

Proceedings of the IX International Conference ION 2012, Kazimierz Dolny, Poland, June 25–28, 2012

Multicomponent (Ti–Zr–Hf–V–Nb)N Nanostructure Coatings Fabrication, High Hardness and Wear Resistance

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First results in the field of synthesis and research of the multicomponent (Ti–Zr–Hf–V–Nb)N nanostructured coatings are presented in the paper. Influence of processes of spinodal segregation and mass-transfer on single-layered or multilayered crystal boundary (second phase) forming were explored. Superhard nanostructured coatings were investigated before and after annealing at the temperature 600 °C using unique methods (slow positron beam, proton microbeam particle induced X-ray emission- μ , Rutherford backscattering-analysis, scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffraction analysis was performed using DRON-4 and nanoindentor). Diffraction spectra were taken point-by-point, with a scanning step $2\theta = 0.05$ to 0.1° . We detected that positron trapping by defects was observed on the nanograins boundaries and interfaces (vacancies and nanopores which are the part of triple and larger grain's boundary junction). The 3D distribution maps of elements obtained by the proton microbeam (particle induced X-ray emission- μ) together with the results obtained by slow positron microbeam gave us comprehensive information about physical basis of the processes, connected with diffusion and spinodal segregation in superhard coatings.

DOI: [10.12693/APhysPolA.123.816](https://doi.org/10.12693/APhysPolA.123.816)

PACS: 61.46.–w, 62.20.Qp, 62.25.–g

1. Introduction

One of the most important tendencies of modern science is constructing new materials, in particular, creation of multicomponent nanocomposite coatings with the grain characteristic dimensions between 2 and 50 nm. Nanocomposite coatings are the new generation of materials [1–3]. They consist at least of two phases with nanocrystal and/or amorphous structure. Due to small (≤ 10 nm) grain size and more important role of surrounding boundary zones nanocomposite materials act differently and show absolutely different properties in comparison with common materials (with the grain size ≥ 100 nm) [3, 4]. Therefore, creation and study of new nanocomposite (nanostructure) (Ti–Zr–Hf–V–Nb)N coatings using vacuum-arc deposition is a topical problem.

It is well known that Hf, Zr and Ti form continuous hard solutions with each other and have fcc crystal lattice at room temperature and bcc crystal lattice at higher temperatures. Nb and V form a continuous series of solid solutions. At the same time, Hf, Zr, Nb and V

are β -stable for Ti. In this combination both Nb and V (regulators for the fcc lattice), and high-melting elements Hf, Zr, Ti due to high similarity to nitrogen [5] provide an opportunity to form a nitride phase, based on a high-entropy single-component alloy.

Positron annihilation (feasible interval of defects analysis is in the range from 10^{-6} to 10^{-3} defects per atom) is one of the most effective, sensitive and reliable methods of studying unconfined spaces in nanocrystal materials, including compaction ones. Part of positrons can be captured in the boundary of two neighbouring nanograins or in the junction of three neighbouring nanocrystallinities. It gives an opportunity to solve one of the most complicated and interesting problems of understanding interface regions structure (including electron one), because interface regions length or volume defines basic properties of nanocomposite coatings.

2. Results and discussion

The results of the Rutherford backscattering spectroscopy (RBS) (Fig. 1a,b) and energy dispersive X-ray spectroscopy (EDX) analysis (see Table) indicate that the certain stoichiometry formed in the obtained coatings, strongly depends on the bias potential, which is applied to substrate. In other words, at the expense of bias potential increasing energy of ion-plasma flux also

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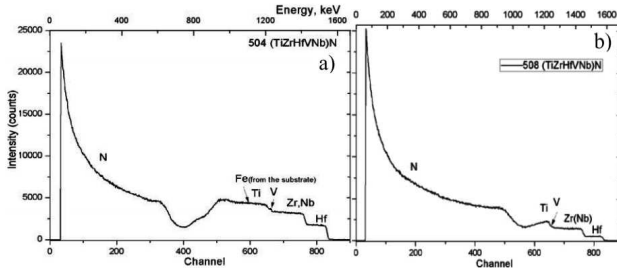


Fig. 1. Results of the RBS analysis spectra for the samples #504 (a) and #508 (b).

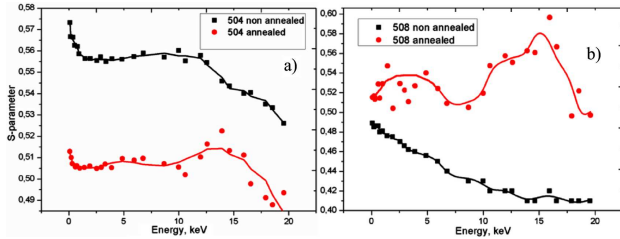


Fig. 2. Dependences of the S -parameter of the annihilation peak of the Doppler shift, which is measured through the thickness of the coating (Ti-Zr-Hf-V-Nb)N in the samples #504 (a) and #508 (b) after deposition and after annealing at 600 °C (50 mbar).

increases, which leads to much higher radiation component. It is well known that in order to form a two-phase nanostructure coating, it is necessary and convenient to increase velocity of atomic diffusion on the grains boundaries, and to keep high temperature (up to 600 °C) from the moment of deposition till the end of spinodal segregation process.

Experimental works show that positrons are located in the regions with lower electron density (i.e. on the vacancy defects — divacancies, conglomerate of vacancies of different types, complexes, made of vacancy and two or three interstitial atoms [6, 7]). As follows from the experimental works, nanostructure materials, which were formed using compaction, seem to be a good baffle for positrons, which annihilate with two or three components of positron lifetime τ_2 , τ_3 , it is connected with the positron annihilation on the grains boundary i.e. quasi-amorphous phase in our case. In Fig. 2a,b it is well seen that defect profiles (S -parameter) significantly differ in the case of different deposition conditions i.e. (V [V] — potential on the substrate and P [Pa] — nitrogen pressure in the chamber), for example have a look at the samples series #504 and #508. At the same time, annealing in the vacuum chamber using rather high residual atmospheric pressure, leads to much higher S -parameter changing through the coating thickness. For the samples series #504 S -parameter changes from $0.58 \div 0.56$ to $0.52 \div 0.51$ after annealing, and only when the positron energy reaches the value $12.5 \div 15$ keV, increase of S -parameter up to value of 0.53 can be observed. For the samples series #508 (Fig. 2b), after the analysis of

TABLE

Parameters of the Ti-Zr-Hf-V-Nb coating deposition, crystallites sizes and hardness for different samples series. El. — element, C — concentration [at.%], P — nitrogen pressure in the chamber [Pa], D — crystallites average size [nm], H — hardness [GPa].

No.	El.	C	P	D	H	V
#504	Ti	44	5×10^{-3}	12	-	-200
	Zr	30				
	Hf	14				
	V	5				
	Nb	5				
	N	2				
#505	Ti	14.85	7×10^{-4}	50-85	50-55	-150
	Zr	13.89				
	Hf	37.45				
	V	5.61				
	Nb	15.37				
	N	12.83				
#508	Ti	57	8×10^{-4}	15	-	-100
	Zr	18				
	Hf	13				
	V	5				
	Nb	5				
	N	2				
#509	Ti	23.04	6×10^{-4}	48-50	45-50	-200
	Zr	13.18				
	Hf	33.34				
	V	4.42				
	Nb	14.12				
	N	11.9				
#510	Ti	18.46	3×10^{-4}	55-57	58	-200
	Zr	13.47				
	Hf	33.71				
	V	5.64				
	Nb	15				
	N	13.72				
#511	Ti	50	8×10^{-4}	17-22	-	-50
	Zr	23				
	Hf	15				
	V	5				
	Nb	5				
	N	2				

Elementary composition was obtained using RBS-method (samples #504, #508, #511) and using EDS JEOL-7000F method (samples #505, #509, #510).

S -parameter dependence in the initial state (after deposition), one can see that there are no positron-sensitive defects through the thickness of the coating, that is why S -parameter is minimal and equals 0.49. After annealing to the temperature 600 °C S -parameter significantly grows to a value of 0.53 in the near-surface regions, and with the depth increasing, S -parameter also increases and approaches the maximal possible value 0.59. In this case the positron energy changes from 14 to 17 keV.

It is well known that S -parameter depends on the concentration of vacancy defects and on their type [2, 6, 7]. In a strong-structured coating sample #504 with high level of compression strain (8 GPa) and deformation strain equals 2.59%, we found high resistance to oxide formation after annealing (5×10^{-3} , -200 V). It is connected with low oxygen diffusion deep into the coating and with high degree of filling of octahedral interstitial with nitrogen atoms during the process of coating forming under high pressure of nitrogen in the working chamber. Thus, there is no nitride interlayer between the nanograins in this system (due to bad diffusion and high compression stresses); probably there is not enough annealing temperature or energy for interlayer forming. That is why the main source of nitrogen atoms for creation of nitride interlayer is the boundary interphase “coating-substrate” (see S -parameter dependence, where the maximum value 0.56 is observed when the positron beam energy is 15–16 keV).

For the samples series #508 (-100 V), elastic strain is less than the compression stress (1.9% of compression stress). It stimulates diffusion processes, either for nitrogen atoms or for oxygen atoms near to surface, that is why we can see two peaks on the S -parameter plots, when the positron beam energy is $3 \div 5$ keV and $14 \div 17$ keV. It means that new channels for positron annihilation appear. After annealing, defects are well seen on the interphase boundary, and these defects attract positrons with much higher efficiency or much higher velocity. New quasi-amorphous nitrides phases appear as a result. Particle induced X-ray emission- μ (PIXE- μ) analysis confirms these results and shows that oxide film is forming on the surface, due to it S -parameter grows, and inside the coating redistribution of elements can be observed. It means that our theory about ending the process of spinodal segregation and new phases forming on the nanograins boundaries is correct (more details are given in [7–9]).

During annealing up to the temperature 600°C (900 K) grains growth is obviously the most important mechanism of structure relaxation. Nitrogen segregation on the grains interfaces decelerates nanocrystal growing. For the samples series #504 an average size of nanograins is $55 \div 58$ nm, but after thermal annealing it goes up to $67 \div 70$ nm (according to the XRD analysis data using the Debye–Scherrer method). The diffusion length of positrons is $L^+ \approx 100$ nm, it is much higher than nanograins size. According to common theoretical and experimental works, nanopores are usually distributed on the cross-sections of three and more interphases, positron lifetime components intensity relations have to decrease

while crystallite sizes increase. That is why decrease of S -parameter intensity (sample series #504) can be explained by annealing of chilled thermal or interface vacancies. Nanohardness measurements (see Table) shows that the largest hardness $H = 58$ GPa (according to the modern classification the term superhardness [1, 3] can be used) is formed in the coating, when the bias potential during deposition is -200 V.

Acknowledgments

This work has been done under financial support of the Ministry of Science and Education, Youth and Sports of Ukraine within the government program (order No. 411), as well as with funding from the Ministry of Education and Science of the Russian Federation in the framework of State contract No. 16.552.11.7087 and in the collaboration with the National Institute of Material Science, Tsukuba, Japan, Martin-Luther Universität Halle–Wittenberg, Ion Beam Center HZDR, Dresden and, partially, within the project SFFI-041/20, Ukraine. The authors acknowledge Dr. A.A. Andreev (Kharkov, Ukraine) and Dr. G. Abronzis (Dresden, Germany) for their help in conducting these experiments.

References

- [1] A.D. Pogrebnjak, A.P. Shpak, N.A. Azarenkov, V.M. Beresnev, *Phys. Usp.* **52**, 29 (2009).
- [2] A.D. Pogrebnjak, A.G. Ponomarev, A.P. Shpak, Yu.A. Kunitskii, *Phys. Usp.* **55**, 270 (2012).
- [3] J. Musil, *Surf. Coat. Technol.* **125**, 322 (2000).
- [4] S. Vepřek, *J. Vac. Sci. Technol. A* **17**, 2401 (1999).
- [5] S.-C. Liang, D.-C. Tsai, Z.-C. Chang, T.-N. Lin, M.-H. Shiao, F.-S. Shieu, *Electrochem. Solid-State Lett.* **15**, H5 (2012).
- [6] V.I. Lavrent'ev, A.D. Pogrebnjak, A.D. Mikhalev, N.A. Pogrebnjak, R. Shandrik, A. Zecca, Yu.V. Tsvintarnaya, *Techn. Phys. Lett.* **24**, 334 (1998).
- [7] V.I. Lavrent'ev, A.D. Pogrebnjak, R. Sandrik, *JETP Lett.* **65**, 651 (1997).
- [8] A.D. Pogrebnjak, A.P. Shpak, V.M. Beresnev, D.A. Kolesnikov, Yu.A. Kunitskii, O.V. Sobol, V.V. Uglov, F.F. Komarov, A.P. Shpylenko, N.A. Makhmudov, A.A. Demyanenko, V.S. Baidak, V.V. Grudnitskii, *J. Nanosc. Nanotechnol.* **12**, 9213 (2012).
- [9] A.D. Pogrebnjak, Zh.M. Ruzimov, D.L. Alotseva, P. Żukowski, C. Karwat, C. Kozak, M. Kolasik, *Vacuum* **81**, 1243 (2007).