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Nitride Coatings Based on a High-Entropy Alloy Formed by the Ion-Plasma Method

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Abstract—Nitride coatings based on the high-entropy alloy with the elemental composition of TiNbZrTaHf were formed by deposition onto a solid substrate in vacuum from a multi-component gas-metal plasma created by vacuum arc cathode evaporation with plasma assistance in a mixture of nitrogen and argon. It was shown that the coatings are a single-phase (FCC crystal structure; a = 0.4508 nm) nanocrystalline (2.5–3 nm) material with a hardness of 26 GPa and a Young's modulus of 359.2 GPa.

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INTRODUCTION

In 2004, scientific literature began to appear on the research of a new class of materials called high-entropy alloys (HEAs) [1, 2]. Later (in 2004–2005), thin metallic films as well as hard and superhard nitride coatings based on HEAs were formed [3, 4]. It was noted that the use of films and coatings instead of bulk HEAs significantly reduces the cost of products and expands their range of applications [5]. Formation of films and coatings based on HEAs is most commonly carried out using magnetron [6–8], thermal [9, 10], laser [11, 12], arc [13, 14], and some other methods.

The aim of this study was to analyze the structure and properties of ceramic (nitride) coatings based on high-entropy alloys of the elemental composition (TiNbZrTaHf)N, formed on solid substrates using vacuum arc plasma-assisted deposition methods.

MATERIALS AND METHODS

Thin (up to 3 μm thick) ceramic coatings based on HEAs (TiNbZrTaHf)N were used as the research material. Ceramic coatings were formed on substrates made of technically pure titanium Grade 2, steel 12Cr18Ni10Ti, and hard alloy WC-8%Co. The HEA ceramic coatings were formed using vacuum arc plasma-assisted deposition on the "QUINTA" setup. For this purpose, a multi-element TiNbZrTaHf cathode, close to equiatomic, was used. The coatings were obtained using an electromagnetic filter of the droplet fraction. The following deposition parameters were used: arc discharge current of 75 A, deposition in a mixture of argon and nitrogen at equal ratios and a pressure of 0.3 Pa, bias voltage of –150 V. The coating growth rate was 7.2 μm/h. The elemental and phase composition and defect substructure of the coatings were investigated using scanning electron microscopy (Philips SEM-515 with EDAX ECON IV microanalyzer) and transmission electron diffraction microscopy (JEM-2100F, JEOL). The phase composition and structural parameters of the films were studied using X-ray structural analysis on the XRD-6000 diffractometer with Cu Kα radiation. The analysis of the phase composition was carried out using PDF 4+ databases, as well as the POWDER CELL 2.4 program for full-profile analysis. The microhardness of the HEA films was determined using a PMT-3 device (measurements were carried out using the Vickers method, with a load on the indenter of 0.5 N). The hardness and Young's modulus were determined using the TTX-NHT instrument, with a load on the indenter of 30 mN. Tribological studies of the HEA films were carried out on the Pin on Disc and Oscillating TRIBOtester (TRIBOtechnic, France): a WC-8%Co hard alloy ball with a diameter of 6 mm, a wear track radius of 2 mm, a load on the indenter of 2 N, a track length of 50 m, and a sample rotation speed of 25 mm/s. The degree of material wear was determined based on the results of the profilometry of the formed track obtained during the tests. It should be noted that in recent years, synchrotron and neutron research methods have been successfully used for the analysis of the structure and properties of films and coatings, including those based on HEAs [15–19].

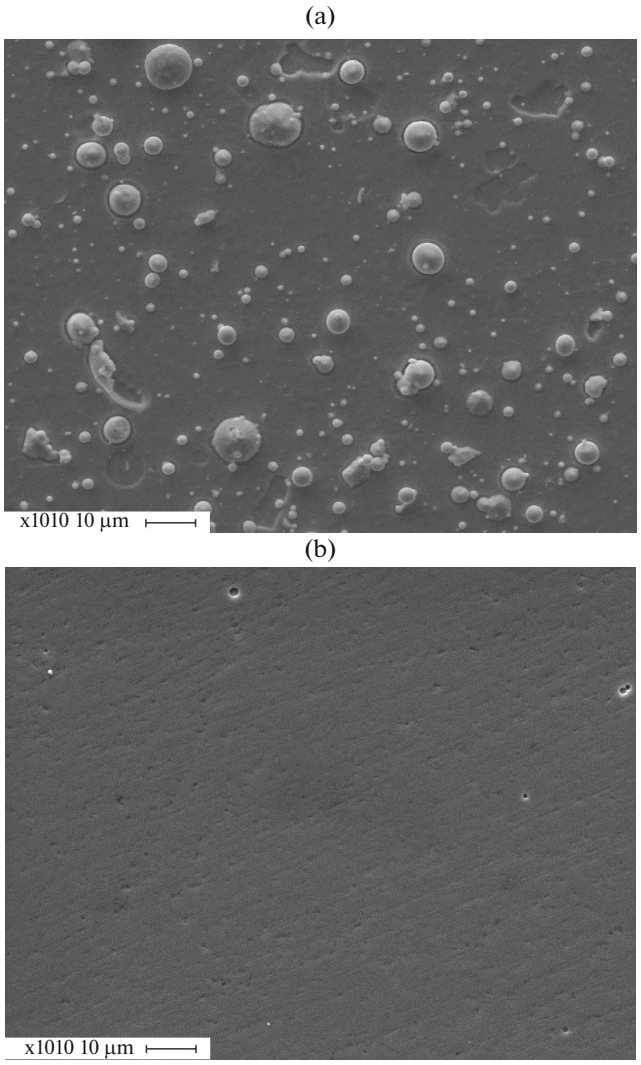

Fig. 1. Electron microscopy image of the structure of a nitride coating obtained without (a) and with (b) an electromagnetic filter for the droplet fraction during deposition.

RESULTS AND DISCUSSION

Using X-ray microanalysis methods, it was determined that the cathode used in this study has the following averaged elemental composition (at %) over five areas of 0.043 mm^2 each: 20.8Ti–19.5Nb–19.1Zr–18.8Ta–21.8Hf. This alloy has a body-centered cubic crystal lattice with a lattice parameter of a = 0.3424 nm. The size of the coherent scattering regions is D = 85 nm; the magnitude of the microstrains of the crystal lattice is $\Delta d/d = 5 \times 10^{-3}$. The microhardness of the TiNbZrTaHf alloy is 3.3 GPa. It should be noted that the microhardness of the initial components of the alloy does not exceed 1.5 GPa [20].

Research on the surface structure of ceramic (nitride) coatings has been carried out. It has been shown that coatings formed without an electromagnetic filter are characterized by the presence of a large number of microdroplets of various sizes (Fig. 1a). This disadvantage of the vacuum-arc deposition method has been noted in many studies [20, 21]. The use of an electromagnetic filter practically eliminates the entry of droplet particles into the forming coating (Fig. 1b).

X-ray microanalysis revealed that the ceramic coating used in this study has the following average elemental composition (at %) over five areas of 0.043 mm^2 each: 5.6Ti–14.1Nb–15.0Zr–8.6Ta–11.7Hf–45.0N, i.e., 55Me–45N.

The nitride coating as determined by X-ray phase analysis, has a face-centered cubic crystal lattice with a lattice parameter of a = 0.4508 nm. The size of coherent scattering regions is D = 75 nm, and the magnitude of microstrain $\Delta d/d = 3.6 \times 10^{-3}$.

The electron microscopy images presented in Fig. 2 indicate that the (TiNbZrTaHf)N nitride coating has a columnar structure.

The dark field analysis revealed that the coating has a nanocrystalline structure with crystal sizes ranging from 2.5 to 3 nm (Figs. 2c, 2d). The crystals form blocks with sizes ranging from 15 to 20 nm. The analysis of the microelectronogram shown in Fig. 2b indicates that it corresponds (in terms of interplanar spacing) to the microelectronogram obtained from a material with a face-centered cubic crystal lattice. This result is in good agreement with the results obtained by X-ray diffraction analysis. It should be noted that in [21], the cluster structure of the HEA coating was revealed by high-resolution electron microscopy. The clusters are characterized by variation in the elemental composition, which allows for the preservation of the material's phase composition with a slight deviation of the lattice parameter in each cluster.

The microhardness (measured at an indenter load of 0.5 N) of the (TiNbZrTaHf)N nitride coating formed on the WC-8%Co hard alloy is 26.0 GPa. The hardness measured at an indenter load of 30 mN is 23.8 GPa, and the Young's modulus (with a Poisson's ratio of 0.25) is 359.2 GPa. It should be noted that the hardness and Young's modulus of the coating depend significantly on the technological factors of the process (such as nitrogen pressure, negative bias voltage, etc.) and can vary widely [21], even with the same elemental composition of the sputtering target.

Tribological tests were conducted, and it was found that the wear parameter (which is inversely proportional to wear resistance) of the (TiNbZrTaHf)N nitride coating is $k = 3.3 \times 10^{-5}$ mm^3 N^{-1} m^{-1}, and the coefficient of friction is $\mu = 0.89$.

CONCLUSIONS

A vacuum arc plasma-assisted method for forming nitride coatings based on a high-entropy alloy from a

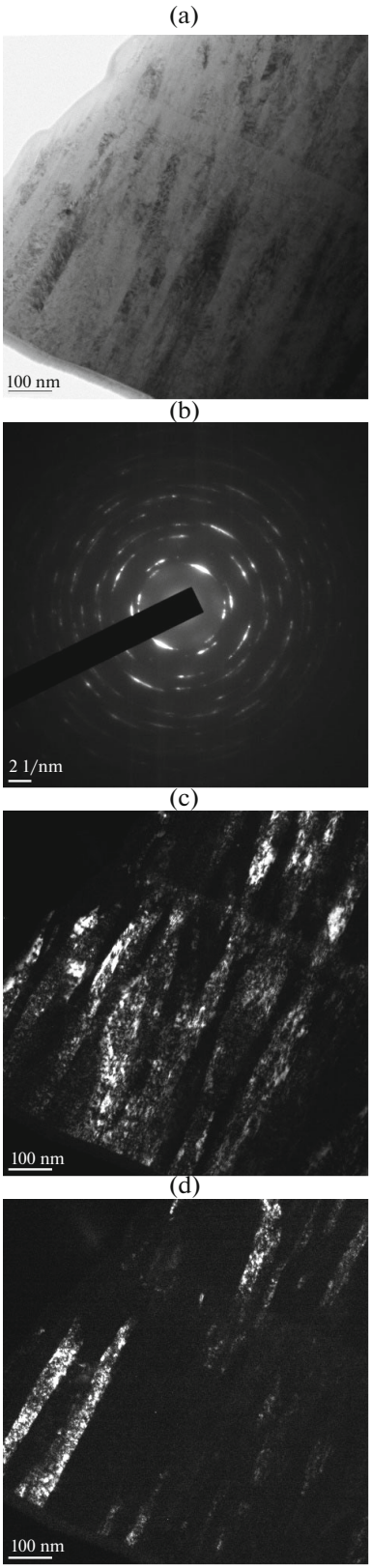

Fig. 2. Electron-microscopic images of the structure of a coating based on the nitride of the HEA of composition (TiNbZrTaHf)N: (a) bright field, (b) microelectronogram, (c, d) dark fields obtained in the [111] reflection. The reflex in which the dark field was obtained is indicated by an arrow in (b).

multi-component gas-metal plasma generated by evaporating a multi-element cathode has been proposed. A mode has been identified that allows for the deposition of thin (a few micrometers) (TiNbZrTaHf)N HEA nitride coatings. It has been found that nitride coatings obtained by evaporating a multi-element cathode are a single-phase nanoscale material with a face-centered cubic crystal lattice with a lattice parameter of $a = 0.4508$ nm and a crystallite size of 2.5–3 nm. The hardness of the nitride coatings is HV = 26 GPa, and the Young's modulus (with a Poisson's ratio of 0.25) is 359.2 GPa. The wear parameter (a value inversely proportional to wear resistance) of the (TiNbZrTaHf)N nitride coating is $k = 3.3 \times 10^{-5}$ $mm^3\ N^{-1}\ m^{-1}$, and the coefficient of friction is $\mu = 0.89$. In the near future, studies of the thermal stability of the formed nitride coatings using synchrotron radiation diffraction methods are planned.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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