THE FORMATION OF SUPERHARD COATINGS ≥ 48 GPa IN TI-HF-N (Fe) AND ANALYSIS OF THEIR STRUCTURE AND PROPERTIES.

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Abstract

Superhard nanostructured Ti–Hf–N(Fe) coatings are prepared. The formation of local regions of (Ti, Hf)N, FeN, and Hf is detected using μ-PIXE (ion microbeam). It is revealed that the synthesized coatings have a nanohardness of 48 ± 1 GPa and are composed of nanograins with a size of 4.8–10.6 nm, which are enveloped by finer entities of other phases (Ti, Fe)N and FeN. There is a good correlation between the results derived by XRD, TEM, AFM, and SEM and microanalysis, which in turn are complemented by the analysis results obtained using an ion microbeam and PIXE.

Keywords: Superhard, nanostructured, Ti–Hf–N(Fe), μ-PIXE, ion microbeam, nanohardness.

I Introduction

It is known that the unique properties of nanostructured nanocomposite coatings are a high volume fraction of the interfaces and their strength, the absence of dislocations inside the crystallites, the possibility of changing the ratio of fractions of the crystalline and amorphous phases, and the mutual solubility of the metallic and nonmetallic components [1–3]. The strength of the interface contributes to an increase in the strain resistance of nanostructured coatings, and the absence of dislocations inside the crystallites increases the elasticity of the coatings. Therefore, it is a high priority problem of materials science and solid state physics to study the physical causes of the high physicomechanical properties of nanostructured materials (coatings). Ti–Hf–N(Fe) films with a thickness of 1.5 μm were deposited on steel samples with a diameter of 20 and 30 mm and a thickness of up to 3 mm in a vacuum chamber using a vacuum arc source in a high-frequency (HF) discharge and employing a Ti–Hf(Fe) cathode (sintered by an electron gun in an Ar atmosphere). The deposition parameters are listed in the table 1.

Experiment and discussion

To analyze the properties of the Ti–Hf–N(Fe) coatings, we used a scanning nuclear microprobe based on an electrostatic accelerator designed at the Institute of Applied Physics, National Academy of

Sciences of Ukraine [3]. Analysis was performed using Rutherford backscattering (RBS) and proton induced characteristic X-ray emission (PIXE and μ-PIXE) at an initial energy of Ep = 1.5 MeV, a beam size of 2-4 μm, and a current of $\approx 10^{-5}$ A [5]. The total PIXE spectrum was analyzed using the GUPIXWIN software, which provided information on the quantitative content of elements and stoichiometry. To compare the elemental composition and to analyze the morphology, we used a Quanta 200 scanning electron–ion microscope with an EDS detector. A Bulat-3T vacuum arc source with an HF generator was used [5]. A bias potential was applied to the substrate from the HF generator, which generated decaying oscillation pulses at a frequency of ≤ 1 MHz, Ti–Hf–N(Fe) coating deposition parameters; crystallite sizes and hardness for different sets of samples. A pulse duration of 60 μs, and a repetition frequency of 10 kHz.

Table 1 – Deposition parameters and coatings characteristics of Ti–Hf–N(Fe).

No.	P, nitrogen pressure in the chamber, Pa	Substrate potential, V	Nanohardness, GPa	Average crystallite size, nm
7(direct)	0,3	-200	41.82	6.4
11(separated)	0,5	-200	47.17	4.8

The negative substrate auto-bias voltage, owing to the HF diode effect, was 2–3 kV. In addition, we used an RBS scheme with 1.3-MeV He^+ ions, a registration angle of $\theta = 170°$, and a detector resolution of 16 keV. The dose of helium ions was ≈5 μs [5]. XRD analysis of the nanostructured films was carried out using two diffractometers: DRON-4 and X'Pert PANlytical (Holland) with a step size of 0.05° at a tube voltage of U = 40 V and a current intensity of I = 40 mA; the emitter was copper Cu$K\alpha$. The analysis of morhology, structure, and elemental composition on the cross sections of the coatings was performed using a Quanta 200 3D scanning electron–ion microscope. The mechanical properties i.e., hardness, nanohardness, and elastic modulus were studied using two Nanoindentor G 200 instruments (MES System, United States) employing Berkovich and Vickers pyramids; in addition, we employed a Rockwell C indenter with a radius of curvature of about 200 μm. Figure 1 shows the distribution maps for the elements in the coating, which were obtained using an ion microbeam, depending on color (dark regions with a low concentration, lighter regions with a high concentration of elements).

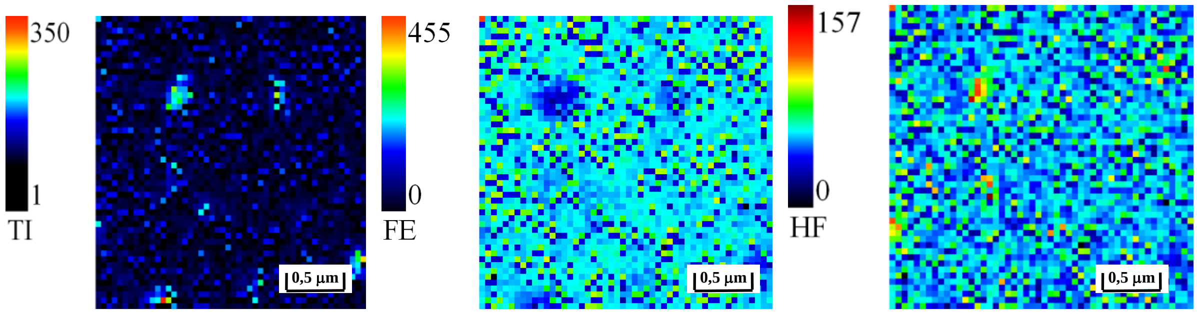


Fig. 1. Element (Ti; Hf; Fe) distribution maps derived for the steel samples with a deposited Ti–Hf–N(Fe) coating. In particular, there are local regions with sizes of from 2–4 to 6–10 μm that consist of Hf and Ti inclusions, in which the concentration of Fe greatly decreases.

The PIXE-derived quantitative analysis and its stoichiometry are represented in Fig. 2. The results (the concentration integrated over depth is about 2 μm) show that a thin AlC film is formed on the surface, which is probably the result of exposure to a proton beam, and the main concentration of the elements is as follows, at %: Fe ≈ 77, Ti ≈ 11, Hf ≈ 11.05, Mn ≈ 0.9, and Cr =0.01; the last-mentioned elements apparently are part of the substrate.

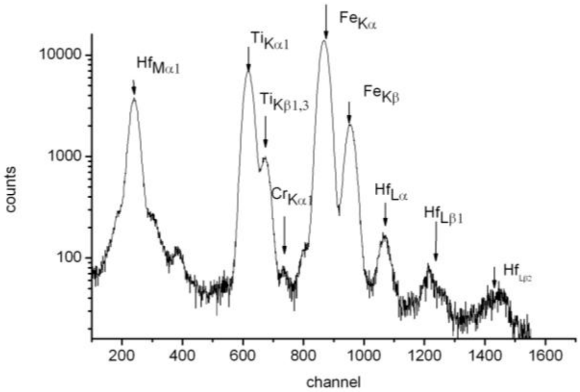
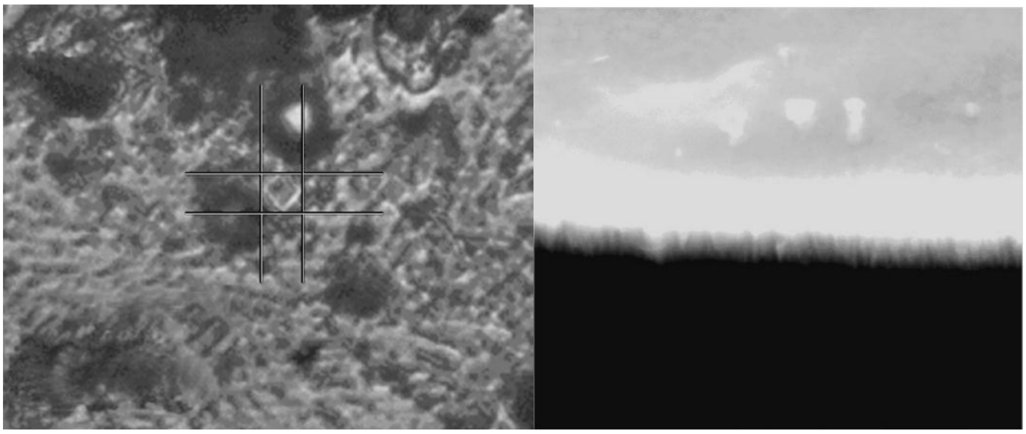


Fig.2 Total PIXE spectrum (in a logarithmic scale) derived from the sample with an Hf–Ti–N–Fe coating in the analysis using a 1.5-MeV proton beam (the spectrum was recorded using a silicon detector).

Figure 3b depicts an image of a region of the surface area of the coating with the imprint of the indenter, which is equivalent to the nanohardness of 48 ±1 GPa; this nanohardness value is very high about 50 GPa and, according to the modern classification scheme, corresponds to a superhard coating [6, 7]. At the same time, the nanohardness of the coating measured using a Vickers pyramid is 36.4 GPa, because a softer steel substrate is located under the coating (Fig. 3b). The XRD analysis results obtained for the samples with this coating type show that the coatings are composed of at least two phases (Ti, Hf)N, (Ti, Hf)N, or FeN and the nanograin sizes determined from the diffraction peak widths by the Debye–Scherrer technique are 4.8–10.6 nm. In addition, by changing the coating deposition parameters, we can specify the stoichiometry (composition) of the film; that is, by changing the substrate potential of 0–100, and –150 to –200 V, at the same pressure of nitrogen (or an Ar/N mixture), we can change the coating structure from columnar (Fig. 3a) at low pressures to nanograin at a high potential. Three dimensional islands on the surface of the films with a columnar structure emerge on the surface of the faces of individual grains (Fig. 3a). Surface undulation is attributed to the growth mechanism and the formation of individual islands on the surface (Volmer–Weber mechanism). In addition, measurement of the XRD spectra in the coating in the θ–2θ geometry and the $\sin_2\varphi$ method revealed compression microstresses, which are formed in nanograins and correspond to a compression value of ≈2.6%. The compression stresses that occur in the film growth plane, which were measured according to the position of the diffraction line peaks by the $\sin_2\varphi$ method, were ≈2.78%.



a) b)

Fig. 3. (a) Cross section of the Hf–Ti–N–Fe coating with a columnar structure; (b) imprint of a four-sided Vickers pyramid on the Ti–Hf–Fe–N coating with a nanohardness of H_V = 36.4 GPa.

The represented distributions of elements over the coating surface and to a depth of 2 μm show that, in fact, the segregation process has not been completed; therefore, the derived hardness values of ≈50 GPa can be increased (by 15–25%) owing to rapid diffusion and the completion of the spinodal segregation process [4, 5]. That is, we can state that the "self-hardening" effect in superhard coatings can lead to an increase in nanohardness up to 60–65 GPa. The μ-PIXE results imply that, apparently, it will be possible to control the self-hardening process or the grain-boundary diffusion acceleration and, thereby, to in situ control the spinodal segregation and the distribution of elements.

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