DOI 10.1007/s11003-021-00557-8
Materials Science, Vol. 57, No. 3, November, 2021 (Ukrainian Original Vol. 57, No. 3, May–June, 2021)

SPECIFIC FEATURES OF THE STRUCTURE AND ELECTROPHYSICAL CHARACTERISTICS OF NITRIDE COATINGS BASED ON Ti–V–Zr–Nb–Hf HIGH-ENTROPY ALLOY

V. F. Horban,[1] **I. V. Serdiuk,**[2] **O. M. Chuhai,**[3] **O. O. Voloshyn,**[3]
S. V. Oliinyk,[3] **H. H. Veselivska,**[4,5] **M. I. Danylenko,**[1]
D. V. Sliusar,[3] **V. A. Stolbovyi,**[2] **and O. S. Kalahan**[6]

UDC 539.21: 621.793

The composition, morphology, and electrophysical properties of vacuum-arc nitride coatings based on a high-entropy Ti–V–Zr–Nb–Hf alloy are investigated. Significant changes in the chemical composition of the high-entropy alloy along the samples are established. At the same time, for the studied regions, the deviations of the averaged atomic radii of elements do not exceed 1.5%. It is shown that the surface morphology of samples is characterized by three types of inclusions with different chemical compositions, sizes, and shapes. Some of these inclusions are drops typical of the vacuum arc method of deposition of the coatings and the remaining inclusions are cleavages. It is shown that the distributions of the AC resistance and quality factor along the sample are characterized by the presence of bursts. We also establish the relationship between the surface morphology and the presence of oxide layers on the surface.

Keywords: vacuum-arc nitride coatings, high-entropy alloy, electric AC resistance, quality factor, surface morphology, oxide layers.

Introduction

In contemporary mechanical engineering, high requirements are imposed on the physical and technical characteristics of machine parts. This primarily applies to the surface properties of cutting tools operating under extreme conditions. As a possibility of increasing the strength and wear and corrosion resistances of the tools, we can mention the application of coatings made of high-entropy alloys (HEA) [1]. In [2, 3], it was shown that the application of nitride coatings based on high-entropy Ti–V–Zr–Nb–Hf alloys and deposited by the vacuum-arc method is a promising method of hardening of the tools. An important condition for getting the best possible engineering characteristics of these coatings is the uniformity of their physical properties. To monitor the uniformity of mechanical properties of the coatings with high degree of localization, it is customary to use the microhardness method. However, the application of this method requires significant amounts of time to analyze

---

[1] I. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Kyiv, Ukraine.

[2] "Kharkiv Institute of Physics and Technology," National Science Center, National Academy of Sciences of Ukraine, Kharkiv, Ukraine.

[3] "M. Zhukovsky Kharkiv Aviation Institute," National Aerospace University, Kharkiv, Ukraine.

[4] Karpenko Physicomechanical Institute, National Academy of Sciences of Ukraine, Lviv, Ukraine.

[5] Corresponding author; e-mail: fminanu1978@gmail.com.

[6] Lviv National Agrarian University, Lviv, Ukraine.

Translated from Fizyko-Khimichna Mekhanika Materialiv, Vol. 57, No. 3, pp. 132–136, May–June, 2021. Original article submitted December 29, 2020.

1068-820X/21/5703–0428

the heterogeneity of properties in the entire sample. In [4], the authors of the cited work proposed a method for detection of inhomogeneities in the properties of coatings by analyzing the electrophysical characteristics of a specimen in the form of a rectangular plate. In the present work, we apply this method to study the heterogeneous chemical compositions and structures of nitride coatings based on the high-entropy Ti–V–Zr–Nb–Hf alloy.

Materials and Methods

The specimens were investigated by using a "Bulat-6" modified vacuum-arc installation. A cathode for the deposition of vacuum-arc coatings was made of the following alloy (wt.%): 25 Ti; 25 Zr; 25 Nb; 15 Hf, and 10 V, obtained by the method of vacuum-arc melting in an atmosphere of high-purity argon [2]. After the evacuation of a vacuum chamber down to a pressure of 0.001 Pa, the surface of substrate was cleaned and activated for 5 min by applying the procedure of bombardment with metal ions of the evaporated alloy. After this, the coating was deposited under the conditions of a constant negative potential of 50–200 V formed on the substrates for an arc current of 85 A under a nitrogen pressure varying within the range 0.05–0.66 Pa. The specimens had the form of rectangular plates $12 \times 4 \times 2$ mm in size.

The hardness of materials and coatings was investigated by using a "Micron-Gamma" installation at room temperature (under a load $P = 0.5$ N) with the help of a Berkovich diamond pyramid ($\alpha = 65°$). The accuracy of the applied load P was 10^{-3} N and the depth of indentation h of the indenter was 2.5 nm. The level of hardness (H_{IT}) and the modulus of elasticity (E_r) were measured according to ISO 14577-2002. The data spread was equal to $\pm 2\%$ for hardness and — $\pm 5\%$ for modulus of elasticity. We also used the characteristic of normalized hardness (H_{IT}/E_r), which is sensitive to the structural state of the material as indicated in [5].

The composition and surface morphology of the specimens was studied by using an REM-106 scanning electron microscope. The local chemical composition of the specimens was analyzed with the help of a JEM-2100F microscope for an electron probe with a diameter of 0.5 nm. The inhomogeneity of electric resistance of specimens to alternating current was investigated in the direction perpendicular to their surface by using a well-known procedure [4]. The quality factor or the loss-angle tangent of dielectric was measured parallel with the capacitance of the studied object depending on the ratio of the active and reactive components of electric resistance.

Results and Discussion

The investigated alloy is a solid solution based on the BCC lattice, which has high hardness even in the cast state (Table 1). For the metal coating, its phase composition remains constant but we observe a certain decrease in the lattice parameter. The reduced lattice parameter and the nanostructured state of these coatings guarantee their hardness higher than 8 GPa. The H_{IT}/E_r ratio for the cast state exceeds 0.04, which corresponds to the nanostructured state for metals. The abnormally high hardening typical of the as-cast HE is explained by their cluster structure [3]. For the nitride coatings based on high-entropy Ti–V–Zr–Nb–Hf alloys, we record high values of hardness (up to 60 GPa). The spread of these values in all analyzed states does not exceed admissible values, which reveals fairly homogeneous hardness parameters of the coatings.

As an important specific feature of the HEA, we can mention the impossibility to preserve homogeneous chemical composition in the cross section of the specimen. Moreover, the presence of atoms with different radii in the lattice leads to the appearance of distortions in different planes.

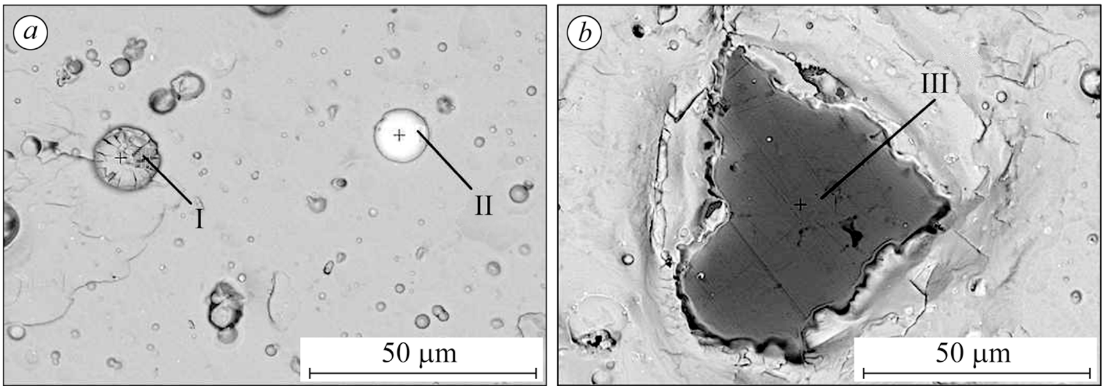

Fig. 1. Micrographs of inclusions from groups I and II (a) and from group III (b).

Table 1
Characteristics of the High-Entropy Ti–V–Zr–Nb–Hf Alloy Depending on the State

State	Lattice type	Lattice parameter, nm	H_{IT}, GPa	E_r, GPa	H_{IT}/E_r
Initial	BCC	0.3389	4.2 ± 0.2	90 ± 3	0.047
Metal coating	BCC	0.3264	8.1 ± 0.3	106 ± 5	0.077
Nitride coating	FCC	0.4462	56.0 ± 3.5	405 ± 20	0.138

As a result, in order to preserve the value of the lattice parameter, it is necessary to modify the chemical composition of the HEA. This agrees with the results of investigations of the chemical composition of Ti–V–Zr–Nb–Hf–Ta alloy [3]. In the cited work, the researchers revealed significant fluctuations that should be reflected in local distortions of the crystal lattice affecting the physicomechanical properties of the metal and, hence, of coatings made of this metal.

The analysis of the structures of nitride coatings shows that they contain three groups of inclusions with different composition, shapes, and sizes. The largest group (I) contains regularly shaped inclusions with sizes varying from one micrometer to tens of micrometers (Fig. 1a). The chemical composition of these particles undergoes insignificant variations as compared with the matrix (up to 5%), with the exception of Ti (7.9%) and V (25.5%) (Table 2). Inclusions from group II (Fig. 1a) are encountered much less frequently. For these inclusions, the deviations of the concentrations of chemical elements from their concentrations in the matrix are much more pronounced as compared with group I. These inclusions are also of regular shape and their sizes vary within the range 5–30 μm. Note that the images of these inclusions in reflected electrons differ by their contrast from the images of the largest group.

A separate group (III) is formed by inclusions with Fe, Cr and Ni predominant in their chemical compositions. They have irregular shapes and have a maximum size of 50–100 μm (Fig. 1b). The inclusions from groups I and II are drops, which is a specific feature of the vacuum-arc method of coating deposition. At the same time, inclusions from group III are cleavages on the surface of the substrate formed under the action of high internal microstresses.

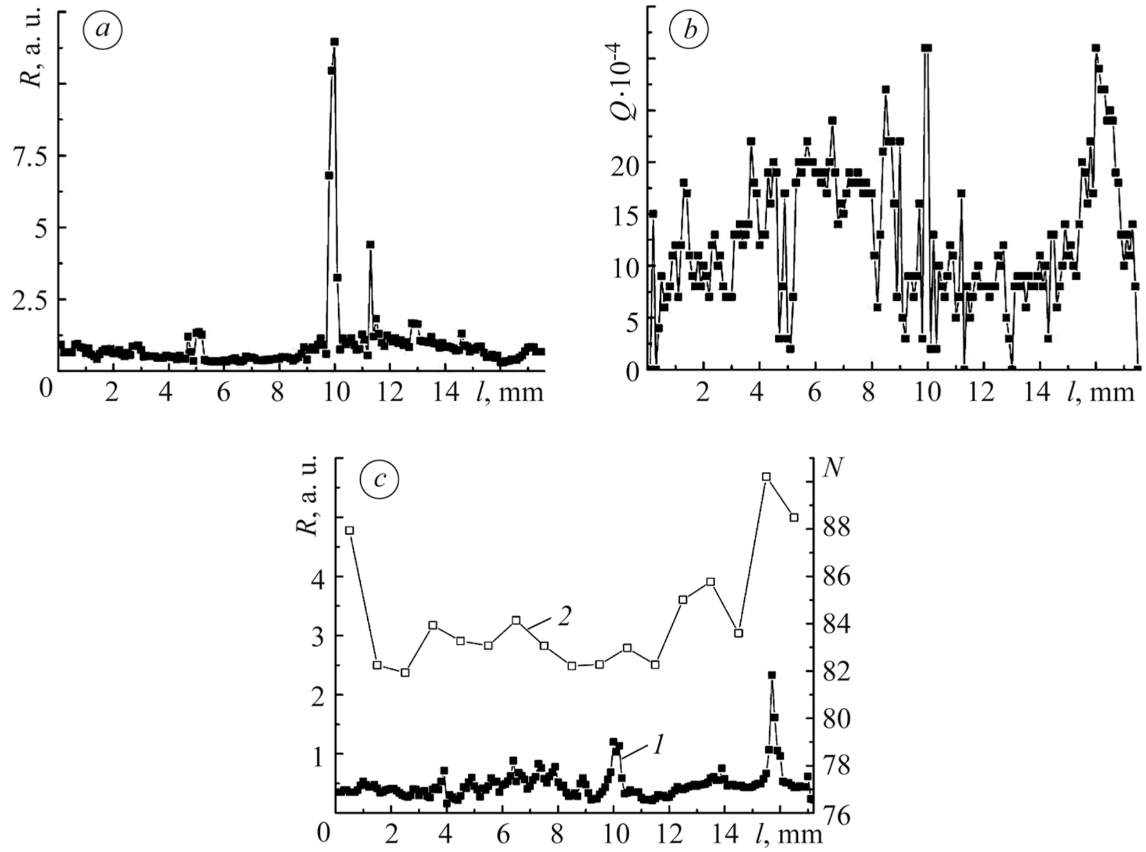

Fig. 2. Changes in electric resistance [(a) and (c) curve 1], quality factor (b), and the number of inclusions [(c) curve 2] along the specimen.

Table 2
Chemical Compositions of the Matrix and Inclusions

Content, at.%		Zr	Hf	You	Nb	V	Fe	Cr	Ni
Matrix		33.5	31.9	17.7	11.4	5.5	–	–	–
Inclusion	I	35.0	32.9	16.3	11.7	4.1	–	–	–
	II	44.2	35.9	0.10	19.6	0.20	–	–	–
	III	3.1	1.9	1.5	1.9	0.90	66.5	18.1	6.1

In Fig. 2, we show the dependences of the AC resistance R (Fig. 2a) and quality factor Q (Fig. 2b) on the displacements of the electrode along the object typical of the analyzed specimens. It is easy to see that the Q-bursts observed within linear zones with lengths of 0.2–0.5 μm are quite frequent unlike the behavior of electric resistance.

To establish the relationship between the functions $R(l)$ and $Q(l)$ and the above-mentioned types of inclusions, we used the procedure of automatic counting for the number of inclusions N in a domain $10 \times 40\ \mu\text{m}^2$

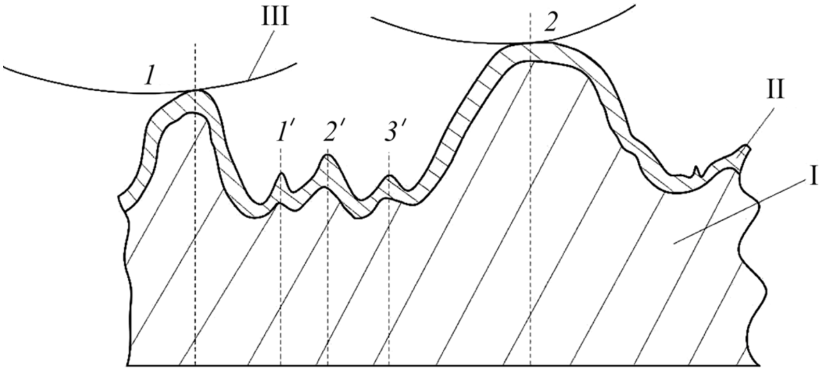

Fig. 3. Schematic representation of the electric contact in the course of motion of the electrode along the specimen: (I) HEA; (II) oxide; (III) moving electrode.

in size. To this end, we used the Image J computer program [6]. It was discovered that N correlates with the electric resistance of the specimen (Fig. 2 c).

To explain these relations, it is necessary to take into account two factors, namely, the morphology of the surface and the presence of oxide layers (in fact, insulating) on this surface. Despite their small thicknesses (up to 1 μm [7]), these layers determine the electric resistance of the entire electrode–sample electric system because typical resistances of various high-entropy alloys do not exceed several hundreds of $\mu\Omega \cdot \text{cm}$ [8].

In the course of motion of an electrode along the specimen, the electric contact between them is realized only in the zones of the highest asperities on the surface (Fig. 3, points 1, 2). Thus, the function $R(l)$ reflects the sequence of such contacts.

Another role is played by relatively low asperities separated from the moving electrode by an air layer. These asperities form electric capacitance C together with the surface of moving electrode. Therefore, the process of motion of the electrode from point 1′ to points 2′ and 3′ on the specimen (Fig. 3) affects mainly the electric capacitance but not the electric resistance of the system. This explains the above-mentioned frequent bursts in the function $Q(l)$.

CONCLUSIONS

The investigated vacuum-arc nitride coatings based on high-entropy Ti–V–Zr–Nb–Hf alloy are characterized by a complex surface morphology, which contains inclusions with different compositions, sizes, and shapes. The investigations of these materials in alternating electric fields performed with the use of systems with flat and moving cylindrical electrodes reveal the presence of regions with sharp changes in the electric resistance and quality factor of the specimens. Moreover, the latter occur much more frequently. This feature of the electric properties is explained by significant difference between the local chemical composition of the material and complex morphology of the surface coatings. This requires additional improvements in the technology of deposition of these coatings with an aim to minimize local heterogeneities of their structure and properties.

REFERENCES

1. S. A. Firstov, A. A. Andreev, V. Gorban’, N. I. Danilenko, N. A. Krapivko, and V. A. Stolbovoy, “New class of superhard nitride coatings based on multicomponent high-entropy alloys,” in: *Proc. Internat. Conf. “Nanotechnologies of Functional Materials,” St. Petersburg, June 27–29 (2012),* pp. 572–577.

2. O. V. Sobol', A. A. Andreev, V. Gorban', N. A. Krapivko, V. A. Stolbovoy, I. V. Serdyuk, and V. E. Filchikov, "On the reproducibility of a single-phase structural state of a multielement Ti–V–Zr–Nb–Hf high-entropy system and high-hardness nitrides based on this system in the course of their formation by the vacuum-arc method," *Lett. ZhTF,* **38**, Issue 13, 40–46 (2012).
3. S. A. Firstov, V. F. Gorban', N. I. Danilenko, M. V. Karpets A. A. Andreev, and E. S. Makarenko, "Thermal stability of superhard nitride coatings based on multicomponent high-entropy alloy of the Ti–V–Zr–Nb–Hf system," *Poroshk. Metallurg.,* No. 9/10, 93–102 (2013).
4. O. N. Chugai, S. L. Abashin, A. V. Gaidachuk, D. P. Zherebyat'ev, E. A. Zhuk, A. A. Poluboyarov, S. V. Sulima, I. S. Terzin, and Yu. A. Yatsyna, "Compositional and dielectric inhomogeneities in melt-grown CdZnTe crystals," *Neorgan. Mater.,* **51**, No. 10, 1054–1059 (2015).
5. V. F. Gorban' and E. P. Pechkovskii, "Relationship between the elasticity parameters obtained by the method of instrumental indentation and the structural state of the material," *Poroshk. Metallurg.,* No. 7/8, 54–62 (2010).
6. T. J. Collins, "Image for microscopy," *Biotechniques,* **43**, No. 1, 25–30 (2007).
7. N. P. Zhuk, *A Course in Theory of Corrosion and Protection of Metals* [in Russian], Metallurgiya, Moscow (1976).
8. M.-H. Tsai, "Physical properties of high entropy alloys," *Entropy,* No. 15, 5338–5346 (2013).