A new type of (TiZrNbTaHf)N/MoN nanocomposite coating: Microstructure and properties depending on energy of incident ions

A.A. Bagdasaryana,b, A.V. Pshykb,c, L.E. Coyb, P. Konarskic, M. Misnikc,d, V.I. Ivashchenkoe, M. Kempiński b,f, N.R. Mediukhe, A.D. Pogrebnjak,a, V.M. Beresnev, e, S. Jurga b

a Sumy State University, 2, Rymsky Korsakov Str., 40007, Sumy, Ukraine
b NanoBioMedical Centre, Adam Mickiewicz University, 85, Umultowska Str., 61-614, Poznań, Poland
c Yeł & Radio Research Institute, 11, Rakowiecka Str., 03-450, Warsaw, Poland
d Department of Atomic, Molecular and Optical Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Poland
e Prantsievich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3, Kryzhanykovskogo Str., 03680, Kyiv, Ukraine
f Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614, Poznań, Poland
g Kharkiv National University, Svobody Sq., 4, 61022, Kharkiv, Ukraine

ARTICLE INFO

Keywords:
Nitride coatings
Multilayer structure
Nanocomposite
Solid solution
Microstructure
Mechanical properties

ABSTRACT

A novel (TiZrNbTaHf)N/MoN nanocomposite coatings, which consist of the nitride of the high-entropy alloy and the binary nitride, were synthesized by vacuum-arc deposition at various substrate biases. The elemental composition, chemical bonding state, phase structure, microstructure and mechanical properties of the coatings were studied by high-resolution experimental methods: SIMS, GDMS, XPS, XRD, HR-TEM and nano-indentation. It was found that the chemical state of the (TiZrNbTaHf)N/MoN coatings has a complex nature, which consist of a mixture of nitrides of constituting elements. It was also shown that the coatings are based on B1 NaCl-structured γ-Mo2N-phase with a mixture of crystallographic orientations (111), (200), (220) and (311) together with the B1 NaCl-structured (TiZrNbTaHf)N solid-solution phase. First-principles calculations demonstrated that the metal sub-lattice of the (TiZrNbTaHf)N solid solution can be based on Ti1-xHfyTa1-x-y,Zr1-xHfyTa1-x-y, Zr0.25Ti0.25Ta0.5 ternary alloys, which have the lowest mixing energy. The HR-TEM results showed that the nanocomposite nitride coatings have nano-scale multilayer structure with modulation periods ranged from 20 nm to 25 nm. The maximum hardness of approximately 29 GPa demonstrated the coating deposited at a higher energy condition (~200 V) with the thinnest modulation period of bilayer of 20 nm (15 nm of (TiZrNbTaHf)N and 5 nm of Mo2N).

1. Introduction

The recent breakthrough in the last century in engineering materials is design of nanocomposite coatings, which possess superior mechanical and chemical properties, such as high hardness, stiffness, wear resistance, low coefficient of friction, low thermal conductivity etc., in contrast with single layer coatings [1–15]. Such nanocomposite materials are nano-multilayer composites, which have large amount of two or more separated nanocrystalline phases with different elastic modulus and lattice parameters. In order to obtain multilayer coatings with superior functional properties, it is important to adjust carefully their elemental composition and modulation wavelength. It was found that the optimum properties occur in multilayer coatings with bilayer period A in the range of 4–50 nm depending on elemental composition and deposition conditions [16,17].

Nanocomposite architecture allows to achieve excellent functional properties, especially high hardness and low coefficient of friction. There are several hardening mechanisms acting at the same time but at different degrees in the multilayer coatings. First, the hardness alteration could be due to the hindering of dislocation across the layer interfaces. Also, if the constituent layers with different lattice parameters are grow epitaxially, the resulting coherence stress field at the interfaces act as obstacles for dislocation movements [18–20]. Few publications showed another mechanism of hardening, known as Orowan strengthening, which act in structures with nanometer modulation wavelength [21,22]. The improvement in hardness according to this effect occurs at the expense of the precipitation, stopping of dislocation and formation of obstacles, such as “Orowan loop”. Despite the great variety of strengthening mechanisms in multilayer structures, the overall hardness enhancement originates from contributions of all.
mechanisms. In addition, the effects acting in single-layer coatings, especially in multi-principal elements alloy, such as Hall-Petch effect, solid solution hardening, should be taken into account [23].

In the last decade, it has developed a new approach to designing engineering materials that possess a wide range of unique properties, high-entropy alloys (HEAs) or multi-principal elements alloys (MPEAs). There are two major definitions of HEAs: based on the composition and on the configurational entropy [24-28]. According to D.B. Miracle et al. [25], HEAs are the alloys, which contain at least 5 constitutional elements with an atomic percentage between 5 and 35%. Moreover, these alloys can be defined as materials maximum value configurational entropy of which is 1.61 R (where R is the gas constant, 8.314 \text{j} \times \text{k}^{-1} \times \text{mol}^{-1}) and minimal value is 1.36 R. In accordance with these definitions, the basic concepts of HEAs is high entropy of mixing, which can promote the stabilization of a disordered solid solution (SS) and prevent the formation of ordered compounds, like intermetallics (IM) due to the lattice distortion effect and sluggish diffusion, which can be explained by kinetic theory [26].

Since the appearance of the first studies of HEAs [29,30], more than 1000 scientific works have been published to date. The relationship between microstructure of the new alloys, which can include SS (with BCC, FCC and HCP structures), IM and even amorphous state [31-33] and their physical properties was investigated [34-36]. It was shown that the HEAs possess different outstanding functional properties, like superconductivity with transition temperature \( T_c = 7.3 \text{ K} \) [37], high level electrical resistivity [38], high saturated magnetization [39,40], high corrosion resistance [41-43], good hydrogen storage properties [44-47]. Moreover, HEAs were used as a template for graphene production [48], high-entropy steel and transformation-induced plasticity-assisted dual-phase high-entropy alloys [49-52]. For achievement superior mechanical behavior and thermal stability HEAs were alloyed by (TiZrNbTaHf)N [53], (AlMoNbSiTaTiVZ)N [54], (TiVCrZnHf)N [55], (TiTaCrZrAlN)N [56], (CrTaTiZn)N [57], (TiZnNiTa)N[C] [58], (MgNiCoCuZrY) [59], (AlCrTaTiZnO) [60], (MgCoNiCuZnO) [61], CuCoNiZrAlFe [62] and others [63-67].

Since the appearance of first publication by Koehler, the variety of different type of multilayer composites, like metal/metal (Ni/Ti, Co/Ni, Fe/Ni [68-70]), ceramic/metal (TiN/AI, NbN/Al, Ta/TaN [71-74]) and ceramic/ceramic (CrAlSiN/TiVN, AlCrSiN/AlCrSiN, TiN/TiAIN[9,17,75]) have been intensively investigated. Recent papers have shown the possibility of using different type of composites based on HEAs with intrinsic multilayer architecture, like: AlCoCrCuFeNi/Mg [76], (TiHfZrVNbTaN) + DLC [77], (FeCoNiMnCr) + MeC [78], TiAlSiC/Ni/SiC [79]. However, the research work devoted to the composites with a HEA layer is still very limited. The only pure metals [76] and carbide interlayers [77-79] have been studied, assuming that the preparation of intermediate nitrides, will affect the Nitride based HEAs. Nevertheless, although it is worth to assume a large diffusion due to the complex stoichiometry of HEAs, especially in similar interfaces, such as in case of Metal-Nitride/Metal-Nitride, these effects have remain unexplored.

It is well known, that the deposition parameters, like temperature of deposition, energy of incident particles, pressure of working gas and others have a significant influence on structural state and overall properties. In our work we developed and investigated a novel (TiZrNbTaHfN)/MoN nanocomposite coatings, which deposited by vacuum arc deposition under different energy conditions. The chemical stability and growth of such complex nanocomposites have been poorly studied. Moreover, the influence of overall ions deposition energy on crystallization process and as a result on interaction between nanolayers should be taken into account and analyzed in order to avoid malfunction of nanocomposite coatings. Clearly, the understanding of microstructural features of such nonhomogeneous complex systems is essentially needed in order to move further towards the improvement of the physical properties of high-entropy based nanocomposite thin films. This article contributes to the gaining of knowledge about the growth mechanism, structural evolution and functional properties of a novel (TiZrNbTaHfN)/MoN nanocomposite nitride coatings based on the high entropy alloy. In order to achieve this aim, six transition metals Ti, Zr, Nb, Hf, Ta and Mo are selected due to the their similar electronic configuration, which is favored by the octahedral grouping of the metal atoms around a central nitrogen atom, which will allow to achieve a single-phase stable structure.

2. Experimental methods

2.1. Growth and characterization

The five-element TiZrNbTaHf cathodes were obtained by vacuum-arc melting method. Ingot were melted at least six times to achieve necessary compositions homogeneous. All the samples have been prepared by vacuum-arc deposition in “Bulat-6” chamber. The deposition was carried out from the two different cathodes (1 – TiZrNbTaHf alloy, 2 – Mo), diatomically opposed to the substrate holder during continuous rotation of the holder during 1 h. Steel discs and plates (12H18N9T steel – C ≤ 0.12 wt %; Si ≤ 0.8 wt %; Mn ≤ 2.0 wt %; Cr – 17 – 20 wt %; Ni - 8 - 11 wt %; Ti < 0.8 wt %.) with Ø = 45 mm and thickness of 4 mm were used as a substrate. The working gas pressure used during deposition was 0.53 Pa while a negative bias of –100, –200 and –300 V was applied to the substrate (see Table 1). The temperature of deposition was 400°C.

The X-ray photoelectron spectroscopy (XPS) measurements were performed in UHV conditions using the monochromatic Al Kα X-ray source and Sphera II photoelectron energy analyzer (Scienta Omicron). All measurements were made in the ultra-high vacuum chamber at a pressure around \( 10^{-9} \) mbar. The spectra were taken at 20 eV pass energy and 0.1 eV resolution.

SIMS measurements were done with the use of 5 keV Ar+ ion beam. SIMS analyser model SAJW-05 is equipped with Physical Electronics 06-350E ion gun and QMA-410 Balzers quadrupole mass analyser with 16 mm diameter rods.

Glow discharge mass spectrometry (GDMS) analysis was conducted with a SAWJ-01 instrument and SRS-300 quadrupole mass analyzer with 6 mm diameter rods. The 1.8 kV DC glow discharge voltage was applied and Ar working pressure was 0.2 Torr.

The structure and elemental composition was analyzed using Scanning electron microscopy (SEM JEOL 7001TTLs) with Energy dispersive X-ray spectroscopy. The electron transparent lamellas of the coatings for TEM measurement were prepared using a focused ion beam (FIB) operating with Ga ions. High-resolution transmission electron microscope (HRTEM JEOL ARM 200F) operating at accelerating voltage of 200 kV was used to image the microstructure of the coating and evaluating of thickness period of multilayers. The microscope was also equipped with an EDX detector used to determine the distribution of the elements.

The crystal structure was characterized by X-ray diffractometer PANalytical using filtered Cu-Kα radiation (1.5418 Å) with PIxcel 3D detector in Bragg-Brentano geometry. Spectra were recorded in continuous scanning mode at room temperature (300 K), with the 2θ ranging from 20.0° to 80.0° and scanning step was 0.006°. Data were processed in the PANalytical XPert software.

<table>
<thead>
<tr>
<th>№</th>
<th>Coatings</th>
<th>I, A</th>
<th>Uin, V</th>
<th>P30, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(TiZrNbTaHfN)/MoN</td>
<td>90/ 150</td>
<td>–100</td>
<td>0.53</td>
</tr>
<tr>
<td>2</td>
<td>(TiZrNbTaHfN)/MoN</td>
<td>90/ 150</td>
<td>–200</td>
<td>0.53</td>
</tr>
<tr>
<td>3</td>
<td>(TiZrNbTaHfN)/MoN</td>
<td>120/ 140</td>
<td>–300</td>
<td>0.53</td>
</tr>
</tbody>
</table>
The nanoindentations were performed at room temperature on (TiZnNbTaHf)N/MoN coatings using Hysitron Tribolindenter 950 equipped with a Berkovich diamond tip Ti-0039 (conical angle 142.3° and 100 nm tip radius) calibrated against the fused silica sample. In order to measure the hardness and reduced elastic modulus of the coatings at different depth, the multiple load function in the form of trapezoidal sinus was applied to the indenter with continuously increasing load up to a maximum 10 mN load. The measurements were repeated several times. The hardness and the elastic modulus were evaluated using the standard procedure proposed by Oliver and Pharr [80].

The elastic modulus of the coatings was calculated using the following formula [80]:

\[
\frac{1}{E_i} = \frac{1 - \nu_i^2}{E_e} + \frac{1 - \nu_i^2}{E_i},
\]

where \(E_i\) and \(\nu_i\) are Young's modulus and Poisson's ratio of the coating material, \(E_e\) and \(\nu_e\) are Young's modulus and Poisson's ratio of the Berkovich diamond indenter (\(E_i = 1140\) GPa and \(\nu_i = 0.07\), respectively).

2.2. Computational details

We considered the 8 atoms cubic cells to model Zr\(_x\)Ti\(_y\)Ta\(_{1-x-y}\)N, Zr\(_x\)Hf\(_y\)Ta\(_{1-x-y}\)N and Ti\(_x\)Hf\(_y\)Ta\(_{1-x-y}\)N (x, y = 0.0, 0.25, 0.5, 0.75 and 1.0) solid solutions (alloys) with the B1 structure (space group Fm-3m, No. 225). These cells were used in first-principles calculations that have been carried out using the Quantum-ESPRESSO code [81]. The details of the calculations can be found in our previous work [63], therefore, we note only the following main approaches. In particular, Vanderbilt ultra-soft pseudo-potentials were used [82]. For exchange-correlation energy, the generalized gradient approximation (GGA) of Perdew et al. [83] was employed. The structures were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [84]. For Hf and Ta the 4f states are not considered as the valence states, because they are completely filled and chemically inert. The mixing energy of an alloy (\(E_{mix}\)) was:

\[
E_{mix}(\text{Me}_x\text{Me}_y\text{Me}_{1-x-y}N) = E_{tot}(\text{Me}_x\text{Me}_y\text{Me}_{1-x-y}N) - x \times E_{tot}(\text{Me}N) - y \times E_{tot}(\text{Me}N) - (1-x-y) \times E_{tot}(\text{Me}N),\]

where Me, Me, Me = Ti, Zr, Hf and Ta.

3. Results

3.1. Elemental composition and chemical bonding

Before analyzing of elemental composition by SIMS and GDMS methods, it will be useful to analyze the chemical bonding states of (TiZnNbTaHf)N/MoN nanocomposite coatings by means of XPS. The XPS survey spectrum (see Fig. 1 (a)) contains peaks, which associated with titanium, zirconium, molybdenum, niobium, tantalum, nitrogen and oxygen. Carbon (peak at 284 eV) and oxygen (peak at 532 eV) peaks are due to the contamination of the coating by the small amount of residual gases in vacuum chamber during the deposition and contamination of the coating surface by ambient atmosphere [85]. For analyzing, we selected Ti2p, Mo3d, Zr2p, and Nb3d core-level peaks due to the absence of overlapping effects of these peaks with the other constituent elements of the coating. Importantly, Hf was detected in the coating as well, but the intensity of Hf4f and Hf4p\(_{1/2}\) peaks was very low and inappropriate for analysis, while the Hf4s may overlap with O1s.

The Zr3d spectrum (Fig. 1 (b)), containing peaks corresponding to the spin-orbit split 3d\(_{3/2}\) and 3d\(_{5/2}\) electrons, was de-convoluted into 2 doublet components: (1) peaks at 183.04 eV and 179.42 eV, respectively, and (2) peaks at around 184.44 eV and 181.89 eV, respectively. According to the literature data, the energy position of the first component can be due to ZrN\(_x\) bonds, while the second component is attributed to ZrO\(_2\) bonds in the coating [86].

The Ti2p XPS spectrum was de-convoluted into 3 spin-orbit doublets. In this study, the peaks of Ti2p\(_{3/2}\) and Ti2p\(_{1/2}\) at 458.15 eV and 464.15 eV, respectively, are associated with the presence of TiO\(_2\); the components at around 455.16 eV and 460.76 eV, respectively, are related to Ti-N bonds. Besides these chemical states, the intermediate state was found in the coating, which corresponds to Ti-N-O bonds at 456.60 eV for Ti2p\(_{3/2}\) peak and 462.44 eV for Ti2p\(_{1/2}\) peak, which is in good agreement with binding energy reported in the literature [87,88].

The Nb3d spectrum was fitted into 3 spin-orbit doublets. The spin-orbit split 3d\(_{3/2}\) and 3d\(_{5/2}\) peaks at around 206.97 eV and 203.74 eV, respectively, are corresponding to the binding energy of NbN. The components at around 206.52 eV (Nb3d\(_{3/2}\)) and 209.46 eV (Nb3d\(_{5/2}\)) can be assigned to NbO\(_x\), and at 204.79 eV (Nb3d\(_{3/2}\)) and at 207.64 eV (Nb3d\(_{5/2}\)) – to NbO [89,90].

The Mo3d\(_{3/2}\) and Mo 3d\(_{5/2}\) peaks of the Mo3d spectrum have been de-convoluted into 3 chemical states: molybdenum nitride, MoO\(_2\), and MoO\(_3\) with binding energies of 228.19 eV (Mo3d\(_{3/2}\)) and 231.41 eV (Mo3d\(_{5/2}\)) and 229.31 eV (Mo3d\(_{3/2}\)) and 231.34 eV (Mo3d\(_{5/2}\)), 232.69 eV and 235.19 eV (Mo3d\(_{3/2}\)) and respectively [91].

Fig. 2 shows typical depth profile of (TiZnNbTaHf)N/MoN coatings. It is clearly visible that the signal from all elements are well distinguished. The intensity can be related to a semi-quantitative concentration of the ion fragments of constituent elements along the coating thickness. Analysis of these results confirms the presence of secondary ion current oscillation, which corresponds to formation of multi-layered structure consisting of (TiZnNbTaHf)N and MoO\(_N\) layers. The decreasing of intensity of the oscillations with an increasing of sputter time is not due to the destruction of a multilayer structure. In our opinion, this kind of changes could be explained by changes in sputtering rate and increasing of the curvature of the layers.

In case of GDMS analysis (see Fig. 3) it was shown, that the ion current intensities of constituent elements decreases with the increasing of thickness of each samples (see Fig. 3). This effect is due to the developing conditions of the glow discharge during the analysis. It is worth to note that nitrogen and tantalum signals are burdened by high background levels. In fact, N ion signal (measured as N\(_2^+\) ion current) is high due to high nitrogen background in the glow discharge cell and Ta signal is high due to the use of tantalum diaphragm as an intermediate cathode in the glow discharge cell. Nevertheless, the distribution of all the remaining elements is close to uniform, except Hf, which signal is close to the noise level.

3.2. Structural analysis and microstructure

Diffraction patterns from (TiZnNbTaHf)N/(MoN) multilayer nanocomposite coatings deposited on steel under different substrate bias are presented in Fig. 4. As we can see, XRD patterns contain FCC \(\gamma\)-Mo\(_N\) (111), (200), (220) and (311) together with (TiZnNbTaHf)N (111), (200), (220), (222) and (311) peaks.

In Table 2, the calculated lattice constants for TiN, ZrN, HfN and TaN in a comparison with the corresponding experimental and theoretical values are showed. One can see that the calculated lattice parameters are in good agreement with those gained in experimental and theoretical investigations of other authors. Nevertheless, there is a strong deviation of the calculated values from the experimental ones for TaN, which could be ascribed to nonstoichiometry of the experimental TaN samples.

From these XRD patterns, we can observe the changing of preferred orientation from (111) + (311) to (200) under different substrate bias. At low \(U_s\), the highest peaks are at (20) = 69.67°, β = 54.65°, which correspond the (311) and (111) planes of the (TiZnNbTaHf)N layer and (20) = 36.11° responsible for (111) plane of the \(\gamma\)-Mo\(_N\) layer. When substrate bias increases to −200 V, the intensity of (111) planes of...
(TiZrNbTaHf)N and γ-Mo2N layers reach maximum and weak (200) (TiZrNbTaHf)N, (222) (TiZrNbTaHf)N and (311) γ-Mo2N peaks can be observed. The preferred orientation of (TiZrNbTaHf)N/MoN grains was dramatically changed from (111) to (200) (TiZrNbTaHf)N, (200) γ-Mo2N and (220) γ-Mo2N at −300 V.

Figs. 5 and 6 present TEM cross-sectional images and SAED patterns of (TiZrNbTaHf)N/MoN multilayered coatings deposited under −100 V and −300 V, respectively. STEM analysis of the (TiZrNbTaHf)N/MoN multilayered coatings, Figs. 5 and 6 b, confirm the columnar growth with dark and bright layers. Taking into account the different sputtering coefficient of the constituent atoms and EDX mappings, the bright layers on Fig. 5 b and 6 a can be as assigned to (TiZrNbTaHf)N with thickness 15–20 nm and dark layers to Mo2N with thickness of around 5 nm. From SAED patterns, which show in Fig. 5 c and 6 (the inset), the reflections (111), (200), (220), (222) and (311) corresponding to the FCC phases are clearly identified. The reflections corresponding to fcc-

![Fig. 1. XPS spectra of (TiZrNbTaHf)N/MoN coating deposited at Uab = −200 V: a) XPS survey spectrum; b) Zr3d, Ti2p, Nb3d, Mo3d.](image)
(TiZrNbTaHf)N and fcc-Mo2N phases are very close to each other, which is in good agreement with the results shown in XRD patterns. The modulation period estimated from the TEM images was 20 nm for the coating deposited at −100 V and 25 nm at −300 V. The changes in the modulation period are associated with the increase of the TiZrNbTaHf target current during deposition of the coating under −300 V.

The HRTEM images and its corresponding inverse FFT images, provide a hint of the internal structure of the columnar grains observed in the coatings (see Fig. 5 (d, e) and Fig. 6 (c, d)) demonstrating the formation of randomly oriented nanocrystalline sub-grains of (TiZrNbTaHf)N/MoN multilayered nanocomposite coatings with sizes between 5 and 15 nm (see Table 3). The inverse FFT filtering of (311) oriented grains of fcc-(TiZrNbTaHf)N and (311) oriented grains of fcc-Mo2N phase of the coating deposited under −100 V (Fig. 5 e) revealed that the corresponding lattice fringes are maintained through the interface of the corresponding layers without interruption during the grain growth. Importantly, these observations imply that the grains grow "epitaxially" with fcc-(TiZrNbTaHf)N(311)||fcc-Mo2N(311), or at least, highly coherently between interfaces. This local cube on cube epitaxial growth is due to the fact that both layers have the same crystalline structure, with a lattice mismatch of around 4.6%. The same growth was observed for other orientations. Arcing of the (311)-assigned reciprocal-lattice points on the FFT pattern (Fig. 6 d, inset) points on a slight misorientation of the corresponding grains. Several arrays of mismatch dislocations were observed in HRTEM images (not showed here), which are introduced due to the relaxation of coherency strains accumulated as a result of the lattice mismatch. It should be noted, that these dislocations caused lattice distortion, which can lead to the formation of sub-grain structure.

The increase in bias voltage up to 200 V caused degradation of the (311)-oriented grains of Mo2N phase, but promoted the development of (111) texture, as clearly visible on XRD pattern. Therefore, the same local epitaxy with cube on cube growth can be expected, although texturized in the (111). However, an abrupt change of the growth mechanism is observed for the coating deposited at 300 V. A complete degradation of (111) oriented MoN grains and significant sharpening of

Fig. 2. SIMS analysis of N+, Mo+, Zr+, Nb+, Hf+, Ti+ and Ta+ ion emission in time of erosion of (TiZrNbTaHf)N/MoN samples at different substrate bias. The secondary ion current data is shown in linear scale versus erosion depth.

Fig. 3. GDMS analysis of (TiZrNbTaHf)N/MoN samples deposited at −100 V, −200 V and −300 V substrate bias. The ion current data is shown in logarithmic scale.
the (200) reflections of both phases, as well as a shift of other reflections of (TiZrNbTaHf)N phase to higher angles are observed. Due to much lower lattice mismatch of around 2.2%, the (200) oriented grains of both lattices demonstrated cube on cube epitaxial growth (not showed here). At the same time, the absence of (111) oriented Mo2N grains renders impossible the coherent growth of (111) (TiZrNbTaHf)N grains with Mo2N layer, effect that is clearly demonstrated in Fig. 6 (c, d). Importantly, there is no crystallographic coherence between the (111) (TiZrNbTaHf)N and (200) Mo2N grains and therefore the arrays of stacking faults are introduced at the interface between the layers visible as a smearing of the reciprocal-lattice points on the FFT pattern acquired at the interfaces (Fig. 6 (e, g)).

3.3. Nano-indentation measurements

Hardness and Young’s modulus values of (TiZrNbTaHf)N/MoN multilayer nanocomposite coatings are presented on Fig. 7 as a function of the indenter displacement. It is important to remark that at low penetration, roughness of the films overcomes the Berkovich shape, thus stable values can be observed above penetrations of 50 nm.

The hardness and Young’s modulus strongly depend on substrate bias (see Fig. 7). The initial increase of substrate bias from −100 V to −200 leads to increase of the hardness and Young’s modulus from 29 to 306 GPa to −200 V–33 and 315 GPa, respectively. At the highest substrate bias (at −300 V) the hardness and Young’s modulus decreases dramatically to 20 and 349 GPa. It should be noted, that the drastic decrease of hardness of the coatings at −300 V can be explained by development of (200) preferred orientation, which is less densely packed that (111) and by increasing of grain size. Based on oscillation of the signal of constituent elements (see Fig. 3), we can conclude that the (TiZrNbTaHf)N and Mo2N layers have sharp and distinguished interfaces. However, the increasing of substrate bias leads to large

![Fig. 4. XRD spectra of (TiZrNbTaHf)N/MoN multilayered nanocomposite coatings under different substrate biases.](image)

![Fig. 5. Cross-sectional STEM image of the (TiZrNbTaHf)N/MoN multilayered coating obtained under −100 V (a), low-magnification bright-field TEM image (b), corresponding SAED pattern (c), high-resolution TEM image and corresponding FFT pattern as an inset (d) and inverse FFT image (e) of the image (d). The Mo2N (311) oriented grains are colored in green color in figure e, while (TiZrNbTaHf)N grains with (311) and (220) orientations are colored in blue and red color, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)](image)

<table>
<thead>
<tr>
<th>TiN</th>
<th>ZrN</th>
<th>HfN</th>
<th>TaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.247</td>
<td>4.592</td>
<td>4.537</td>
<td>4.407</td>
</tr>
<tr>
<td>4.241</td>
<td>4.600</td>
<td>4.525</td>
<td>4.340</td>
</tr>
<tr>
<td>4.25</td>
<td>4.60</td>
<td>4.54</td>
<td>4.408</td>
</tr>
<tr>
<td>4.275</td>
<td>4.583</td>
<td>4.54</td>
<td></td>
</tr>
</tbody>
</table>

* Experiment [92].

First-principles pseudo-potential method (VASP code) + GGA [93].

First-principles ultrasoft pseudo-potential method + GGA [94].
di
ffusion of elements in the coatings, to the loss of independent inter-
faces and probably to incomplete layers.

Elastic strain to failure $H/E^*$ and resistance to plastic deformation
$H_3/E^{**}$ were calculated from the nanoindentation data (Fig. 7). The best
ability to resist the plastic deformation ($H_3/E^{**}$) of 0.38 GPa and
highest elastic strain prior to failure of 0.1 among the studied coatings
demonstrates the multilayer coating deposited under $-200$ V substrate
bias voltage.

The coefficient of thermal expansion (CTE) of the investigated nano-
composite coatings can be estimated according to the rule of mixing from
the CTEs of binary nitrides of constituent elements:

$$\alpha_{TiN} = 8.1 \times 10^{-6} \text{ K}^{-1}, \quad \alpha_{ZrN} = 7 \times 10^{-6} \text{ K}^{-1}, \quad \alpha_{HfN} = 10.1 \times 10^{-6} \text{ K}^{-1}, \quad \alpha_{MoN} = 3.6 \times 10^{-6} \text{ K}^{-1}, \quad \alpha_{NbN} = 6.5 \times 10^{-6} \text{ K}^{-1}, \quad \alpha_{TaN} = 0.442 \text{ nm} \quad [92].$$

As a result, the overall CTE (see Table 4) can be found from the equation [95]:

$$\alpha_{TiZrNbTaHf/MoN} = \alpha_{TiN} \cdot C_{TiN} + \alpha_{ZrN} \cdot C_{ZrN} + \alpha_{HfN} \cdot C_{HfN} + \alpha_{TaN} \cdot C_{TaN} + \alpha_{MoN} \cdot C_{MoN} + \alpha_{NbN} \cdot C_{NbN},$$

where $C_i$ is the concentration ratio of the individual target element to the
total target elements in the coating [95]. The significant difference of CTEs
of (TiZrNbTaHf)N/MoN and substrate ($\alpha_{Fe31Ni29Pt}$ steel $= 18 \times 10^{-6} \text{ K}^{-1}$)
could lead to evolution of larger thermal stress in the coatings. For calcula-
tion of the Young's modulus of the coatings (Table 4) by means of formula
(1), we used Poisson ratio equal to $\nu = 0.25$, which is the most frequently
value for nitride films reported in the literature [95,99–101].

4. Discussion

4.1. Morphology

Our experimental analysis of chemical bonding state, elemental
composition, structural-phase state and microstructure using different
high-resolution methods such as SIMS, GDMS, XPS, XRD and HRTEM
have shown that the (TiZrNbTaHf)N/MoN nanocomposite coatings
deposited by vacuum arc deposition at different substrate bias grow
with local cube on cube epitaxy of fcc-MoN and fcc-(TiZrNbTaHf)N
grains. The growth of such structure can be explained by the following
considerations.

Nitride coatings, like (TiZrNbTaHf)N, based on MPEAs with ran-
domly distributed atoms tend to form a disordered solid solutions with
a simple crystal structures [53–57]. It is important to note, that the
crystal structure of the binary nitrides of constituent elements and their
lattice parameter are approximately equal (TiN $\text{FCC with lattice}
\text{parameter, } a = 0.424 \text{ nm}; \text{ZrN } \text{FCC, } a_{ZrN} = 0.459 \text{ nm}; \text{NbN } \text{FCC,}
a_{NbN} = 0.442 \text{ nm}; \text{TaN } \text{FCC, } a_{TaN} = 0.44 \text{ nm}; \text{HfN } \text{FCC,}
a_{HfN} = 0.453 \text{ nm}) [92]. In our case the lattice parameter of (TiZrNbTaHf)N
is 0.446 and 0.448 nm for the coatings deposited under $-100$ V and
$-200$ V, respectively, which is close to the lattice parameter of
binary nitrides of constituent elements. The N p-orbitals interact with
the transition metals d-orbitals forming sp$^3$d$^2$ hybridization typical for
the transitional metal nitrides with NaCl structure. Therefore, there is a
high probability of forming NaCl structured solid-solution where the

<table>
<thead>
<tr>
<th>Substrate bias, Usb, V</th>
<th>Thickness, μm</th>
<th>Bilayer period, A, nm</th>
<th>Crystallite size, (TiZrNbTaHf)N, D, nm</th>
<th>Crystallite size, (Mo2N), D, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-100$</td>
<td>11.5</td>
<td>20</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>$-200$</td>
<td>10</td>
<td>25</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>$-300$</td>
<td>12.2</td>
<td>25</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3

Thickness, bilayer period ($A$) and crystallite size ($D$) of the (TiZrNbTaHf)N/ (MoN) multilayered coatings.

Fig. 6. Cross-sectional bright field TEM image with SAED as an inset (a), STEM image (b), and high resolution cross-sectional TEM image (c) of the (TiZrNbTaHf)N/MoN multilayered coating obtained under $-300$ V with corresponding inverse FFT image (d) and the local FFTs acquired from the MoN/ (TiZrNbTaHf)N interface in the lower left part of figure c (b), from the (TiZrNbTaHf)N layer (e) and (TiZrNbTaHf)N/MoN interface in the upper right part of figure c (f). The Mo$_2$N (200) oriented grains are colored in green color in figure d, while (TiZrNbTaHf)N (111) oriented grains are colored in purple color. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

A.A. Bagdasaryan et al.
Composites Part B 146 (2018) 132–144
transition metals occupy the metallic sub-lattice cites. It is well known that the metals (Ti, Zr, V, Nb, Ta, Mo, W) which belong to IV-VI groups can form binary and ternary compounds with nitrogen that are metastable disordered solid solution with FCC structure [102]. However, limited information are available on the structural phase state of multicomponent coatings. That’s why we employed first-principles calculations for obtaining the general picture of phase formation in (TiZrNbTaHf)N/MoN multilayered coatings.

In our theoretical interpretation of the experimental results, we concentrate on the binary and ternary alloys. However our approach is quite justified because the goal of our theoretical study is to show the possibility of the formation of different phases in the complex (TiZrNbTaHf)N solid solutions that form the hard coatings considered above. The phase stability is based on an analysis of mixing energy. Positive mixing energy implies that a solid solution is not stable, and will decompose into separate phases with the chemical driving force \( E_{\text{mix}} \). Unstable alloys can be thermally stabilized in some range of compositions, because the configurational entropy is always positive and promotes a decrease in Gibbs free energy. On the contrary, a stable solid solution has negative mixing energy.

In Fig. 8, the mixing energies of the binary alloys based on titanium, zirconium, hafnium and tantalum nitrides with the B1 structure are showed. For the sake of comparison, the mixing energies calculated by a first-principles pseudo-potential method (VASP code) using the 32-atom cells with the randomized arrangement of transition metal atoms in the sites of the metallic sub-lattice [93]. For \( \text{Zr}_{1-x}\text{Ti}_x\text{N} \) and \( \text{Ti}_{1-x}\text{Hf}_x\text{N} \), all non-end-member structures have positive \( E_{\text{mix}} \). There is a little asymmetry of \( E_{\text{mix}}(x) \) leaning to TiN-side in \( \text{Zr}_{1-x}\text{Ti}_x\text{N} \) but much more in \( \text{Ti}_{1-x}\text{Hf}_x\text{N} \) in agreement with the results [93]. Our \( E_{\text{mix}} \) values are slightly higher compared to those calculated in Ref. [93], which is supposed to be due to the ordered cells used in our calculations. The positive mixing energies are observed in \( \text{Ti}_{1-x}\text{Ta}_x\text{N}, \text{Zr}_{1-x}\text{Ta}_x\text{N} \) and \( \text{Hf}_{1-x}\text{Ta}_x\text{N} \), indicating that these alloys can be stable in a wide range of temperatures. The minimums of \( E_{\text{mix}}(x) \) is located closer to TaN-side, especially in \( \text{Zr}_{1-x}\text{Ta}_x\text{N} \). In our previous work [63], we have shown that the most values of mixing energy for \( \text{Ti}_{1-x}\text{Nb}_x\text{N} \) in the range of \( 0.25 \leq x \leq 1 \) are negative, which indicates that such alloys can be stabilized as solid solutions at moderate temperatures.

Table 4 shows the calculated mixing energy for the ternary \( \text{Zr}_{1-x}\text{Ti}_x\text{Ta}_{1-x-y}\text{Zr}_{1-x}\text{Hf}_{x}\text{Ta}_{1-x-y} \) and \( \text{Ti}_{1-x}\text{Hf}_{x}\text{Ta}_{1-x-y} \) alloys. The results presented in Table 5 enable us to estimate an effect of the substitutional atoms on the stability of the binary alloys considered above. The comparison of the results presented in Fig. 8 and Table 4 shows that:

1) \( \text{Zr}_{1-x}\text{Ti}_x\text{N} \) and \( \text{Ti}_{1-x}\text{Hf}_x\text{N} \) can be stabilized by the substitution up to 50% of Zr, Ti, Hf atoms by Ta atoms;
2) The substitution up to 50% of Ti, Hf and Ta atoms by Zr atoms in \( \text{Ti}_{1-x}\text{Ta}_x\text{N} \) and \( \text{Hf}_{1-x}\text{Ta}_x\text{N} \) leads to an increase in \( E_{\text{mix}} \) of these alloys;
3) \( \text{Zr}_{1-x}\text{Ta}_x\text{N} \) is destabilized due to the substitution up 50% of Zr or/and Ta atoms by Ti atoms.

An analysis of the results presented in Table 5 and in our work [63] shows that along with the transition metal mononitrides and the stable binary solid solutions shown in Fig. 8, the following ternary alloys, such as \( \text{Ti}_{1-x}\text{Hf}_{x}\text{Ta}_{1-x-y} \), \( \text{Zr}_{1-x}\text{Hf}_{x}\text{Ta}_{1-x-y} \), \( \text{Zr}_{0.25}\text{Ti}_{0.25}\text{Ta}_{0.5}\text{N} \), \( \text{Ti}_{1-x}\text{Nb}_x\text{N} \) can form in the (TiZrNbTaHf)N disordered solid solutions. It follows that the metallic matrix of the deposited nanocomposite coatings can contains transition metal mononitrides and their solid solutions, depending on deposition conditions. Due to the low mixing energy of the mentioned ternary alloys, the decomposition of corresponding solid solution phases can take at a relatively high temperature, thus will be responsible for the stability of the coating system at high thermal loads.
It is worth to note that Mo is a weaker nitride-forming element characterized by low enthalpy of formation $\Delta H_{\text{MoN}} = -81.6$ kJ/mol in contrast with strong nitride-forming elements, like Ti, Zr, Nb, and Nb, with easy nucleation: $\Delta H_{\text{TiN}} = -335$ kJ/mol, $\Delta H_{\text{HN}} = -373.6$ kJ/mol. Nevertheless, the obtaining of solid solution with simple structure in (Ti-Zr-Nb-Hf-Ta)N/MoN coatings can be anticipated based on the aforementioned fact.

Thus, according to Hume-Rothery rules [103], the formation of the solid solutions is very favourable as a consequence of the relatively low atomic size mismatch between the constituent atoms, the small electronegativity difference and the small valence difference between Nb, Ta, Hf, Zr and Ti in addition to the mentioned above a low energy difference between the corresponding nitride phases. Indeed, the difference fraction points associated with (TiZrNbTaHf)N phase of the coatings deposited under $-100$ V and $-200$ V are in the intermediate position between stress-free TiN and HfN. This can be assigned to NaCl lattice dilatation due to random occupation of the metal sub-lattice sites by bigger atoms than Ti ($r_{\text{Ti}} = 1.40$ Å) such as Hf ($r_{\text{Hf}} = 1.55$ Å), Ta ($r_{\text{Ta}} = 1.45$ Å), Zr ($r_{\text{Zr}} = 1.55$ Å) and Nb ($r_{\text{Nb}} = 1.45$ Å).

MoN layers from investigated samples are polycrystalline exhibiting diffraction peaks related to cubic $\gamma$-MoN phase. Recently, I. Jauberteau et al. [104], have reported that there are three molybdenum nitride phases which are stable in thermal equilibrium ($\gamma$-MoN with cubic structure of NaCl B1-type, $\beta$-MoN – tetragonal modification of $\gamma$-MoN phase and $\delta$-MoN – hexagonal structure). Molybdenum nitride also can be synthesized in the thermodynamically unstable stoichiometric MoN phase of NaCl-B1-type cubic structure. The formation of such phase place demands high temperature and concentration of nitrogen. It should be noted that, it is difficult to determine the kind of phases of MoN from XRD studies. Especially it related to $\gamma$-MoN and $\beta$-MoN phases, which have a similar intense of reflection at low Bragg angles [4,105]. In our case, the lattice parameter of 0.416–0.418 nm of MoN (obtained from XRD peak positions) is close to the values obtained by Bull et al. [106], Hara et al. [107], Stöber et al. [108], which correspond $\gamma$-MoN phase of $\text{Fm3m}$ space group.

It was shown that the application of different substrate biases leads to microstructural modification in terms of the films preferred crystal orientation. At low $U_s$ a strong (111) and (311) peaks of (TiZrNbTaHf)N and (111) of MoN was found. Under higher energetic conditions (at $-300$ V) more closed packed (111) plane reduced and eventually disappeared (in the case of MoN) and there is an evolution of more open channeling planes: (200) of (TiZrNbTaHf)N and (220) of MoN. Such textural changes are known due to the competition between thermodynamic and kinetic forces: enhanced ad-atom mobility, plasma sheath, re-sputtering yield, anisotropy in surface diffusivities, cascade effects, free surface and strain energies.

It should be noted, that the more intensive (311) orientation, which is parallel to the sample surface. In contrast, the (111) orientation can attributed to the difference in growth rates between the two crystallographic planes and by a preferential re-sputtering of the N atoms lying on the (111) planes under high ion bombardment deposition at $-300$ V [109,110]. Moreover, the clearly visible XRD peak-shift of (TiZrNbTaHf)N reflections toward higher angle positions for the coating deposited under $-300$ V substrate bias is a consequence of the lattice shrinking. This is a result of the depletion of the plasma flow on big atoms that is well demonstrated by EDS analysis (Table 6). As a possible explanation of this depletion one can consider the increase of the target current during the deposition of the coating deposited under $300$ V. The increase of the target current from 90 A to 120 A, give rise to the increment of the target temperature, thus increasing its poisoning by N. The formation of the nitrides of the constituent elements on the target results in the preferential erosion of more easily eroded phases compared to HfN ($T_m = 3310$ °C) and TaN ($T_m = 3090$ °C) whose depletion is observed. This preferential erosion may subsequently influence the composition evolution of the plasma and the resultant film.

| Table 5 |
| Mixing energy ($E_{\text{mix}}$) for the ternary alloys. |
| Solid solution | $E_{\text{mix}}$ (meV/atom) | Solid solution | $E_{\text{mix}}$ (meV/atom) | Solid solution | $E_{\text{mix}}$ (meV/atom) |
| $Zr_{0.25}Ti_{0.25}Ta_{0.5}$ | -10.9 | $Zr_{0.25}Hf_{0.25}Ta_{0.5}$ | -7.8 | $Ti_{0.25}Hf_{0.25}Ta_{0.5}$ | -25.1 |
| $Zr_{0.25}Ti_{0.25}Ta_{0.5}$ | 13.1 | $Zr_{0.25}Hf_{0.25}Ta_{0.5}$ | -3.6 | $Ti_{0.25}Hf_{0.25}Ta_{0.5}$ | -4.8 |
| $Zr_{0.25}Ti_{0.25}Ta_{0.5}$ | 20.5 | $Zr_{0.25}Hf_{0.25}Ta_{0.5}$ | -1.9 | $Ti_{0.25}Hf_{0.25}Ta_{0.5}$ | -11.7 |

EDS quantification of metallic elements for (TiZrNbTaHf)N/MoN coatings deposited at $-100$ V, $-200$ V and $-300$ V substrate bias. (*- means that the element was not quantified due to its low concentration).

<table>
<thead>
<tr>
<th>$U_s$</th>
<th>Ti</th>
<th>Zr</th>
<th>Nb</th>
<th>Hf</th>
<th>Ta</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>16.07</td>
<td>12.10</td>
<td>5.34</td>
<td>12.16</td>
<td>10.91</td>
<td>43.41</td>
</tr>
<tr>
<td>200</td>
<td>15.66</td>
<td>11.44</td>
<td>10.35</td>
<td>6.39</td>
<td>6.03</td>
<td>50.13</td>
</tr>
<tr>
<td>300</td>
<td>43.23</td>
<td>13.01</td>
<td>19.45</td>
<td>-</td>
<td>0.08</td>
<td>24.23</td>
</tr>
</tbody>
</table>
composition visible as enrichment on Ti and Nb.

Recently, many works have shown the influence of substrate bias on the orientation of growth plane, like the transition from (111) to (200) preferred orientation in different nitride systems: Cr-Mo-N [111], Ti-Al-N [112], CrN/AlBN [113], TiAlN [114], TiN-MoS [115], TiAlSiN [116], (AlxCrNybSiz)2TiN, [117] and others [55,118,119]. However, the detailed physical mechanism of the development of preferred orientation under the influence of substrate bias is not yet fully understood.

The textural evolution of (TiZrNbTaHf)N/MoN multilayered nanocomposite coatings can be described through a complex of interplay between thermodynamic and kinetic forces, which have been recently studied for TiN [120–125]. From the point of view of modern thermodynamics, minimal total energy, which consist of surface, stopping and strain energy responsible for evolution of (200), (220) and (111) planes, respectively. According to this mechanism, the (111) crystallographic orientation is more favorable in the case of low ion-bombarding-energy conditions; this is due to the occupation of lower-energy position by the adatoms. In this case, the probability of growth of the (111) already nucleated grain is higher than the probability of nucleation of a new grain. Moreover, the higher Ti adatom mobility on (200) compared to (111) surface, for which Ti adatom chemical potential is μTi,111 < μTi,200 promotes Ti adatoms moving off the (200) islands and to their adjacent (111) grains. Thus, with increasing bias voltage the collision, and therefore the mobility of adatoms also increases, consequently the deposition conditions closely approach the thermodynamic equilibrium, which leads to prevailing of thermodynamic forces under kinetic regimes. Therefore, the development of planes with minimum surface energy during nucleation and coalescence stages, which is preferred to less compact (200) orientation, is observed under high ion irradiation conditions. Additionally, the increase of adatom mobility at 300 V increases the probability of (200) islands to expand laterally.

However, there are some works [126–129], which suggest that the model, which we have described above, is doubtful. Recently, different mechanism of growth process (anisotropy in surface diffusivities, collisonal cascade effects and adatom mobility’s) based on kinetic driving force was proposed [121,128,129]. The high-energy condition of deposition at 300 V leads to development and evolution of more open channel directions (e.g. 200, 220) due to the larger penetration depth of incident ions (collision cascade effects). The higher energy of ions leads to the increasing of density of defects, and as a result the most close packed plane (111) in FCC crystal structure become more affected by different type of cascades.

4.2. Mechanical properties

The main mechanism responsible for the hardening of the (TiZrNbTaHf)N layer is solid-solution strengthening due to impeding dislocation motion at local stress fields created by the solute atoms. The solid-solution hardening in the coating deposited at 300 V has lower contribution to the hardening because of lower amount of solute elements in the lattice.

Multilayer architecture allows to achieve higher hardness comparing with monolithic coatings due to the impeding dislocation motion across the interfaces and due to the difference in elastic modulus of the layers. Moreover, the enhancement of hardness is due to the reduction of grain size (Hall-Petch strengthening), which is a result of the increasing of volume fraction of grain boundaries with high interfacial energies [130]. The formation of strong MeN chemical bonds and low modulation period (5–20 nm) also a reason for the enhancements of hardness. In our case, the highest hardness 29 GPa has the coating with the thinnest bilayer period (20 nm).

The high H/E ratio imply that a typical tribo-contact during sliding/abrasive wear can remain elastic and recover due to the increased ability of the coating material to absorb energy during deformation up to fracture at high stresses. Therefore wear resistance of the coating with H/E × ratio in the range of 0.1 [131] can be improved at high loads due to absence of plastic deformation. The high H/E2 ratio means that the coating possess higher fracture toughness among the studied coatings suggesting that the resistance of the coating to the cracking sufficiently high and contributes to the protective efficiency of the coating exposed to the external load [132].

5. Conclusions

1. The deposited (TiZrNbTaHf)N/MoN multilayered nanocomposite coatings obtained by vacuum-arc deposition under different energy conditions have a complex chemical composition, which consists of nitrides of constituent elements. The presence of contaminations H+, C+, Na+, K+ and Cr+ ions from ambient atmosphere was found in the coatings.

2. The formation of (TiZrNbTaHf)N and MoN phases with FCC crystal structure was revealed in all coatings. The change of preferred orientation from (111) & (311) to less packed (200) under conditions of high substrate bias was observed. Using first-principles calculations it was shown that the metallic matrix of the (TiZrNbTaHf)N coatings can contain transition metal mononitrides and their solid solutions, depending on deposition conditions.

3. The HR-TEM observations revealed that the coatings have columnar growth and consist of multilayers with modulation period between 20 and 25 nm. The sub-grain structure of the columnar grains is composed of nanodimensional grains, which grow with local cube on cube epitaxy with coherent interfaces. The elemental inter-diffusion process between intrinsic layers was identified by EDS line scan.

4. The maximum hardness of approximately 29 GPa was obtained at a bias voltage of −200 V and the thinnest modulation period of bilayer (20 nm). The enhancement of mechanical properties was attributed to Hall-Petch strengthening, solid-solution strengthening, formation of strong MeN chemical bonds and low modulation period. Good ability to resist the plastic deformation (H/E2 ratio) allows to use (TiZrNbTaHf)N/MoN multilayered nanocomposite coatings as a protective materials.

Authors contributions


Acknowledgement

Presented work was financially supported by Erasmus Mundus Eminence scholarship and by budget programs “Development of material science basis of structural engineering vacuum plasma superhard coatings to achieve the required functional properties” (No 0115U000682) and “Multilayer and multicomponent coatings with adaptive behavior in wear and friction conditions” (No 0118U003579). A.P. gratefully acknowledge partial financial support from the National Science Centre of Poland within PRELUDIUM, under project number UMO-2015/19/N/ST5/01764.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compositesb.2018.04.015.
References


