GENERAL REGULARITIES AND DIFFERENCE OF NANOSTRUCTURED COATINGS BASED ON NITRIDES OF Zr, Ti, Hf, V, Nb METALS AND THEIR COMBINATIONS

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Abstract

Using the vacuum-arc source with the HF discharge, nano-structured hard and super-hard coatings based on Ti-Hf-N(Fe), Ti-Hf-Si-N, Ti-Zr-Si-N, and (Ti, Zr, Hf, Nb, V)N of 1.2μm to 2.5μm thickness were manufactured. The coatings were studied using the proton micro-beam μ-PIXE, RBS, SIMS, SEM with EDS, XRD, and tested for adhesion resistance, wear, and nano-hardness. It was found that a concentration of Ti, Zr, Hf, V, and Nb metals as well as a bias potential applied to a substrate and residual pressure in a chamber (N or Ar/N) affected the formation regularities of solid solutions and quasi-amorphous phases based on α-Si_3N_4. Hardness of the resulting coatings reached 48GPa to 52GPa, their elastic modulus was 420GPa to 535GPa. The friction coefficient was 0.12 to 0.2, and temperature resistance was as high as 1300°C.[1]

Coating structures varied from a columnar to a nanosized one. Grain sizes of the phases of the solid solutions were from 4nm to 10nm or 12nm. Those of α-Si_3N_4 inter-layer were from 0.8nm to 1.2nm.

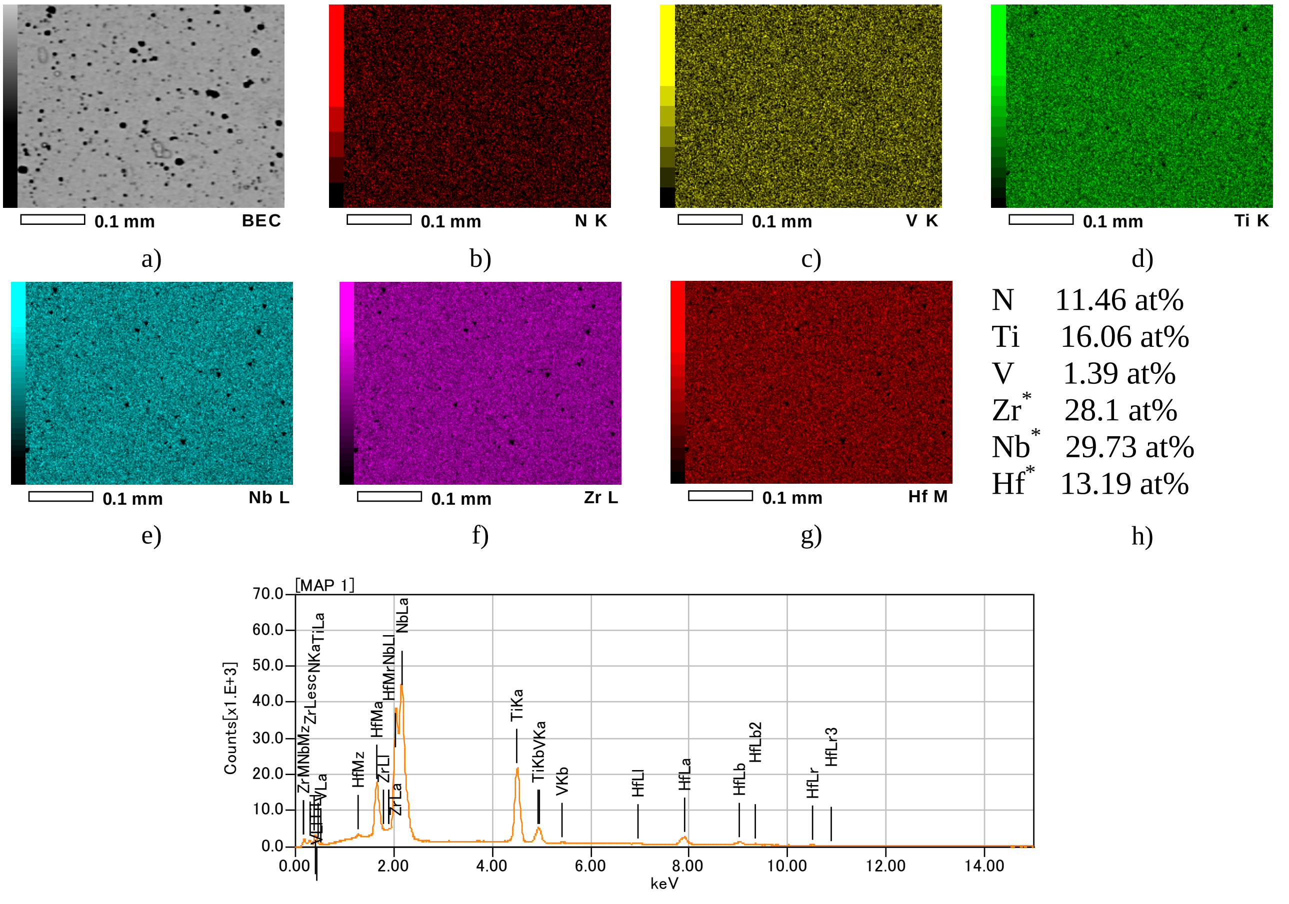
Keywords: super-hardness, adhesion, friction, nano-grains, thermal stability

I Introduction

The purpose of the given work is creation of the new multycomponent nanostructure coatings based on (Ti-Zr-Hf-V-Nb)N using the cathode vacuum-arc deposition, investigation of its structure, morphology, physical-mechanical and frictional properties. As the cathode we used material, melted from the powder with (Ti; Zr; Hf; V; Nb)N composition on the device, being well described in the work [1,2].

For element and composition analysis we used such methods, as scanning electron microscopy with microanalysis (EDS), on Jeol 7000 F, Japan; RBS analysis on ion accelerator 4.5 MeV Tandentron, NIMS, and on another ion accelerator, Van de Graaff, Dresden, with ion energy 2MV, and we built element profiles through the coating thickness and detected stoichiometry of the coating. We investigated structure and phase composition using XRD analysis in sliding geometry on the device XPert PANanalitical (Holland), U = 40kV, I = 40 mA, cathode – copper. Also, on the samples with coatings we made cross-sections (using ion-beam) in order to analyze its structure, thickness and coating morphology. Nanohardness and elasticity modulus were detected using nanoindentor Nanoindentor II GSM, frictional characteristics were explored using equipment Revetest, Belgorod State University, Russia. On separate samples with coatings we obtained profiles of defects through the coating thickness using slow beam of positrons at the Halle University, Germany. Deposition of the sample was held in the chamber with a residual pressure of P = 8×10^{-4} to 5×10^{-3} Pa, potential applied to the steel substrate U = 40 - 200 V, with concentration of coating elements changes, for example, for N from 8.4 to 16 at.%, for Ti from 14.8 to 27 at.%, for V from 1.4 to 5.6 at.%, for Zr from 13 to 28 at.%, for Nb from 13 to 29.7 at.%, and for Hf from 13 to 37 at.%.

As the example, on the fig. 1 we presented map of the (Ti-Zr-Hf-V-Nb)N coating surface in the element contrast. Sample spectrum was shown on the insertion. Analysis of defects through the coating thickness was shown on the fig. 2a. It is obvious, that positron beam energy is enough for penetration through the coating thickness. Annealing with the step 150^0C up to the temperature of 600^0C, spinodal segregation ending on the boundaries of the grains showed, that some part of positrons actually annihilates on the vacancy defects, laying on the grains boundaries. Further XRD analysis showed, that in the system, made of Hf-Ti-Si-N, an amorphous α-Si_3N_4 phase was formed with the high weighting ratio in comparison with the coating, which was obtained using the deposition method (under room temperature). From theoretical works [3] it is well-known, that maximum hardness and plasticity of nanocomposite coatings is reached when interphase boundary between nanograins is 1 ML or less, and volume fraction of the interphase boundary is 30-50%.



a) b) c) d)

e) f) g)

N	11.46 at%
Ti	16.06 at%
V	1.39 at%
Zr^*	28.1 at%
Nb^*	29.73 at%
Hf^*	13.19 at%

h)

i)

Fig. 1. Element composition of the coating made of (Ti-Zr-Hf-V-Nb)N in contrast of elements (colored images MAP); a), b), c), d), e), f), g) – energy-dispersive spectrum, obtained on the coating; h) – concentration of elements in the coating, measured in atomic percent.; i) – EDS spectrum of the coating.

From the results presented on Fig. 2 a, b it is clearly seen that the defect profiles (S-parameter) vary significantly for different deposition conditions (for example see samples 504 and 508). At the same time, annealing in vacuum chamber with a sufficiently high residual atmosphere pressure leads to even greater changes (S-parameter) at a depth of coating.

In case of sample 504, the value of S-parameter decreases from (0,58 ÷ 0,56) to (0,52 ÷ 0,51) after annealing and only approaching to the energy (12,5 ÷ 15) keV of positron analyzing the magnitude of S-parameter increases to 0.53. In case of sample 508 (Fig. 2b) S-parameter before annealing does not show any defects in depth and it's value is minimal, i.e. 0.49. But after annealing up to 600ºC, it's value increases significantly to 0.53 in the surface layer of coating, and then increases with depth from the positron energy (10 – 17) keV, while the value of S-parameter increases further and becomes maximum, approaching 0.59 (the maximum possible value).

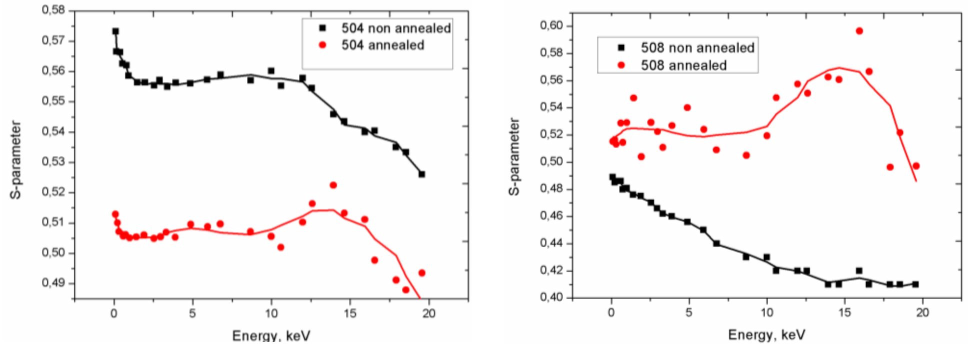


Fig. 2a, b Dependence of S-parameter of Doppler broadening of the annihilation peak measured at a depth of coating (Ti,Zr,Hf,Nb,V)N (samples 504 (a) and 508 (b)) before and after annealing up to 600ºC (50 mbar).

According to Fig.3, in direct-flow mode without separation the non-textured polycrystalline coatings are formed. Rather high intensity of the peaks at XRD-patterns of (Ti,Hf)N solid solutions is attributed to relatively large concentration of hafnium, which has larger reflectance value than titanium.

In case of beam separation the coatings have different texturation. At low substrate potential (100 V) coatings have [110] texture, and coatings consist of textured and non-textured crystallites. The volume content of textured crystallites is about 40% of total amount of the crystallites, and their lattice parameter enlarged in comparison to non-textured crystallites. We suppose that the increased lattice parameter may be caused by the inhomogeneous distribution (mainly in the lattice sites of the textured crystallites) of the hafnium atoms in coating.[4,5,6]

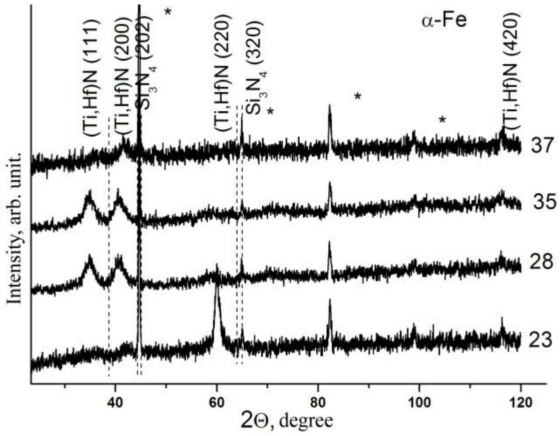


Fig. 3 XRD spectra of the coatings deposited on a steel substrate at modes (1-(23) – 100V, separated, 2-(28)-200V, non separated, 3 (35)-100V, non separated, 4 (37)-200V, separated).

Conclusion

Thus, in the work we studied the processes of impurities segregation on the boundaries of nanograins after finishing of the process of spinodal segregation. We used the unique methods of analysis: SEM with EDS, XRD, Nanoindentor, Test “Revest”, Positron Microbeam (Positron Annihilation), Microbeam (PIXE, RBS) Finally, we obtained solid multycomponent nanostructure coatings (Ti-Zr-Hf-V-Nb)N with high physical and mechanical properties.

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