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GRADIENT AND MULTI-LAYERED NITRIDE COATINGS DEPOSITED BY VACUUM-ARC METHOD

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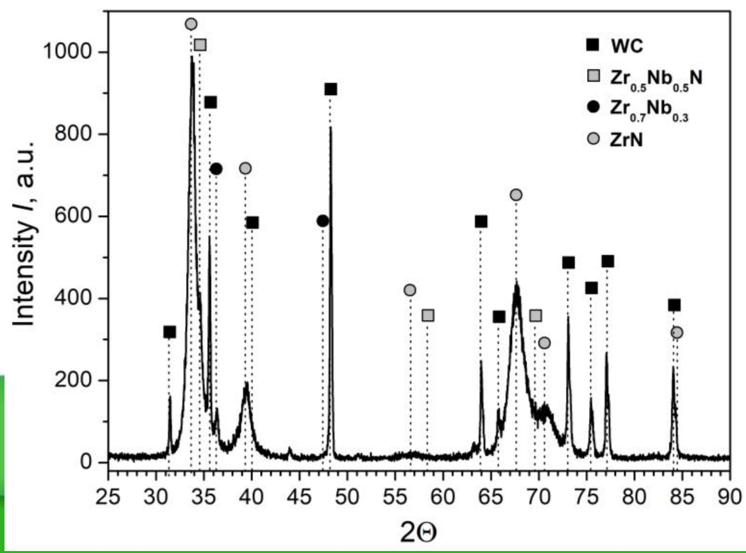
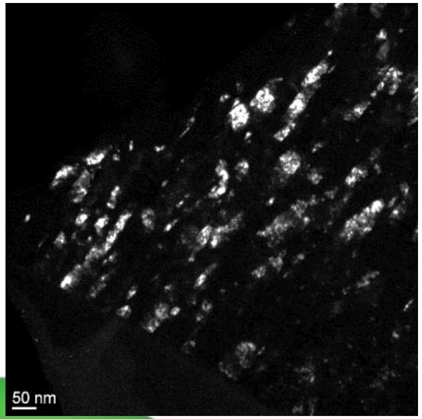
Introduction

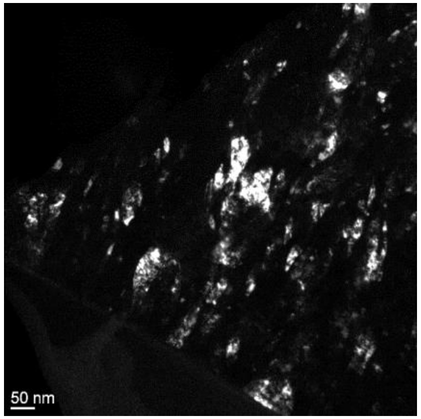
The synthesis of the ternary nitride coatings (ZrSiN, TiCrN, TiAlN, AlSiN, and ZrNbN) with a stoichiometric composition reduces their adhesive strength to the substrate due to high compressive stresses, which can destroy the coating. Thus, deposition of multi-layered coatings with alternating soft and hard layers or gradient composition is a potential solution. According to literature, the ZrN and (Zr,Nb)N homogeneous coatings offer good protective properties, such as high hardness and adhesion as well as increased wear, corrosion, and radiation resistance, and resistance to high-temperature oxidation. These systems have a high potential to provide scratch-resistant coatings that also satisfy decorative demands as well as the literature accounts of cutting tool applications for these system coatings. Practical applications of gradient and multi-layered (Zr,Nb)N coatings are not entirely defined because the amount of research is not sufficient. The scope of this coating can be analogical of ZrN and (Zr,Nb)N homogeneous coatings, but the aspects for their application is significantly high due to the properties mentioned above.

Results of earlier work. Single-layered (Zr,Nb)N coatings

№	I_{d1}, A	C_{Nb}, at.%	$HV_{0.03}$, GPa	E, GPa	W	μ_{av}	V, 10^{-5}, $mm^3/N \cdot m$
1	0	2,9	30,5	385	50	0,63	20,70
2	80	7,5	39,0	457	54	0,61	15,69
3	100	9,8	39,4	343	57	0,43	0,94
4	150	10,2	39,1	401	58	0,76	1,14





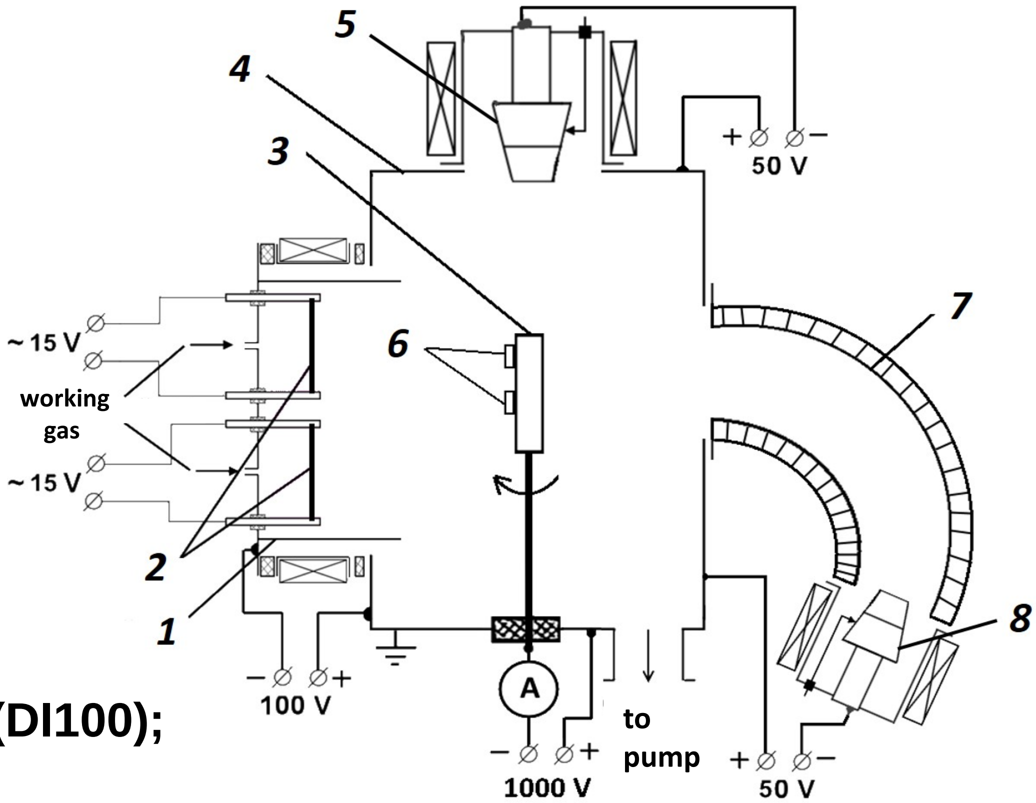


***h* = (7,0-22,8) nm;**
***d* = (2,9-7,4) nm.**

Goal of the present work:

- The deposition of gradient wear-resistant (Zr,Nb)N coatings using a vacuum-arc method, synthesized by varying ion current densities at the arc evaporation of a Nb cathode;
- The investigation of their structure, phase composition, and mechanical and tribological properties in detail.

QUINTA ion-plasma equipment



1 **– hollow cathode;**
2 **– thermionic cathodes;**
3 **– manipulator;**
4 **– anode (chamber walls);**
5 **– arc evaporator with Nb-cathode (DI100);**
6 **– specimens;**
7 **– magnetic filter housing;**
8 **– arc evaporator with Zr-cathode (DI80).**

Simplified scheme of experimental setup

Details of experiments

Materials of evaporated cathodes:

Zr-2.5 wt. % Nb zirconium alloy;
niobium alloy (99.8 wt. % Nb).

Materials of substrates:

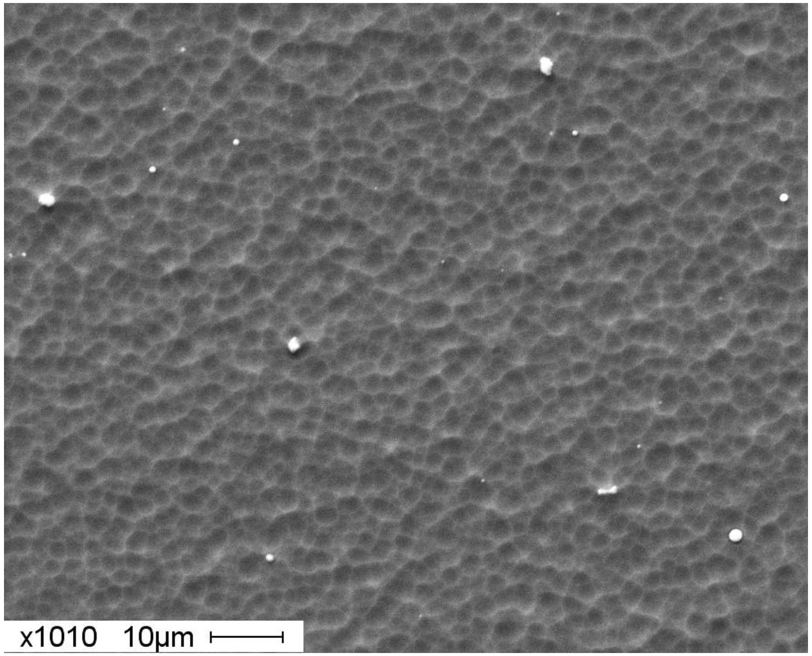
hard alloy WC-8%Co ($HV_{0.5}$ = 13.5 GPa);
commercially pure titanium Grade 2 ($HV_{0.5}$ = 2.2 GPa).

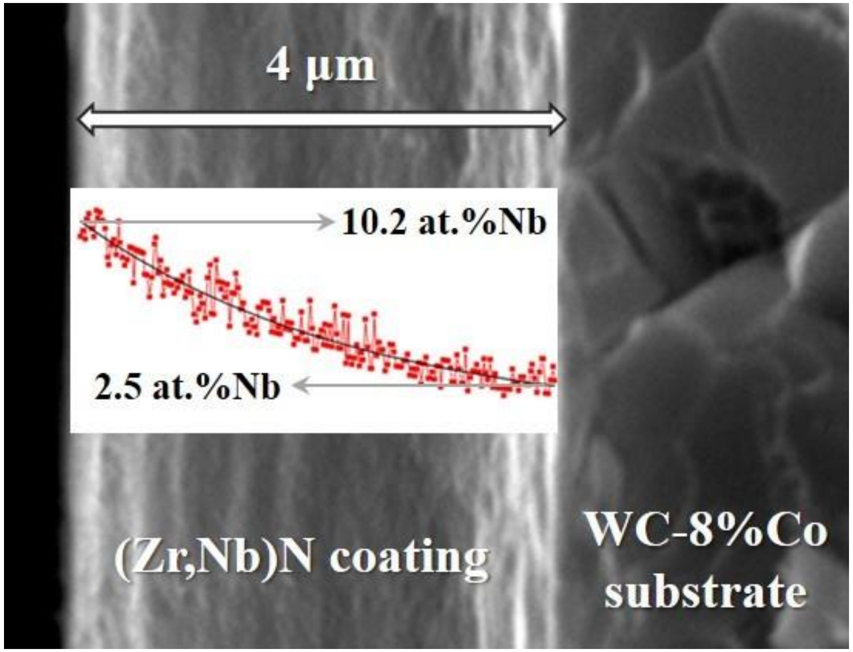
Parameters of vacuum-arc deposition of coatings:

$Ar/N_2 = 1$; p = 0,2 Pa;
I_{Zr} = 150 A;
I_{Nb} = 80÷150 A (j_{Nb} = 0.7–1.9 mA/cm^2);
U_b = -150 V;

- **the substrate holder rotation speed – 3 rpm;**
- **the (Zr,Nb)N coating growth rate – 4-5 μm/h.**

SEM images and elemental composition of (Zr,Nb)N coatings





The (Zr,Nb)N gradient coatings with a thickness of 3–4 μm did not have visible defects, such as spalls and delaminations, as confirmed by the results of scanning electron microscopy (SEM) investigations. The X-ray microspectral analysis supported the observation that the concentration of Nb increases from the substrate to the upper border from 2.5 up to 10.2 at.%.

Properties of (Zr,Nb)N coatings

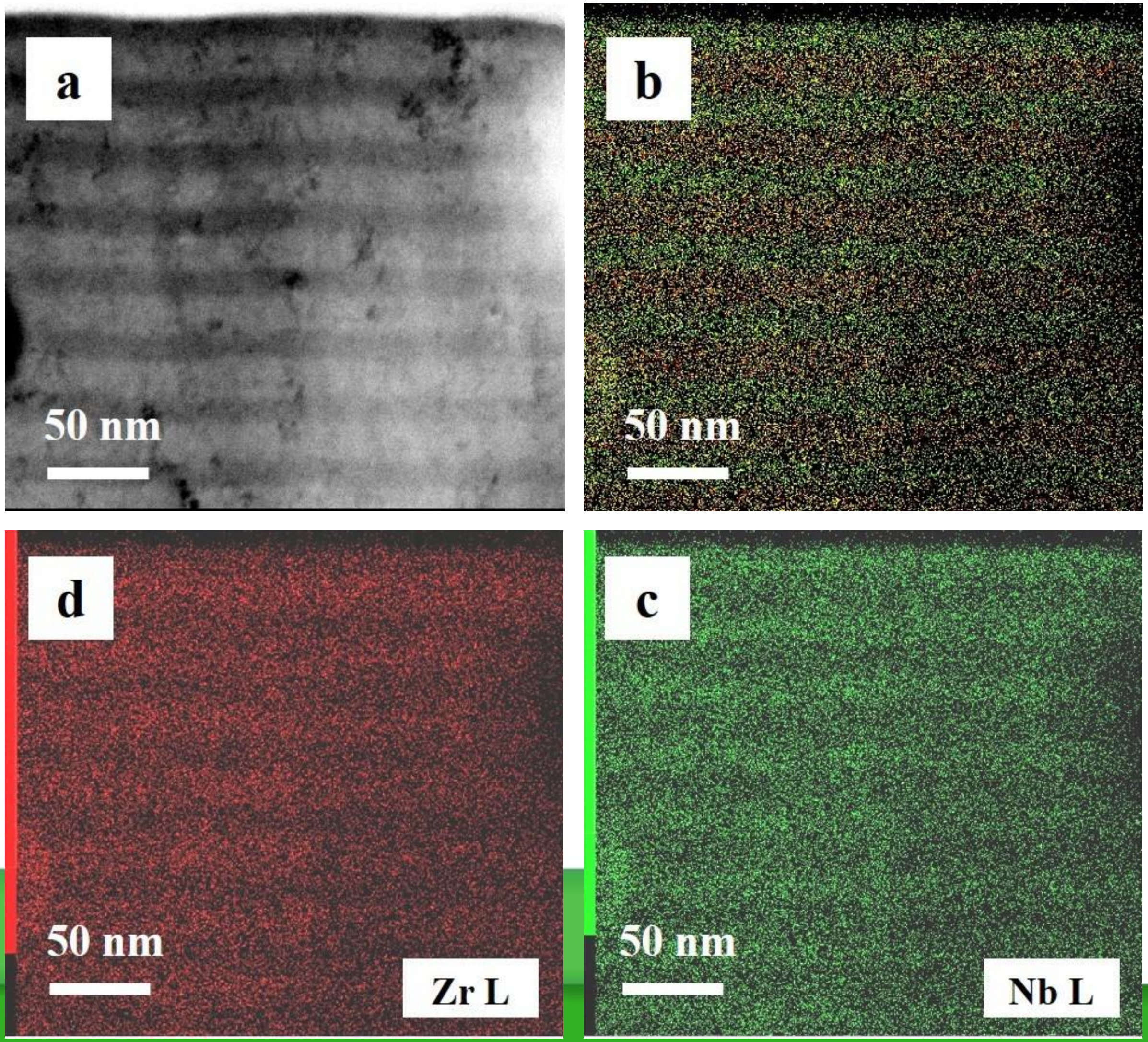
The roughness and tribological properties of the (Zr,Nb)N coatings

Type of coating	Roughness R_a, µm	Roughness R_z, µm	Friction coefficient µ	Wear rate V, $\cdot 10^{-6}$ $mm^3N^{-1}m^{-1}$
homogeneous	0.03	0.44	0.43	9.4
gradient	0.03	0.34	0.31	1.3

The nanoindentation study results for the gradient (Zr,Nb)N coatings

Load P_n, mN	Hardness HV, GPa	Young's modulus E, GPa	Elastic strain to failure H/E	Elastic recovery W, %
30	36.2	222	0.16	69
50	35.3	348	0.10	59
100	34.0	317	0.10	59

Elemental composition of (Zr,Nb)N coatings



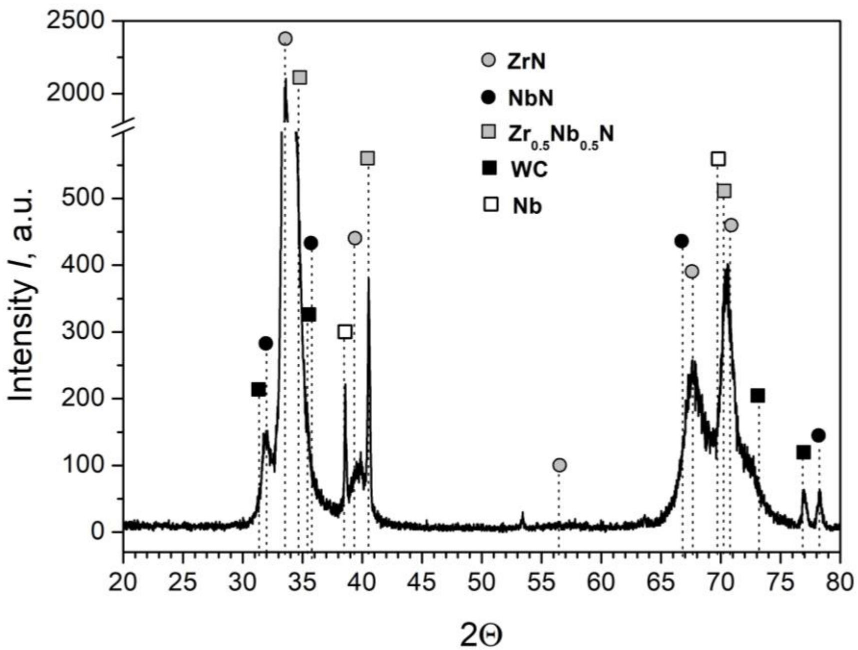
STEM images of (a) an area of the (Zr,Nb)N coating, in the characteristic X-ray radiation of (c) Nb and (d) Zr atoms, where (b) is an overlap of (c) and (d).

The analysis was carried out on the coating area in the near-surface region at approximately 4 μm from the substrate.

The thickness of the Nb-enriched layers varies from h_1 = 11.4–14.2 nm and that of the Zr-enriched layers varies from h_2 = 15.9–18.8 nm.

Phase composition and structure of (Zr,Nb)N coatings

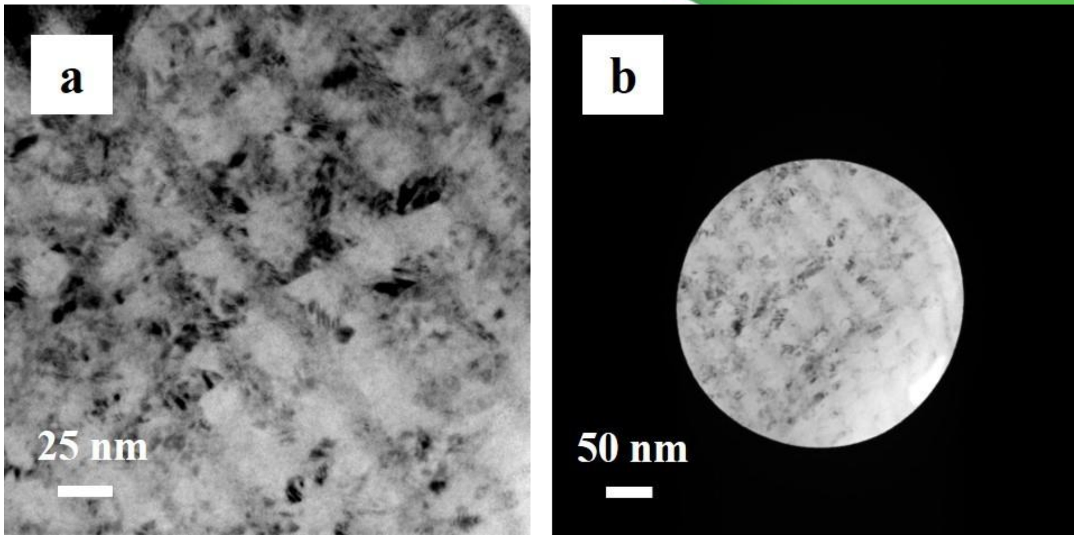
Revealed phases, crystal lattice type	Phase content, wt.%	Lattice parameters, Å	Crystal scattering region, nm	Lattice microdistortion $\Delta d/d$, $\cdot 10^{-3}$
ZrN, cubic	77.1	a = 4.5928	16.98	6.396
$Zr_{0.5}Nb_{0.5}N$, cubic	12.5	a = 4.4484	-	-
Nb, cubic	9.7	a = 3.2958	13.05	3.230
NbN, hexagonal	0.8	a = 2.9027 c = 2.7923	-	-



The X-ray diffraction pattern of the gradient (Zr,Nb)N coating synthesized on a WC–8%Co carbide substrate.

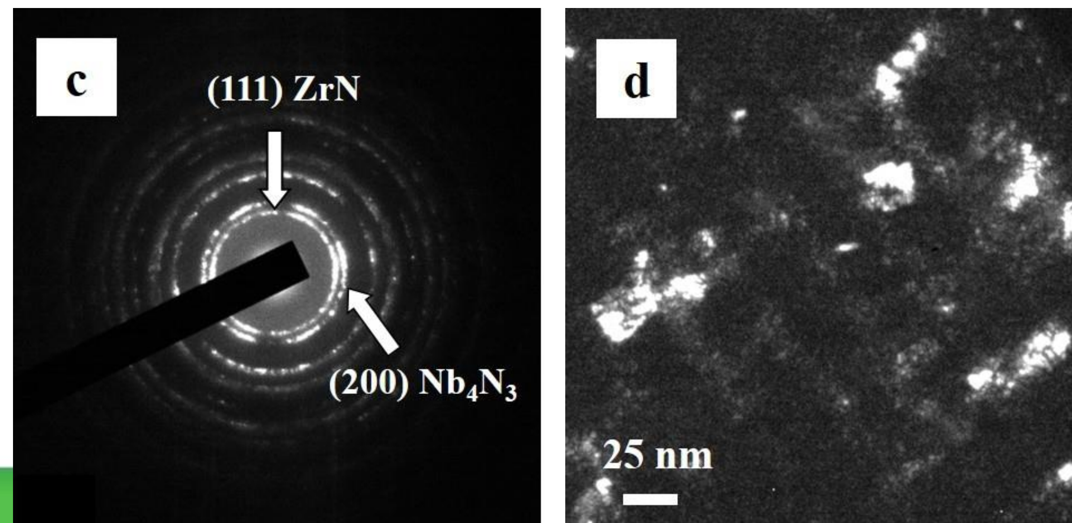
* The lattice parameter of ZrN crystallite for ZrN coating a = 4.6000 Å.
The Nb atom radius is 146 pm.
The Zr atom radius is 160 pm.

Structure of (Zr,Nb)N coatings



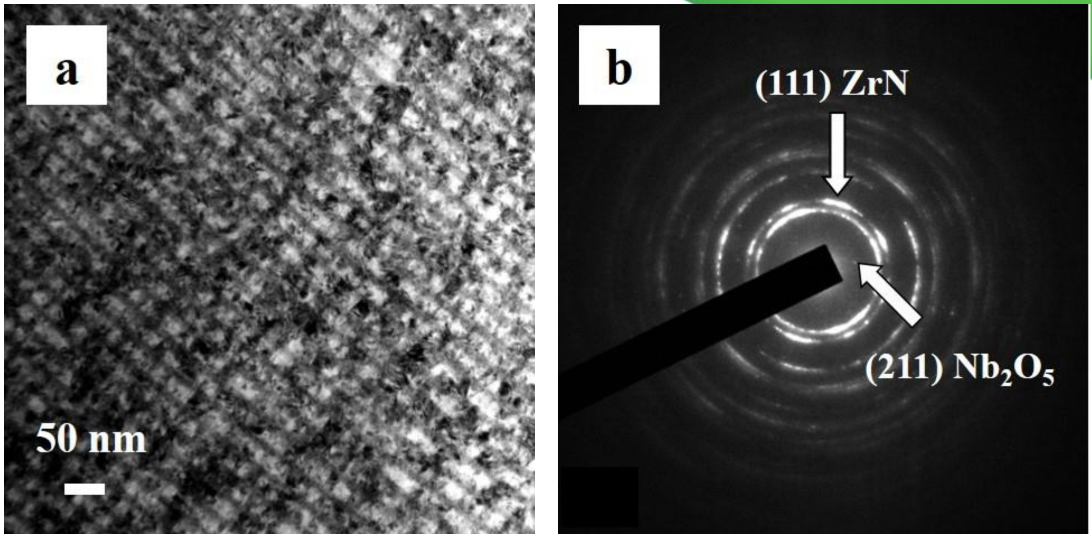
Electron microscope images of the (Zr,Nb)N coating structure of the near-surface region at approximately 4 μm from the substrate. Bright-field images in (a) and (b).

Micro-diffraction pattern in (c), and dark-field (d) obtained in the [111] ZrN phase reflex. The arrows indicate the [111] ZrN reflex on (c), and the obtained dark-field and the [200] Nb_4N_3 reflex (d).



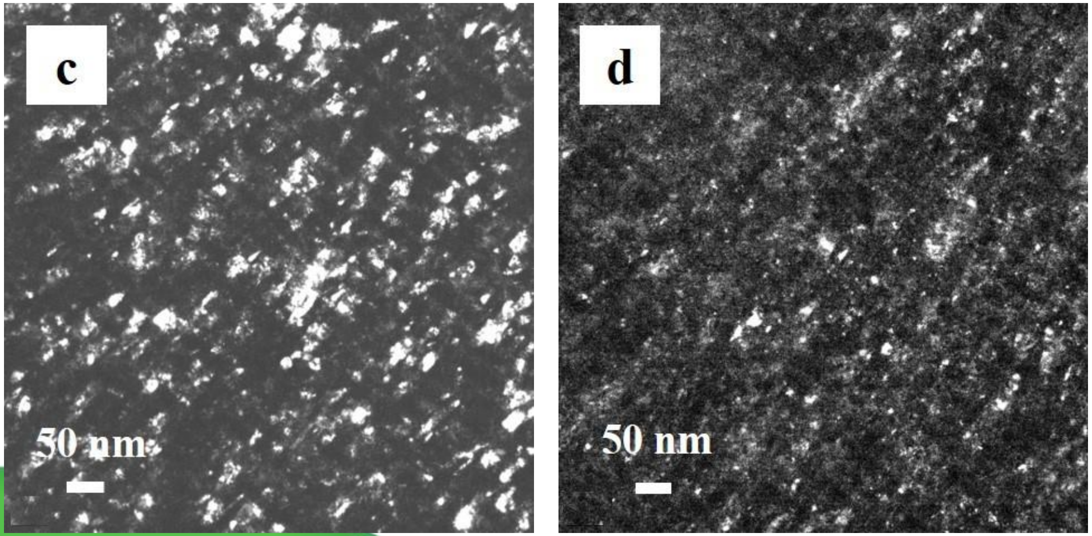
For the crystallites of the main phase (ZrN):
***h* = (5,8-17,0) nm;**
***d* = (2,4-6,9) nm.**

Structure of (Zr,Nb)N coatings



Electron microscope images of the (Zr,Nb)N coating structure of the central region at approximately 2 μm from the substrate. Bright-field image (a), micro-diffraction pattern (b).

Dark-field obtained in the [200] ZrN reflex (c), and dark-field obtained in the [211] Nb_2O_5 reflex (d). The arrows indicate the reflexes on (c) where the dark-fields were obtained.



For the crystallites of Nb_2O_5 *d* = (2,9-7,5) nm; for the crystallites of Nb_4N_3 *d* = (1,2-2,0) nm.

The TEM results show the phases of Nb_4N_3, Nb_2O_5, NbN, Nb_2N, $ZrN_{0.28}$, NbO_2, and ZrO_2.

Conclusion

Multi-layered gradient (Zr,Nb)N coatings were deposited with vacuum-arc evaporation of pure Zr and Nb metal cathodes. The gradient of the Nb concentration through the thickness was obtained by varying the arc discharge current with a Nb cathode within 80–150 A under the constant pressure of a working Ar/N_2 gas mixture and a constant current of arc discharge with a Zr cathode.

The synthesized (Zr,Nb)N coatings include a multiphase and multilayered nanocrystalline structure with alternation of only those layers with higher and lower Nb concentrations. These consist primarily of the ZrN crystallites with a cubic crystal lattice, and $Zr_{0.5}Nb_{0.5}N$, Nb, and NbN crystallites with the volume fraction of up to 23%. In addition, there exist a small amount (3%) of other phases with Nb_2N, Nb_4N_3, $ZrN_{0.28}$, NbO_2, Nb_2O_5, and ZrO_2. These coatings feature high hardness of up to 36.2 GPa, relatively low Young's modulus of 222 GPa, relatively high elastic strain to failure of approximately 0.2, high degree of elastic recovery of up to 69%, low arithmetic average surface roughness of 0.03 μm, low coefficient of friction of 0.31, and a low wear rate of $1.3 \cdot 10^{-6}$ $mm^3N^{-1}m^{-1}$. Therefore, deposited multi-layered gradient coatings have the potential for engineering applications for consumer products as they perform well as protective wear-resistant coatings.

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Thank you for your attention !!!

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