequently, the plasma flow were generated in a coaxial magnetoplasma accelerator with graphite electrodes. A mixture of dispersed precursors was placed into the plasma structure formation channel between the central and barrel electrodes. The high-entropy carbide was synthesized by using powders of pure metals Ti, Zr, Nb, Hf, Ta (purity 99.9%, mean size $\leq 10\ \mu\text{m}$) (Rare Metals, Russia) and carbon carrier Sibunit (purity 99.0%, specific surface area $\sim 340\ \text{m}^2/\text{g}$) (Boreskov Institute of Catalysis SB RAS, Russia); the powders were mixed until achieving the equiatomic ratio of metals and fivefold atomic content of carbon necessary to form a structure close to TiZrNbHfTaC_5 . The accelerator was supplied with power by a capacitive energy storage device ($W = 27.0\ \text{kJ}$, $U_C = 3.0\ \text{kV}$, $C = 6.0\ \mu\text{F}$).

Application of a potential difference to the accelerator electrodes initiates in the plasma structure formation channel between the central and barrel electrodes a breakdown of the inter-electrode gap accompanied by sublimation of precursors into the plasma state. Magnetic fields of the barrel electrode and external inductor

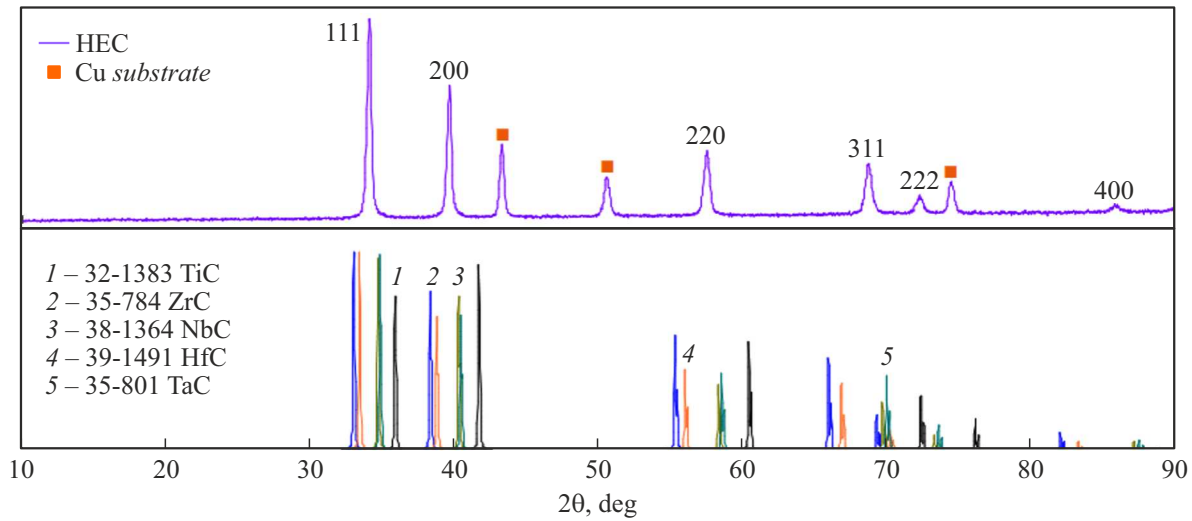


Figure 1. X-ray diffraction pattern of the synthesized coating on the substrate.

Calculations of the lattice constants a of the HEC cubic crystalline phase in the synthesized coating, as well as of the X-ray maxima positions hkl

hkl																		a_{av} , Å	$a_{veg}(HEC)$, Å
111			200			220			311			222			400				
d , Å	2θ , deg	a , Å	d , Å	2θ , deg	a , Å	d , Å	2θ , deg	a , Å	d , Å	2θ , deg	a , Å	d , Å	2θ , deg	a , Å	d , Å	2θ , deg	a , Å		
2.62	34.20	4.54	2.27	39.69	4.54	1.61	57.35	4.54	1.37	68.46	4.54	1.31	71.95	4.54	1.14	85.40	4.54	4.54	4.51651

accelerate the plasma jet and make it flowing into the reactor chamber filled with inert gas (argon) kept at room temperature and atmospheric pressure. In the experiment, the following energy parameters were achieved: maximum arc-stage voltage $U_{max} = 1.25$ kV, discharge current amplitude $I_{max} = 100.80$ kA, discharge power amplitude $P_{max} = 126.28$ MW, released energy $W = 20.06$ kJ, pulse duration $t = 310$ μ s, mean discharge power $P_{av} = 64.72$ MW. To form the coatings, a copper plate was installed in the reactor chamber in the path of the plasma jet propagation at the distance of 65 mm from the accelerating channel edge, which ensured deposition of a shaped high-entropy compound (with the spot diameter of up to 25 mm). Since many high-entropy materials are metastable phases whose synthesis needs both high temperatures (above 3000 K) and high crystallization rates (above 10^7 K/s), the substrate material used in fabricating the carbide-based coatings in question fundamentally affects the rate of heat removal and, as a result, the synthesized item structure and composition. Therefore, to ensure high cooling rates of the deposited coating, copper of high thermal conductivity (395 W/(m·K)) was used as a substrate. In addition, copper does not chemically interact with carbon and does not form with it solutions or directional valence bonds typical for metal carbides;

this allows focusing only on the chemical system including elements of sputtered plasma.

Phase compositions of the synthesized and initial materials were analyzed by X-ray diffractometry (Shimadzu XRD-7000, $CuK_{\alpha 1}$, $\lambda_1 = 1.5406$ Å); diffraction peaks were identified using program code Crystallographica Search-Match and structural database PDF4+. Fig. 1 presents in comparison with the reference patterns the X-ray diffraction pattern of the obtained coating which clearly shows the presence of copper peaks from the metal substrate. In the coating material itself, only the cubic crystalline phase *fcc* with the rock salt (NaCl) structure and space group *Fm3m* (N 225) has been identified. As shown by the positions of intensity maxima, this cubic phase definitely does not correspond to any of the single carbides of metals Ti, Zr, Nb, Hf, Ta, which, jointly with the absence of peaks of unreacted precursors in the material diffraction patterns, indicates formation of a unified high-entropy compound, namely, a carbide including atoms of all the five metals.

The Table presents the calculations of the mean lattice constant a_{av} of the cubic crystalline phase determined by the X-ray maxima positions $2\theta_{hkl}$ with Miller indices (111), (200), (220), (311), (222), (400) and relevant interplanar distance d_{hkl} . A comparison of a_{av} with lattice parameter $a_{veg}(HEC)$ calculated according to the Vegard's rule for a compound with the given stoichiometry at the

equiatomic ratio of metals provides full grounds to believe that plasmadynamic synthesis results in formation of high-entropy carbide TiZrNbHfTaC_5 .

To study the microstructure and properties of the obtained material, the coating specimen section was prepared according to a standard procedure including grinding and polishing. The results of the coating cross-section analysis by scanning electron microscopy (SEM) (Tescan Mira 3LMU with the energy-dispersive X-ray microanalysis system) are shown in Fig. 2. As per the data obtained, thickness of the synthesized product layer reaches $\sim 20\ \mu\text{m}$. The structure of the synthesized material is quite dense and uniform and contains a minimum number of pores and cracks. The estimated value of porosity determined from micrographs is $\sim 7\%$. This result is excellent for the plasma method with high sputtering rate, intense heating and cooling, and with accounting for the significant difference in the linear thermal expansion coefficients of the coating and substrate [9,10]. According to the data of EDS analysis, contrasting light areas along the coating–substrate line correspond to high-atomic-number chemical elements Ti, Zr, Nb, Hf and Ta and confirm the formation of a coating based on a high-entropy material.

To demonstrate physical properties of the obtained material, nanoindentation of the coating layers was performed (Table Top Nanoindentation Tester (TTX-NHT)) by the Vickers method at the load of 5 mN and loading rate of 10 mN/min. The indenter impressions were applied in accordance with procedure ASTM C1327-15 (2019). As a result, mean values of nanohardness and Young's modulus were calculated from the loading-unloading curves (the Oliver–Pharr method): $H_V = 31.9\ \text{GPa}$ and $E = 303.2\ \text{GPa}$, respectively. The obtained hardness exceeds both the theoretical values for high-entropy carbide $H_V = 27\text{--}29\ \text{GPa}$ and

calculations for individual carbides $H_V(\text{TiC}) = 31\text{--}32\ \text{GPa}$, $H_V(\text{ZrC}) = 23\text{--}25\ \text{GPa}$, $H_V(\text{NbC}) = 19\text{--}25\ \text{GPa}$, $H_V(\text{HfC}) = 19\text{--}25\ \text{GPa}$, $H_V(\text{TaC}) = 16\text{--}23\ \text{GPa}$ [11]. The Young's modulus of the coating appeared to be lower than the theoretically calculated values for the compound under consideration ($E = 464\ \text{GPa}$) but significantly higher than the known experimental values for analogs similar in composition ($E = 188\ \text{GPa}$) [11].

Thus, the approach based on the plasmadynamic method allowed us to synthesize for the first time high-entropy carbide TiZrNbHfTaC_5 in the form of a coating on a metal substrate. When a copper plate is subjected to high-speed plasma jet, a carbide cubic phase with space group $Fm\bar{3}m$ free of any impurities gets formed. The coating $\sim 20\ \mu\text{m}$ thick has a fairly dense and uniform structure. This material can exhibit increased values of hardness $H_V = 31.9\ \text{GPa}$ and Young's modulus $E = 303.2\ \text{GPa}$, which evidences for the possibility of using the synthesized product not only for creating heat-resistant products but also for their significant strengthening. Such UHTC materials based on high-entropy carbide are promising for use as hardening, wear-resistant and heat-protective coatings in the aerospace industry.

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Conflict of interests

The authors declare that they have no conflict of interests.

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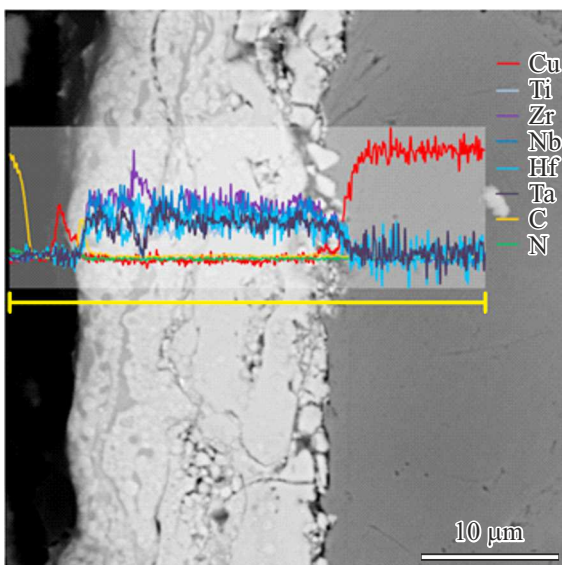


Figure 2. SEM image of the synthesized coating in the BSE mode jointly with results of EDS analysis. The color version of the figure is presented in the electronic version of the article.

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