Stoichiometry, Phase Composition, and Properties of Superhard Nanostructured Ti–Hf–Si–N Coatings Obtained by Deposition from High-Frequency Vacuum–Arc Discharge

A. D. Pogrebnyak*, A. P. Shpak, V. M. Beresnev, G. V. Kirik, D. A. Kolesnikov,
F. F. Komarov, P. Konarski, N. A. Makhmudov, M. V. Kaverin, and V. V. Grudnitskii

Sumy National University, Sumy, Ukraine
Sumy Institute of Surface Modification, Sumy, Ukraine
Kurdyumov Institute of Metal Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine
Kharkiv National University, 61002 Kharkiv, Ukraine
Ukrrosmetall Corporation, Sumy, Ukraine
Belgorod State University, Belgorod, Russia
Belarusian State University, Minsk, Belarus
Tele & Radio Research Institute, Warsaw, Poland
Tashkent University of Informatics (Samarkand Branch), Samarkand, Uzbekistan
e-mail: apogrebnjak@simp.sumy.ua

Abstract—Superhard nanostructured Ti–Hf–Si–N coatings (films) possessing high mechanical properties were obtained by deposition from high-frequency vacuum–arc discharge. The elemental and phase composition and morphology of the films were studied by a combination of methods including RBS, SIMS, GDMS, SEM–EDXS, XRD and nanoindentation techniques at various pressures and bias voltages applied to the coated samples. It is established that, as the average grain size in nc-(Ti,Hf)N (nanocrystalline) coatings decreases from 6.7 to 5 nm and a-Si_3N_4 (amophous or quasi-amorphous phase) interlayers are formed between the nanograins, the nanohardness of coatings increases from 42.7 to 48.4–1.6 GPa. However, the further grain refinement of nc-(Ti,Hf)N to 4.0 nm leads to a slight decrease in the nanohardness. The stoichiometry of the coatings changes from $(Ti_{25}–Hf_{12.5}–Si_{12.5})N_{50}$ to $(Ti_{28}–Hf_{18}–Si_9)N_{45}$, which is accompanied by variation of the lattice parameter of (Ti,Hf)N solid solution grains.

An important current task of the modern materials science is the development of new nanostructured coatings characterized by high hardness (superhardness, $H \geq 40$ GPa), thermal stability ($\geq 1200°C$), and long-term durability [1–5]. As is known, nanocrystalline materials that are characterized, in addition to nanodimensional grain sizes, by the presence of rather extended grain boundaries with partly disordered structures, can possess properties different from those of a coarse-grained material with the same elemental composition. An analysis of the available published data shows that new stable nanocrystalline materials will probably be created based on multicomponent systems characterized by heterogeneous structures, which consist of almost non-interacting phases with linear grain sizes of 2–50 nm, exhibit high thermal stability, and possess properties that remain almost unchanged during the entire working life [2–6].

There is an urgent demand for new coatings possessing high hardness (superhardness) and high elasticity. The present work was aimed at the development of a new type of superhard nanostructured coatings based on Ti–Hf–Si–N compositions and the investigation of their properties.

The coating experiments were performed on carbon steel (St 3 grade) samples in the form of 3-mm-thick disks with a diameter of 20 mm. The coatings with Ti–Hf–Si–N compositions were deposited in a vacuum chamber by the method of high-frequency (HF) arc discharge using a sintered Ti–Hf–Si cathode. In order to provide for the synthesis of nitrides, the chamber was filled with atomic nitrogen at various pressures (p) and the process was carried out at various bias potentials (U) applied to the substrates. The parameter of deposition for some series of samples are listed in the table. The discharge was generated using a vacuum-arc source of Bulat-3T type equipped with an HF generator [5]. The bias voltage applied to a substrate from the HF generator had the form of decaying oscillation pulses with a frequency of ≤ 1 MHz, a pulse duration of 60 µs, and a repetition frequency of about
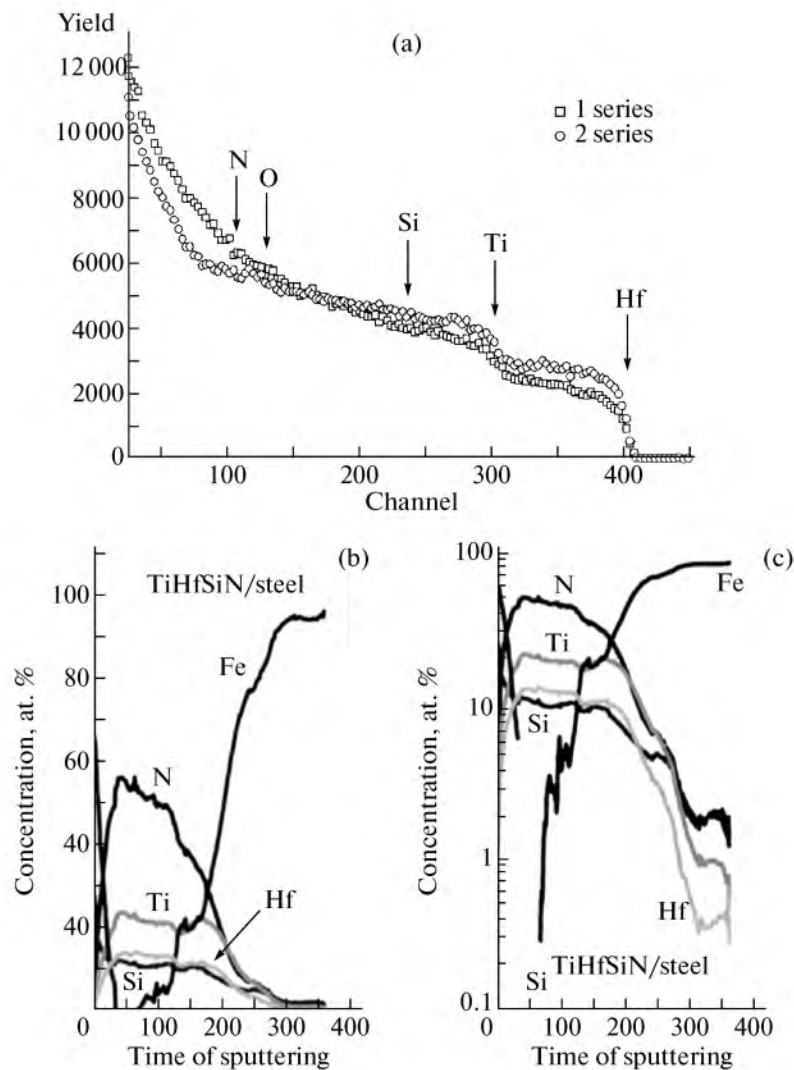
Fig. 1. Analysis of elemental composition of Ti–Hf–Si–N coatings on steel substrates: (a) RBS (1.3-MeV He$^+$) spectra of coatings deposited at (*1*) $U = 100$ V, $p = 0.6$ Pa and (*2*) $U = 200$ V, $p = 0.7$ Pa; (b, c) concentration–depth profiles obtained by SIMS for (Ti$_{25}$–Hf$_{12.5}$–Si$_{12.5}$)N$_{50}$ coatings (series 1) and plotted on the (b) linear and (c) logarithmic scale.

10 kHz. A negative auto-bias voltage on the substrate due to the HF-diode effect was within 2–3 kV.

The elemental composition of deposited coatings was studied using the secondary-ion mass spectrometry (SIMS) on a SAJW-05 instrument equipped with a Balzers QMA-410 quaqdrupole mass analyzer and by glow-discharge mass spectrometry (GDMS) on

SAWJ-01 instrument with an SRS-300 mass analyzer. Additional information on the elemental composition was obtained by the method of Rutherford backscattering (RBS) using 1.3-MeV He$^+$ ions at a 5-μC dose in a scheme with $Q = 170°$ and a detector resolution of 16 keV. The RBS data were processed using a standard international routine [7] for element concentration–depth profiling.

Regimes of deposition, structural parameters, and hardness of Ti–Hf–Si–N coatings deposited in HF vacuum-arc discharge

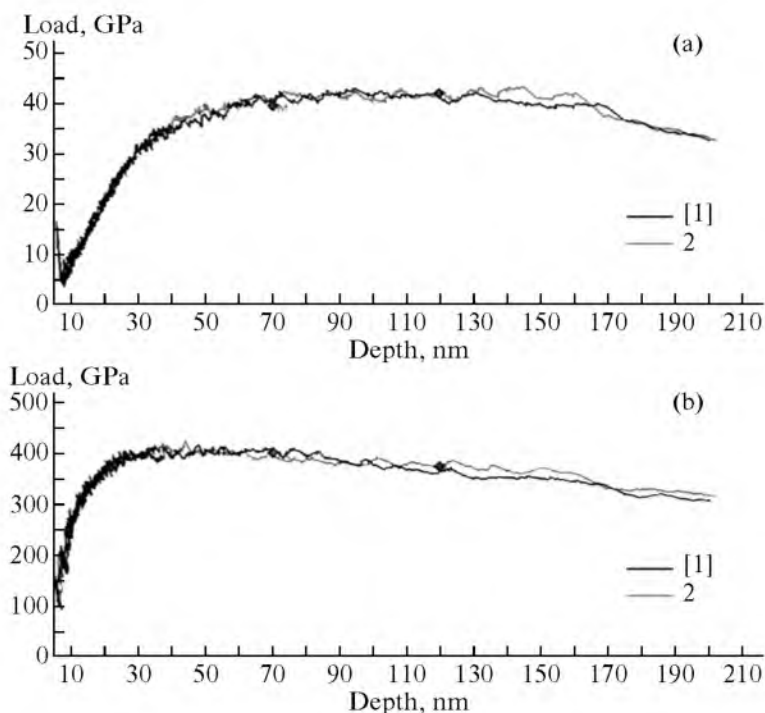| Sample series no.	Nitrogen pressure P, Pa	Substrate bias potential, V	Lattice parameter, nm	Hardness, GPa	Average grain size, nm
23	0.3	−200	0.4294	42.7	6.7
28	0.6–0.7	−200	0.4430	37.4	4.0
35	0.6–0.7	−100	0.4437	38.3	4.3
37	0.6	−100	0.4337	48.8	5.0

Fig. 2. Dependence of (a) nanohardness *H* and (b) elastic modulus *E* on the indentation depth.

The mechanical properties (hardness) were studied by the indentation technique on a Nanoindenter G200 (MES Systems, USA) using a Berkovitz trihedral diamond pyramid with a point tip curvature radius of about 20 nm. The accuracy of determination of the indenter mark depth was ±0.04 nm. The nanohardness of coated samples was determined down to a depth of about 200 nm so as to reduce the substrate effect on the results of hardness measurements. The indentations were made at a distance of 15 μm from each other and no less that five nanoindentations were made on each sample using the continuous stiffness measurement (CSM) technique. The nanoindenter penetration depth was significantly smaller that 1/10 of the coating thickness [1]. The obtained loading curves were processed according to the Oliver–Pharr method.

The structures and phase compositions of deposited coatings were studied by the X-ray (XRD) techniques. The XRD measurements were performed on DRON-4 and X'Pert PANalytical instruments using filtered CuK_α radiation generated at an anode operation regime of $U = 40$ kV, $I = 40$ mA. The angular scans were recorded at a step of 0.05° and a scan rate of 0.05°/s.

The morphology, structure, and elemental; composition profiles were also studied on the transverse sections of coated substrates. These investigations were performed on a Quanta 200 3D scanning ion-electron microscope.

Figure 1 shows the results of determination of the elemental composition of superhard nanostructured Ti–Hf–Si–N coatings in two series of samples studied by three analytical methods (RBS, SIMS and GDMS). As can be seen, the composition of coatings in the first series corresponds to $(Ti_{25}-Hf_{12.5}-Si_{12.5})N_{50}$ (Fig. 1, curve *1*).

As is well known, the RBS is a reference method for determining the concentrations of elements with large atomic numbers and for measuring the thicknesses of thin film. A significant advantage of this method is the nondestructive character. On the other hand, an advantage of SIMS is a higher sensitivity (detection threshold, ~10^{-6} at. %). For this reason, a comparative analysis of the data obtained by RBS, SIMS and GDMS provides a more realistic pattern of the elemental composition and its depth profile. The elemental concentration profiles were obtained over the entire film thickness, including regions both near the outer surface and at the film–substrate interface, including the uncontrolled impurities (O, C) adsorbed from residual atmosphere of deposition chamber.

In the first series of samples with the composition $(Ti_{25}-Hf_{12.5}-Si_{12.5})N_{50}$, the coating thickness was 1 ± 0.012 μm. The second series was obtained upon increasing the bias potential to 200 V and the nitrogen pressure in the working chamber to 0.7 Pa (Fig. 1a, curve *2*). The results of RBS measurements and their comparative analysis together with the EDXS and SIMS data showed that these films had a composition of $(Ti_{28}-Hf_{18}-Si_9)N_{45}$.

The results of nanohardness measurements (Fig. 2) using a Berkovitz trihedral diamond pyramid [5–7] for

the first series of samples gave a nanohardness of $H = 42.7$ GPa and an elastic modulus of $E = 390 \pm 17$ GPa. For the second series of samples, these values were $H = 48.8 \pm 0.8$ GPa and $E = 495 \pm 12$ GPa. Points on the curves of H and E (Fig. 2) indicate the depths at which these values were determined.

The results of determination of the phase composition of coatings by the XRD method and calculations of the lattice parameter showed that the coating represents a two-phase system, which consists of (Ti,Hf)N substitutional solid solution and a-Si_3N_4 amorphous phase. In some series of samples, a predominant orientation of the solid solution was absent. In the samples with maximum hardness (series 37) the (Ti,Hf)N phase had a predominant orientation of (200). It was also established that the lattice parameter of the solid solution increases with the pressure of nitrogen, while being independent of the bias potential applied to the substrate. A minimum lattice constant of (Ti,Hf)N was observed in samples of series 23, which were synthesized at a lowest pressure of nitrogen (see table).

Calculations using the Debye–Scherrer method showed that the size of (Ti,Hf)N grains in samples of the second series with the $(Ti_{28}–Hf_{18}–Si_9)N_{45}$ composition was about 1.5 times smaller than that in the first series (i.e., 4 nm against 6 nm). The thickness of amorphous or quasi-amorphous phase interlayers was also somewhat smaller in the second series that in the first one.

Preliminary results of an HRTEM analysis of electron diffraction on the samples with nanostructured superhard films showed that, by the order of magnitude, the size of nanograins of the nc-(Ti,Hf)N phase is 2–5 nm, in agreement with the XRD data, while the thickness of a-Si_3N_4 interlayers surrounding the (Ti,Hf)N grains is within 1.2–1.7 nm.

The values of nanohardness above 40 GPa are commonly accepted to be indicative of a superhardness of the nanocomposites [1–3], while the values of 80 GPa above correspond to ultrahardness. The investigation of Ti–Hf–Si–N coatings obtained in the first series showed that their properties such as hardness and elastic modulus remain unchanged upon a long-term storage of 6–12 months. Tests for the thermal stability and resistance to oxidation were outside the scope of this study. Now it yet difficult to judge whether the process of spinodal segregation at grain boundaries is competed, since the substrate temperature during deposition did not exceed 350–400°C, which is significantly lower than the temperature of complete grain-boundary segregation (550–650°C) [2, 5, 8, 9].

REFERENCES

1. A. D. Pogrebnyak, A. P. Shpak, N. A. Azarenkov, and V. M. Beresnev, Usp. Fiz. Nauk **179**, 35 (2009) [Phys. Usp. **52**, 29 (2009)].

2. S. Veprek, M. G. J. Veprek-Heijman, P. Karvankova, and J. Prochazka, Thin Solid Films **476**, 1 (2005).

3. J. Musil, P. Baroch, and P. Zeman, *Hard Nanocomposite Coatings: Present Status and Trends, in Plasma Surrace Engineering and Practical Applications*, Ed. by R. Wei (Signpost Publ., 2007).

4. S. Veprek, A. S. Argon, and R. F. Zhang, Phil. Mag. Lett. **87**, 955 (2007).

5. A. D. Pogrebnyak, O. V. Sobol', V. M. Beresnev, P. V. Turbin, S. N. Dub, G. V. Kirik, and A. E. Dmitrenko, Pis'ma Zh. Tekh. Fiz. **35** (19), 103 (2009) [Tech. Phys. Lett. **35**, 925 (2009)].

6. A. D. Pogrebnjak, M. M. Danilenok, A. A. Drobyshevskaya, et al., Vacuum **83**, S235 (2009).

7. A. D. Pogrebnjak, M. M. Danilenok, A. A. Drobyshevskaya, Izv. Vyssh. Uchebn. Zaved., Fiz., No 12, 61 (2009) [Russ. Phys. J. **52**, 1317 (2009)].

8. 9. V. V. Uglov, V. M. Anishcik, S. V. Zlotski, et al., Surf. Coat. Technol. **202**, 2394 (2008).

9. A. D. Pogrebnjak, O. V. Sobol', V. M. Beresnev, et al., in *Nanostructured Materials and Nanotechnolody IV*, Ceram. Eng. Sci. Proc. **31** (7), 127 (2010).

Translated by P. Pozdeev