Structure and Properties of Cermet Coatings Produced by Vacuum-Arc Evaporation of a High-Entropy Alloy

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Abstract: Multilayer cermet coatings based on a TiNbZrTaHf high-entropy alloy were produced on solid substrates by plasma-assisted vacuum-arc deposition. The assisting multicomponent metal-gas plasma was generated by evaporating TiNbZrTaHf cathodes in a gas mixture of nitrogen and argon. It was found that the coatings were nanocrystalline in structure (with nanocrystal sizes ranging from 2.5 to 4 nm). The metallic layer had a body-centered cubic lattice (a = 0.33396 nm), and the ceramic layer had a face-centered cubic lattice (a = 0.44465 nm). Transition layers formed between the substrate and the metallic layer and between the metallic and the ceramic layers were revealed. The hardness of the coatings was 36.7 GPa and their Young’s modulus was 323 GPa.

Keywords: high-entropy alloy; cermet coating; vacuum-arc evaporation; nanocrystalline structure; hardness; wear resistance

1. Introduction

High-entropy alloys (HEAs) are multielement alloys composed of at least five elements, the content of each being no more than 35%. They are equiatomic single-phase thermodynamically stable substitutional solid solutions having predominantly a body-centered cubic (bcc) or a face-centered cubic (fcc) structure. The possibility of producing HEAs was first demonstrated by [1,2]. A five-component Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20} alloy [1], later called the Cantor alloy, was produced by casting and melt spinning. This alloy was a single-phase system with an fcc lattice and a dendritic structure. This approach to designing alloys was suggested as a promising line in materials science and engineering [2]. Somewhat later, the authors of [3,4] reported on the possibility of creating ceramic materials based on HEAs. HEA-based nitride films were produced by ion-assisted DC magnetron sputtering [3]. The sputtering targets were made of Co-Ni-Cr-Cu-Al-Mn and Co-Ni-Cr-Cu-Al_{0.5} HEAs. It was found that the metallic films produced were close in atomic composition to the targets. They had a multiphase structure represented by grains with fcc and bcc lattices or by solid solution grains with an fcc lattice. When the sputtering targets were made of Co-Ni-Cr-Cu-Al-Mn and Co-Ni-Cr-Cu-Al_{0.5} alloys [4], it was observed that as the nitrogen content increased, the size of crystallites (grains) in the nitride films decreased, and the material became more amorphous. The hardness of the films reached 11 GPa.

It was found that nitride coatings based on HEAs, like nitride coatings based on transition metals, had a single-phase nanoscale structure with an fcc lattice [5–8]. The nitride films were produced by reactive RF magnetron sputtering of AlCrTaTiZr HEA targets [5,6]. It was found that they had a crystalline structure with an fcc lattice, while the AlCrTaTiZr metallic films had an amorphous structure. Nitride films with an fcc lattice, the maximum hardness of which was 30 GPa, were also produced by reactive RF magnetron sputtering of AlCrNbSiTiV HEA targets [7]. The authors of [8] report on the preparation of
nitride films with an fcc lattice on (AlMoNbSiTaTiVZr)Nx films having a more complicated composition. Less often, HEA-based nitride coatings were two-phase coatings. Thus, it was shown that AlCrTiZrNbY HEA coatings produced by vacuum-arc deposition consisted of two nanocrystalline phases [9]. One phase had a bcc lattice with an average crystallite size of 15 nm and a lattice period of 0.342 nm, and the other had an fcc lattice with an average crystallite size of 7 nm and a lattice period of 0.437 nm.

Ceramic materials based on HEAs are sometimes considered a separate family of HEAs [10]. However, as noted in [11], these materials are not metal alloys but metal-like compounds in which metallic bonds between metal atoms coexist with ion-covalent bonds between metal and nonmetal atoms. It was found that HEAs and HEA-based ceramic materials have a number of remarkable properties (high corrosion resistance [12,13], excellent mechanical characteristics at high [14] and low temperatures [15,16], high wear resistance [17,18], high strength and plasticity [19,20], high hardness [5,7,8], etc.). It is expected that in the near future the following areas of application of HEAs and ceramic materials based on them may become promising [21–23]. Since HEAs are as light as aluminum alloys and stronger than some metallic glasses, they can be used in transport, aerospace, and power generation industries, where lightweight high-strength materials are in great demand. The HEAs containing refractory elements, such as Nb, Mo, Ta, and Hf, retain high strength at temperatures above 1450 K, outperforming traditional nickel-based superalloys such as Inconel 718 and Haynes 230. They are possible candidates for use as high-temperature materials in gas turbines, rocket nozzles, and components of nuclear reactors. In the aerospace industry, where lightweight materials resistant to high temperatures are in demand, low-density refractory HEAs can be used widely. The high cryogenic properties of HEAs make them excellent materials for cryogenic applications, such as rocket casings and pipelines for transporting and storing liquid oxygen or nitrogen. A surfacing technology holds promise in which HEAs are applied on tools and machine parts by plasma-arc or thermal spraying of HEA rods or powders. It can be expected that HEAs will be used to suppress electromagnetic interferences, especially in electronics. HEAs, as well as HEA-based nitrides, can be used as radiation-resistant coatings on the shells of fuel elements in nuclear reactors, which expands the scope of their high-tech applications.

In most cases, ceramic materials, including those based on HEAs, are used for various types of coatings. Among many types of coatings, multilayer coatings consisting of a combination of layers with different elemental compositions and, therefore, having different physical and chemical properties depending on the thickness and composition of each layer are of chief interest [24–27].

The authors of [24] investigated the mechanism of cracking in SZR-ZrN-(ZrCrAl)N, Cr-CrN-(TiCrAl)N, and Zr-ZrN-(ZrNbTiAl) multilayer composite nanostructured coatings, deposited using technologies of filtered cathodic vacuum-arc deposition, and in Ti-TiAlN-TiAIN coatings, deposited using side rotating cathodes. Typical cracking mechanisms were identified and their influence on the wear kinetics of coated hard-alloy tools was investigated. It was found that all test coatings increased the service life of carbide tools by a factor of three to four in comparison with uncoated tools. Single-layer and multilayer PVD coatings based on Cr and Ti, which are widely used in the tool industry, and coatings based on W and WN, which are not so widespread, were studied by the authors of [25]. They observed that the presence of a metallic interlayer in the test materials additionally improved the adhesion of the coatings because they gradually approached in composition to the substrates. Reviews [26,27] systematically consider the design concept and properties of various types of multilayer coatings, including transition-metal nitride coatings, DLC coatings, and other multilayer coatings. It is shown that the multilayer coatings consisting of a combination of several materials give developers an additional chance to optimize coating properties.

Multilayer coatings with alternating metallic and ceramic layers (La2O3-ZrO2-CeO2, ZrB2-ZrC-SiC, ZrB2 and HfB2, ZrB2-SiC) [28–32] are of much practical interest. Coatings of this type have higher rigidity compared to metals and higher fracture toughness compared
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to single-phase ceramics [33–36]. It was demonstrated [33,34] that the volume fraction of the metallic phase and the size of metal particles of the Al2O3-Ni/Al2O3-Cu-Ni cermet composite can be controlled by varying its hardness and fracture toughness. The authors of [36] studied laminated ZrB2-MoS2SiB2 ceramics with an intermediate Mo-MoS2SiB2 layer. They observed that the fracture toughness and bending strength of the ceramics showed a tendency first to increase and then to decrease with an increase in the ratio of layer thicknesses. High values of fracture toughness (9.89 ± 0.26 MPa m1/2) and bending strength (431.6 ± 15.1 MPa) were obtained for the layer thicknesses ratio equal to 13.

Vacuum-arc coating deposition techniques provide high productivity, and the produced coatings show high density and high adhesive strength to metal and cermet substrates [37]. Therefore, they are considered a promising way of fabricating metallic and cermet coatings.

The study presented in this paper was aimed to analyze the structure and properties of two-layer HEA-based (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coatings produced on solid substrates by plasma-assisted vacuum-arc deposition.

2. Materials and Methods

The HEA-based (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coatings used in the experiment were produced on solid substrates by plasma-assisted vacuum-arc deposition in the QUINTA facility [38]. For this purpose, a sintered multielement cathode of near-equiatomic TiNbZrTaHf composition was used. The experimental arrangement is shown schematically in Figure 1.

![Figure 1. Experimental arrangement for coating deposition using a multielement cathode.](image)

The samples were cleaned with alcohol in an ultrasonic bath, fixed on the substrate holder, and placed in the vacuum chamber opposite the arc evaporator at a distance of 16 cm. With the samples, the vacuum chamber was evacuated with a turbomolecular pump to a limiting pressure of 5 × 10⁻³ Pa. Thereafter, argon was supplied into the chamber until its pressure reached 0.3 Pa, the PINK-P generator, having an exit aperture of 40 mm × 400 mm, was turned on, and the surfaces of the samples were cleaned with argon plasma using plasma-ion etching for 20 min. In this case, the discharge current of the PINK-P generator was 50 A and the repetitively pulsed bias voltage was −900 V with 50% pulse duty cycle. The temperature of the samples during surface cleaning reached 350 °C in 20 min. After cleaning, the arc evaporator (75 A discharge current), comprising a multielement composite cathode, was switched on, and the substrate surface was bombarded with high-energy metal ions at a constant bias voltage (−900 V) for 2 min. Thereafter, the bias voltage was reduced to −35 V, the pulse duty cycle was increased to 85%, and a HEA metal layer was deposited on the substrate. When a HEA ceramic layer was deposited, the bias voltage...
was increased to $-150$ V with the same pulse duty factor (85%). Depending on the type of supplied gas, either HEA metallic or HEA ceramic layers were produced. In the first case, only argon was supplied into the working chamber, while in the second case, nitrogen and argon in equal proportions were used. To produce a cermet coating, layer-by-layer deposition of metallic and ceramic films was performed. In our experiment, the metallic layer thickness was $\approx 1$ µm and the ceramic layer thickness was $\approx 3$ µm. After the deposition was completed, the samples were rest to cool in the vacuum chamber to a temperature below 100 °C and removed for examination.

To examine the elemental and phase composition of the coatings and the state of their defective substructure, a scanning electron microscope (Philips SEM-515 with an EDAX ECON IV microanalyzer) (Philips, Amsterdam, The Netherlands) and a transmission electron diffraction microscope (JEOL JEM-2100F) (Akishima, Tokyo, Japan) were used. The phase composition and structural parameters of the coatings were investigated by the method of X-ray diffraction analysis using an XRD-6000 diffractometer (Shimadzu, Kyoto, Japan) with CuKα radiation. Scanning was carried out at a voltage of 40.0 kV, current of 30.0 mA, scan range of 10.0–80.0 deg, scan speed of 2.0 deg/min, sampling pitch of 0.0200 deg, and preset time of 1.00 s. To analyze the phase composition, the PDF 4+ databases and the POWDER CELL 2.4 full-profile analysis code were invoked. The hardness of the HEA films was measured using a PMT-3 (LOMO, Saint Petersburg, Russia) instrument equipped with a Vickers indenter (the load on the indenter was 0.5 N). The physical and mechanical properties of the coatings were investigated using a TTX-NHT nanohardness tester (CSM Instruments, Peuseux, Switzerland). Indentations were made with an acquisition rate of 20.0 Hz using a linear loading to a maximum load of 30.0 mN at a loading/unloading rate of 60.00 mN/min; the time interval between successive loading/unloading cycles was 5.0 s. The indentation depth was less than 10% of the total coating thickness to rule out the substrate effect [39]. The measurement data were analyzed by the Oliver–Pharr method. Tribological investigations of the HEA films were carried out using an oscillating pin-on-disk tribometer (TRIBOtechnic, Clichy, France) with a WC–8 wt.% Co hard alloy ball 6 mm in diameter. The wear track radius was 2 mm, the indenter load was 2 N, the track length was 50 m, and the sample rotation speed was 25 mm/s. The degree of wear of the material was evaluated from the results of wear track profilometry. The wear rate ($V$) was calculated based on the load ($F$), the distance covered ($L$), the cross-sectional area of the wear track ($A$), and the wear track radius ($R$) using a well-known formula:

$$V = \frac{2 \cdot \pi \cdot R \cdot A}{F \cdot L}, \quad \text{[mm}^3/\text{N} \cdot \text{m]}$$  \hspace{1cm} (1)

The substrate material was made of a WC–8%Co hard alloy, selected to study physical, mechanical and tribological properties, elemental and phase analysis, and AISI 304 non-magnetic stainless steel [(up to 0.08)C; (17.5–20)Cr; (up to) 2%Mn; (8–11)Ni; (up to 0.045)P; (up to 0.03)S; (up to 1)Cu; (up to 0.8)Si; the rest Fe, wt.%] for transmission electron microscopy (TEM) analysis.

3. Results

X-ray microanalysis of one of the samples has shown that the cermet film had the following elemental composition (at.%), averaged over five sections of area 0.043 mm$^2$ each: 4.8Ti-16.7Nb-16.7Zr-9.8Ta-13.9Hf-38.1N, i.e., the metal/nitrogen ratio was 62/38. Figure 2 and Table 1 show the characteristic energy spectra and the results of a quantitative analysis of the elemental composition of one of the analyzed sections of the film.
Table 1. Quantitative results of the elemental analysis of the sample.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
<th>at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>06.45</td>
<td>37.13</td>
</tr>
<tr>
<td>Ti</td>
<td>03.11</td>
<td>05.23</td>
</tr>
<tr>
<td>Hf</td>
<td>29.38</td>
<td>13.27</td>
</tr>
<tr>
<td>Ta</td>
<td>21.15</td>
<td>09.42</td>
</tr>
<tr>
<td>Zr</td>
<td>20.15</td>
<td>17.81</td>
</tr>
<tr>
<td>Nb</td>
<td>19.76</td>
<td>17.14</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis has shown that the HEA cermet film was a multiphase system, the main phases of which were \((\text{TiNbZrTaHf})\text{N}\) and \(\text{Ta}_4\text{N}\) nitrides and a \(\text{TiNbZrTaHf}\) alloy (Figure 3). The lattice parameters and the relative content of these phases are given in Table 2.

Table 2.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Volume Fraction, vol.%</th>
<th>Lattice Parameters, Å</th>
<th>CSR Width, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{TiNbZrTaHf})\text{N})</td>
<td>45</td>
<td>2.5 × 10^{-3}</td>
<td>5 × 10^{-3}</td>
</tr>
<tr>
<td>(\text{TiNbZrTaHf})</td>
<td>29</td>
<td>4.4465</td>
<td>8 nm</td>
</tr>
<tr>
<td>(\text{Ta}_4\text{N})</td>
<td>26</td>
<td>4.1697</td>
<td>3.6 × 10^{-3}</td>
</tr>
</tbody>
</table>

Figure 2. Energy spectra of a section of a \((\text{TiNbZrTaHf}) + (\text{TiNbZrTaHf})\text{N}\) cermet sample obtained by X-ray microanalysis of its elemental composition.

Figure 3. Fragment of the X-ray diffraction pattern of a HEA cermet film produced by evaporating a \(\text{TiNbZrTaHf}\) cathode.
Table 2. Results of X-ray phase analysis of a HEA cermet film produced by evaporating a TiNbZr-TaHf cathode.

<table>
<thead>
<tr>
<th>Detected Phases</th>
<th>Volume Fraction, vol.%</th>
<th>Lattice Parameters, Å</th>
<th>CSR Width D, nm</th>
<th>Crystal Lattice Distortion $\Delta d/d \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TiNbZrTaHf)N</td>
<td>45</td>
<td>$a = 4.4465$</td>
<td>22</td>
<td>7</td>
</tr>
<tr>
<td>Ta$_4$N</td>
<td>26</td>
<td>$a = 6.8272$</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>TiNbZrTaHf</td>
<td>29</td>
<td>$a = 3.3396$</td>
<td>8</td>
<td>5</td>
</tr>
</tbody>
</table>

The data presented in Table 2 indicate that the total content ratio of the nitride phases to the metallic phase was 2.5:1, which correlates well with the thicknesses of the deposited nitride and metallic layers. The (TiNbZrTaHf)N nitride had an fcc lattice with $a = 4.4465$ Å ($D = 22$ nm; $\Delta d/d = 7 \times 10^{-3}$). Preliminary investigations have shown that the separately deposited HEA ceramic film had an fcc lattice with $a = 4.5084$ Å, a width of coherent scattering regions $D = 75$ nm, and a relative lattice distortion $\Delta d/d = 3.6 \times 10^{-3}$. Comparing these data, it can be noted that the ceramic film formed in the cermet system had a smaller (by 0.0619 Å) value of the lattice parameter and smaller (by a factor of 3.4) widths of coherent scattering regions (CSR width) at somewhat larger (by a factor of 1.9) values of the relative lattice distortions in comparison with the single-layer ceramic film. The Ta$_4$N nitride had a tetragonal lattice with $a = 6.8272$ Å and $c = 4.1697$ Å.

The TiNbZrTaHf metallic phase had a bcc lattice with $a = 3.3396$ Å ($D = 8$ nm; $\Delta d/d = 5 \times 10^{-3}$). Preliminary investigations have shown that the sputtered TiNbZrTaHf cathode had a bcc lattice with $a = 3.4278$ Å ($D = 85$ nm; $\Delta d/d = 5 \times 10^{-3}$). Comparing these data, it can be noted that the metallic layer of the cermet coating had a smaller lattice parameter and smaller CSR widths in comparison with the cathode alloy with the same relative lattice distortion. The data obtained by X-ray diffraction analysis obviously indicate the occurrence of elastic stresses in the cermet coating, which was due to the differences in lattice types and parameters between the ceramic and the metallic film. As will be shown below, the stresses partially relaxed due to the transition sublayer formed at the interface between the metallic and the ceramic layer.

The electron microscopic images given in Figure 4a indicate that the (TiNbZrTaHf) + (TiNbZrTaHf)N cermet film was a multilayer system consisting of two main layers (layers 2 and 4) and two transition layers, significantly smaller in thickness (layers 1 and 3). Layers 2 and 4 had a columnar structure (Figure 4b). Analysis of the microelectron diffraction patterns taken from these layers (the sections from which the microelectron diffraction patterns were taken are circled) indicates that layer 2 had a bcc lattice (Figure 4c) and was obviously a metallic layer; layer 4 had an fcc lattice (Figure 4d) and was a ceramic layer. Dark-field analysis has shown that layers 2 and 4 had a nanocrystalline structure with a crystallite size varying between 2.5 and 4 nm, regardless of whether the layer was metallic or ceramic (Figure 4e,f).

Layer 1, which separates the metallic coating from the substrate, had a thickness of 100–110 nm (Figure 5a,b) and consisted of three sublayers (Figure 5c): sublayer 1.1, adjacent to the substrate, was amorphous in structure; sublayer 1.2 consisted of rounded crystallites 2.5–5 nm in size (Figure 5e), and sublayer 1.3, adjacent to the HEA metallic film, was columnar in structure (see Figure 5e). Nanoscale size of the crystallites is evident from the ring structure of the electron diffraction patterns (Figure 5d).
Layers 2 and 4 had a columnar structure (Figure 4b). Analysis of the microelectron diffraction patterns taken from these layers (the sections from which the microelectron diffraction patterns were taken are circled) indicates that layer 2 had a bcc lattice (Figure 4c) and was obviously a metallic layer; layer 4 had an fcc lattice (Figure 4d) and was a ceramic layer. Dark-field analysis has shown that layers 2 and 4 had a nanocrystalline structure with a crystallite size varying between 2.5 and 4 nm, regardless of whether the layer was metallic or ceramic (Figure 4e,f).

Figure 4. Electron microscopic images showing the structure of (a) (TiNbZrTaHf + (TiNbZrTaHf)N) cermet film: (a,b)—light-field images; (c,d)—microelectron diffraction patterns for (b); (e,f)—dark-field images taken from the [112] (e) and the [022] reflex (f). The reflexes from which the dark-field images were taken are indicated by arrows in (e,f). The foil sections from which microelectron diffraction patterns (c,d) were taken are circled in (b). Substrate: AISI-304 stainless steel.
In a study of TiAlCuZrNb HEA films, it was shown that an amorphous-crystalline state was revealed. In addition, it can be speculated that the activation of the substrate surface before deposition of the metallic layer was accompanied by sputtering of the substrate and formation of a transition layer containing HEA atoms and stainless-steel atoms. The atoms of the stainless-steel metallic layer was accompanied by sputtering of the substrate and formation of a transition layer 1, located at the contact boundary of the HEA metallic and ceramic layers, was, as shown above, elastic stresses that arose due to different types and parameters of the crystal lattices. The reason for the formation of transition layer 1, located at the contact boundary between the substrate and the HEA metallic layer, was the sputtering of the substrate atoms and their mixing with particles entered at the substrate, which was followed by the settlement of the mixture on the substrate at the initial stage of coating formation. In addition, this layer was most likely stressed, which was due to its complex elemental composition. It was noted [3,40] that the more chemical elements with very different atomic radii \( \Delta = R_{\text{max}} - R_{\text{min}} \) make up the coating, the greater the intracrystalline deformation and the higher the probability of formation of an amorphous-like state of the alloy. It can be speculated that the activation of the substrate surface before deposition of the metallic layer was accompanied by sputtering of the substrate and formation of a transition layer containing HEA atoms and stainless-steel atoms. The atoms of the stainless-steel components have minimum radii \( R(\text{Ni}) = 0.124 \text{ nm} \) and \( R(\text{Cr}) = 0.125 \text{ nm} \), the HEA atoms have a maximum radius \( R(\text{Zr}) = 0.160 \text{ nm} \), and, hence, we have \( \Delta = R_{\text{max}} - R_{\text{min}} = 0.036 \text{ nm} \). In a study of TiAlCuZrNb HEA films \( \Delta = R(Zr) - R(Cu) = 0.032 \text{ nm} \) [41], the formation of an amorphous-crystalline state was revealed.
The physical and mechanical characteristics of the coatings were investigated using a TTX-NHT nanohardness tester at a normal load of 30 mN. Figure 7 shows a typical loading/unloading diagram obtained during the hardness test of a (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coating ($F_n$ is the normal load and $P_d$ is the penetration depth). The results of calculating the parameters of the diagram are given in Table 3.

Figure 6. Electron microscopic image of a (TiNbZrTaHf + (TiNbZrTaHf)N) cermet film, taken in the region of formation of the second transition layer: (a,b)—light-field images, (c)—microelectron diffraction pattern, (d)—dark-field image taken from the [220] reflex (indicated by the arrow in (c)). The transition layer is indicated by dashed lines in (a).

Figure 7. Loading/unloading diagram obtained during the hardness test of a (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coating.
Table 3. Nanoindentation characteristics of a (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coating.

<table>
<thead>
<tr>
<th>$F_{\text{max}}$, mN</th>
<th>$h_{\text{max}}$, nm</th>
<th>$S_h$, mN/nm</th>
<th>$c_r$, nm</th>
<th>$h_r$, nm</th>
<th>$h_p$, nm</th>
<th>$\epsilon$</th>
<th>$A_p$, nm²</th>
<th>$r/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.12</td>
<td>223.51</td>
<td>0.328</td>
<td>153.94</td>
<td>131.7</td>
<td>90.41</td>
<td>0.76</td>
<td>759362.6</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Notation: $F_{\text{max}}$—maximum load on the indenter; $h_{\text{max}}$—measured displacement of the indenter tip; $S_h$—contact stiffness at the initial stage of unloading; $c_r$—actual depth of indentation of the indenter tip into the sample; $(h_r = h_{\text{max}} - \epsilon (h_{\text{max}} - h_r))$, $h_r$—indentation depth after unloading; $h_p$—elastic deflection of the surface; $\epsilon$—correction factor depending on the indenter geometry, $A_p$—indentation projection area, and $r/V$—Poisson’s ratio.

Table 4 presents the average values of the film physicomechanical characteristics derived from the nanoindentation data given in Table 3. The hardness of the (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coatings produced on the WC–8 wt.% Co hard alloy was 36.7 GPa and their Young’s modulus was 323 GPa (Table 4). Additionally, the hardness of the cermet coatings measured using a PMT-3 instrument at a normal load of 0.5 N was 27.0 GPa.

Table 4. Physicomechanical characteristics of a (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coating.

<table>
<thead>
<tr>
<th>$E_r$, GPa</th>
<th>$H$, GPa</th>
<th>$H/E_r$</th>
<th>$(H^3/(E_r)^2)$, GPa</th>
<th>$\delta_{hr}$, %</th>
<th>$\eta$, %</th>
<th>$\varepsilon_{\text{elast}}$, %</th>
<th>$\varepsilon_{\text{inelast}}$, %</th>
<th>$\varepsilon_{\text{plast}}$, %</th>
<th>$h_r/h_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>322.7</td>
<td>36.7</td>
<td>0.114</td>
<td>0.476</td>
<td>58.9</td>
<td>41.1</td>
<td>31.1</td>
<td>9.95</td>
<td>58.9</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Notation: $E_r$—reduced modulus of elasticity, $H$—hardness parameter, $H/E_r$—wear resistance index, $(H^3/(E_r)^2)$—yield strength parameter, $\delta_{hr}$—plasticity parameter ($\delta_{hr} = h_r/h_{\text{max}} \times 100\%$ [42]), $\eta$—parameter characterizing the degree of elastic recovery of the imprint ($\eta = (h_{\text{max}} - h_r)/h_{\text{max}} \times 100\%$ [43]), $\varepsilon_{\text{elast}}$—percentage of elastic deformation return ($\varepsilon_{\text{elast}} = (h_{\text{max}} - h_r)/h_{\text{max}} \times 100\%$), $\varepsilon_{\text{inelast}}$—percentage of inelastic deformation return ($\varepsilon_{\text{inelast}} = (h_{\text{max}} - h_r)/h_{\text{max}} \times 100\%$), and $\varepsilon_{\text{plast}}$—percentage of plastic deformation accumulation ($\varepsilon_{\text{plast}} = \delta_{hr}$) [42]; the inequality $h_r/h_{\text{max}} < 0.75$ indicates that the deformation along the imprint contour was elastic [41].

For the (TiNbZrTaHf + (TiNbZrTaHf)N) cermet films, the wear parameter $k$ (inversely proportional to wear resistance) was $2.9 \times 10^{-5}$ mm³/N·m and the friction coefficient $\mu$ was 0.71. In preliminary investigations of the TiNbZrTaHfN ceramic films produced by plasma-assisted vacuum-arc deposition, we have found that $k = 3.3 \times 10^{-3}$ mm³/N·m and $\mu = 0.89$. The (TiNbZrTaHf)N ceramic coatings, produced on C45 and M2 stainless-steel substrates by dc magnetron sputtering in confocal geometry in a mixture of argon and nitrogen using an AJA ATC ORION system equipped with Ti, Zr, Nb, Hf, and Ta cathodes (each having a purity of 99.95% and a diameter of 0.0508 m) showed the following characteristics: $HV = 30.9$ GPa, $k = 0.29 \times 10^{-6}$ mm³/N·m, and $\mu = 0.17$ [45].

4. Conclusions

A plasma-assisted vacuum-arc deposition method has been developed and used to produce HEA-based (TiNbZrTaHf + (TiNbZrTaHf)N) multilayer ceramic-metal (cermet) coatings. A multicomponent gas-metal plasma was generated during the evaporation of a multielement cathode made of TiNbZrTaHf alloy of near-equiatomic composition. Depending on the gas supplied into the working chamber, a HEA metallic layer (argon) or a HEA ceramic layer (nitrogen and argon in equal proportions) was formed. The thickness of the metallic layer was 1 µm, and that of the ceramic layer was 3 µm.

The (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coating was a multilayer system consisting of two main layers and two transition layers. It was found that transition layers were formed between the substrate and the metallic layer and between the metallic and the ceramic layers.

X-ray diffraction analysis and transmission electron microscopy have shown that the HEA cermet coatings was a multiphase system, the main phases of which were (TiNbZrTaHf)N and Ta₄N nitrides and a TiNbZrTaHf alloy. The ceramic layer was found to be a two-phase ((TiNbZrTaHf)N + Ta₄N) system. The TiNbZrTaHf metallic phase had a bcc lattice with $a = 3.3936$ Å ($D = 8$ nm; $\Delta d/d = 5 \times 10^{-3}$). The (TiNbZrTaHf)N nitride had an fcc lattice with $a = 4.4465$ Å ($D = 22$ nm; $\Delta d/d = 7 \times 10^{-3}$). The Ta₄N nitride had a tetragonal lattice with $a = 6.8272$ Å and $c = 4.1697$ Å. The cermet coatings had a nanocrystalline structure with a crystallite size of 2.5–4 nm, regardless of whether the layer was metal or ceramic.
The hardness of the cermet coatings was 36.7 GPa and their Young’s modulus (at a Poisson’s ratio of 0.25) was 323 GPa. The wear parameter of the multilayer (TiNbZrTaHf + (TiNbZrTaHf)N) cermet coatings was $2.9 \times 10^{-5}$ mm$^2$/N·m and their coefficient of friction was 0.71.

Due to the high concentrations of many expensive metals, a potential application of presented HEAs-based coatings is depositing HEAs as thin coatings on low-cost substrates. The obtained results may also contribute to the further development of such multilayer coatings for specific applications.

The advantages of the plasma-assisted vacuum-arc deposition method are the ecological safety of the process and the possibility of complete automation of the cleaning of the substrate surface before coating deposition. This method makes it possible to realize a plasma-ion deposition process to produce HEA films of required elemental composition. It also enables a step-by-step formation of metallic, cermet, and ceramic films and coatings with strictly controlled thickness and elemental composition.

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