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Properties of superhard...

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PROPERTIES OF SUPERHARD NANOSTRUCTURED COATINGS Ti-Hf-Si-N

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New superhard coatings based on Ti-Hf-Si-N featuring high physical and mechanical properties were fabricated. We employed a vacuum-arc source with HF stimulation and a cathode sintered from Ti-Hf-Si. Nitrides were fabricated using atomic nitrogen (N) or a mixture of Ar/N, which were leaked-in a chamber at various pressures and applied to a substrate potentials. RBS, SIMS, GT-MS, SEM with EDXS, XRD, and nanoindentation were employed as analyzing methods of chemical and phase composition of thin films. We also tested tribological and corrosion properties. The resulting coating was a two-phase, nanostructured nc-(Ti, Hf)N and α -Si₃N₄. Sizes of substitution solid solution nanograins changed from 3.8 to 6.5 nm, and an interface thickness surrounding α -Si₃N₄ varied from 1.2 to 1.8 nm. Coatings hardness, which was measured by nanoindentation was from 42.7 GPa to 48.6 GPa, and an elastic modulus was E = (450 to 515) GPa. The films stoichiometry was defined for various deposition conditions. It was found that in samples with superhard coatings of 42.7 to 48.6 GPa hardness and lower roughness in comparison with other series of samples, friction coefficient was equal to 0.2, and its value did not change over all depth (thickness) of coatings. A film adhesion to a substrate was essentially high and reached 25MPa.

KEY WORDS: superhard, nanostructured coatings, Ti-Hf-Si-N, stoichiometry, phase composition.

СВОЙСТВА СВЕРХТВЕРДЫХ НАНОСТРУКТУРИРОВАННЫХ ПОКРЫТИЙ Ті-Hf-Si-N А.Д. Погребняк 1,2 , А.П. Шпак 2 , В.М. Береснев 3 , Ф.Ф. Комаров 4 , П. Конарски 5 , В.В. Углов 4 , М.В. Каверин 1 , Н.А. Махмудов 6 , И. Якущенко 2 , В.В. Грудницкий 3 , Д.А. Колесников 7 , Л.В. Маликов 8

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 8 Научный физико-технологический центр МОНМС и НАН Украины, г. Харьков, 61022, пл. Свободы, 6, Украина В работе получены новые сверхтвердые покрытия на основе Ti-Hf-Si-N с высокими физико-механическими свойствами. В процессе синтеза методом вакуумно-дугового осаждения с применением ВЧ напряжения распылялся цельнолитой катод Ti-Hf-Si. Нитриды формировались в среде атомарного азота (N) или в смеси Ar/N, которые напускались в камеру при различных давлениях. Химический и фазовый составы тонких пленок анализировался методами RBS, SIMS, GT-MS, SEM с EDXS, PCA, а твердость определялась наноиндентированием. Исследовались трибологические и коррозионные свойства покрытий. Полученные покрытия являются двухфазными наноструктурированными nc-(Ti, Hf)N и α -Si₃N₄. Размеры нанозерен твердого раствора варьировались от 3,8 до 6,5 нм, а толщина окружающей оболочки α -Si₃N₄ менялась от 1,2 до 1,8 нм. Твердость покрытий H составляла 42,7 ÷ 48,6 ГПа, а модуль упругости H принимал значения от 450 ГПа до 515 ГПа. Определена стехиометрия пленок при различных условиях осаждения. Установлено, что в образцах сверхтвердых покрытий с твердостью 42,7 ÷ 48.6 ГПа наблюдалась более низкая шероховатость по сравнению с другими образцами, коэффициент трения составлял 0,2, и его значение не изменялось по всей глубине (толщине) покрытия. Адгезия пленки к подложке достигла 25 МПа.

КЛЮЧЕВЫЕ СЛОВА: сверхтвердость, наноструктурированные покрытия, Ті-Нf-Si-N, стехиометрия, фазовый состав.

ВЛАСТИВОСТІ НАДТВЕРДИХ НАНОСТРУКТУРОВАНИХ ПОКРИТТІВ ТІ-Hf-Si-N О.Д. Погребняк 1,2 , А.П. Шпак 1 , В.М. Береснєв 3 , Ф.Ф. Комаров 4 , П. Конарскі 5 , В.В. Углов 4 , М.В. Каверін 1 , Н.А. Махмудов 6 , І. Якущенко 2 , В.В. Грудницький 3 , Д.О. Колесніков 7 , Л.В. Маліков 8

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КЛЮЧОВІ СЛОВА: надтвердість, наноструктуровані покриття, Ті-Hf-Si-N, стехіометрія, фазовий склад.

The development of the new nanostructural coating (nc) with high hardness (40 GPa) and thermal stability (> 1200°C) is one of the most urgent problem of the modern material science. According to the previous experimental results it can be considered that not only grains size has strong influence on properties of the solid but also structural states of interfaces (grains boundary). As the quantity of atoms at grains boundary reaches about 30-50%, properties of the material strongly depend on condition of the grains boundary: gap of the border band (in this band lattice parameter deviate from standard value), disorientation of the grains and interfaces, concentration of the defects at boundary and value of the free volume.

порівнянні з іншими зразками, коефіцієнт тертя становив 0,2, і його значення не змінювалося за глибиною (товщиною)

So, nanocrystalline materials, that contain nanosized crystallite along with rather extensive and partially disordered boundaries structure, present new properties by comparison with the large-grained materials.

These stable nanocrystalline materials can be created on base of multi-component compound, since such materials have the heterogeneous structure that include practically non-interacting phases with average linear dimension about 7-35 nm. In this case nanocrystalline materials demonstrate high thermal stability and long-term stable properties [1-7]. Presently, there are many papers related to the research of the structure and properties of the multi-component hard nanostructures (nanocomposite coating based on Zr-Ti-Si-N, Zr-Ti-N and Mo-Si-N etc.) [5-8]. However, the development of the new type of the coating is still continuing. It is well known that superhard coating can be formed on base of nc-TiN or nc-(Zr, TiN) covered with α -Si₃N₄, or BN amorphous or quasiamorphous phase. Hardness of such coating can reach 80 GPa and higher. In addition, the deposition of the coating at temperature about 550 – 600°C allows to finalize spinodal segregation along grain boundaries and hence improve properties of the coatings.

The main goal of the research is the development of the new type of Ti-Hf-Si-N-based superhard nanostructured coatings and analysis of their properties and structure.

EXPERIMENTAL DETAILS

Ti-Hf-Si-N films were deposited on steel 3 substrate (20 mm diameter and 3 mm thickness) with the help of vacuum source in the HF discharge of the cathode, sintered from the Ti-Hf-Si. In order to obtain nitride, atomic N was flooded to the chamber at different pressure and substrate potential. Deposition conditions are presented in Table. Bulat 3T-device with generator was used for the deposition of samples [5]. A bias potential was applied to the substrate from a HF generator, which generated impulses of convergent oscillations with \leq 1 MHz frequency, every duration of the impulse was $60\mu s$, their repetition frequency about 10 kHz. Due to HF diode effect the value of negative auto bias potential at substrate was about $2\div3$ kV.

Secondary mass-spectrometers SAJW-0.5 SIMS with quadruple mass analyzer QMA-410 Balzers and SAWJ-01 GP-MS with glow discharge and quadruple mass analyzer SRS-300 (Poland, Warszawa) were used for studying of the samples chemical composition. In order to obtain complete information about samples chemical composition, 1.3 MeV ion RBS spectrometers equipped with 16 keV resolution detectors were applied. Helium ion dose was about 5 μ C. Standard computer software [7] was used for the processing of the RBS spectra, as a result the depth distribution of the concentration of compound components was plotted.

The research of the mechanical properties of the samples was carried out by the nanoindentation methods with the help of Nanoindenter G200 (MES Systems, USA) equipped with Berkovich pyramid (radius about 20 nm). An accuracy of measured indentation depth was ± 0.04 nm. Measurements of the nanohardness of the samples with coating were carried out till 200 nm depth, in order to decrease influence of the substrate on the nanohardness value. The depth of indentation was substantially less than 0.1 of coating depth [1]. XRD analysis was performed using DRON-4 and X'Pert PANalitical (Holland) difractometers (step size 0.05° , speed 0.05° C, U = 40 kV, I=40 mA, emitter-copper)

The cross-sections of the substrates with coatings were prepared by the ion beam. Further analysis of surface morphology, structure and chemical composition of these cross sections was carried out by the scanning ion-electron

microscope Quanta 200 3D.

RESULTS AND DISCUSSION

Prior to analysis of XRD data, it should be noted that for better understanding of processes occurred at near-surface region during deposition it is necessary to compare formation heats of the probable nitrides. According to [10] standard heats of formation of such nitrides are next: $\Delta H_{298}(HfN) = -369.3$ kJ/mole, $\Delta H_{298}(TiN) = -336.6$ kJ/mole, $\Delta H_{298}(Si_3N_4) = -738.1$ kJ/mole, i.e. values of the formation heats are quite large and negative. It indicates high probability of those systems formation during all stages of transport of the material from target to substrate. In addition, proximity of formation heats for TiN and HfN establish conditions for formation of the sufficiently homogenous (Ti.Hf)N solid solution.

The XRD-analysis revealed the presence of two-phase system. This system was determined as the substitutional solid solution (Ti,Hf)N because diffractions peaks of this phase are located between peaks related to mononitrides TiN (JCPDS 38-1420) and HfN (JCPDS 33-0592). The diffused peaks with less intensity at 2θ values from 40^0 to 60^0 are related to the α -Si₃N₄ phase (Fig.1).

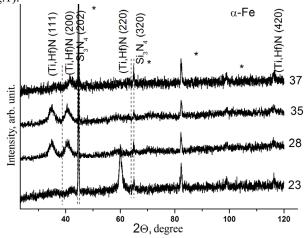


Fig. 1 XRD spectra of the coatings deposited on a steel substrate at modes: 1 - (23) - 100V, separated, 2 - (28)-200V, non separated, 3 - (35)-100V, non separated, 4 - (37)-200V, separated.

The analysis of the XRD data showed that specific structural properties of coating obtained from the same target strongly depend on beam mode (separated or non-separated). The results of XRD-analysis are represented in Table.

According to Fig.1, 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.

At the same time, coating texture leads to increasing of the average grains size of the crystallites along the direction of particle incidence (perpendicular to the growth front). For example, in non-textured fraction of the crystallites the average grains size is about 6.7 nm, whereas in textured crystallites the value of the average grains size is substantially more, namely 10.6 nm. It should be noted that such coatings have the highest nanohardness (Table).

The increase of the substrate potential up to 200 V caused the decrease of average grains size to 5.0 nm. The volume content of textured crystallites is also significantly decreased (less than 20%), moreover the texture axis changed from [100] to [001]. However in this case the lattice parameter is 0.4337 nm and it is larger than for the nontextured fraction in samples obtained at low substrate potential.

According to Vegard law this value of the lattice parameter corresponds to 33 at.% of Hf in metallic (Hf,Ti) solid solutions of the nitride phase (the reference data of the lattice parameters of a TiN=0.424173 nm (JCPDS 38-1420) and a HfN = 0.452534 nm (JCPDS 33-0592) were used).

However, as a rule, the compressive stresses in coatings caused the decrease of the angles of corresponding diffraction peaks during θ -2 θ scan, hence calculated values of lattice parameter can be overestimated. As a result inaccuracy of the calculation of Hf concentration in solid solutions can achieve about 5-10 at. %. Therefore presented results can be considered as estimation of upper limit of the Hf concentration in solid solution.

All above mentioned results are related to samples obtained at typical pressure (0.6-0.7) Pa, whereas in a case of coating deposition at 200 V substrate potential in mode of separation (set of samples 31), the decreasing of pressure up to 0.3 Pa caused the increase of relative content of heavy Hf atoms in coatings (Table). In addition, the average grains size of the crystallites decreased with pressure.

Table.

Results of diffraction spectrums treatment

No॒	Lattice parameter, nm	Average size of crystallite, nm	Hf content in solid solution (HfTi) coming from the size of period ***, at.%	Hardness, GPa	Nitrogen pressure in chamber, Pa	Substrate potential, V
23 (100 V, separated)	0.4294*	6.7**	19	42.7	0.7	-200
28 (200 B, non separated)	0.4430	4.0	65	37.4	0.6-0.7	-200
35 (100 B, non separated)	0.4437	4.3	69	38.3	0.6÷0.7	-100
37 (200 B, separated)	0.4337	5.0	33	48.6	0.6	-100
31 (200 B, separated)	0.4370	3.9	45	39.7	0.3	200

^{*-} in textured crystallites of samples (series №23) with texture axis (220), the period is more than 0.43602 nm, which can be connected with high Hf content in them (about 40 at. %).

Indeed, the decrease in pressure should be accompanied by decrease of the probability of energy loss of atoms during collision between targets and substrate. Thus, atoms at substrates have relatively high energy which can promote secondary sputtering and radiation defect formation. So, secondary sputtering leads to decrease of relative content of heavy Hf atoms, while radiation defect formation provide the decrease of grain size with the increase of nucleus amount.

The coatings obtained under the typical pressure (0.6-0.7) Pa in case of non-separated beam (direct-flow mode) have considerably larger lattice parameter; it can be explained by the high concentration of heavy Hf atoms (Table).

Apparently, the more intensive direct-flow mode leads to the increase of the nucleus density and hence to the decrease of average grain size. In addition, more pronounced decrease of the grains size is caused by the higher substrate potential 200 V. It is obviously because increasing of radiation factor leads to the dispersion of structure [11]. The results of the research of chemical composition of the Ti-Hf-Si-N nanostructured superhard films by the several methods are shown in Fig. 2 (RBS), Fig. 3 (SIMS), Fig. 4 (GT-MS). As follows from Fig. 2 (curves 1) chemical composition of samples from first set is (Ti₄₀-Hf₀-Si₈)N₄₆.

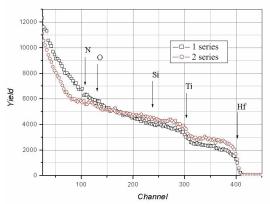


Fig. 2. RBS spectra of He⁺ with 1.3 MeV energy, obtained from steel sample with Ti-Hf-Si-N film: curve 1-potential 100V, p=0.6 Pa, curve 2 - potential 200V, p=0.7 Pa

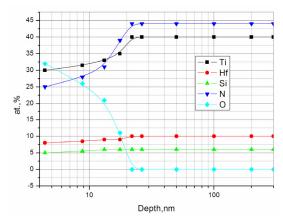


Fig. 3. The depth profiles of elements in the Ti-Hf-Si-N coating, obtained from RBS spectrums (Fig. 2).

^{**-} in the texture axis direction of textured crystallites the average size is larger (10.6 nm).

^{***-} Calculation was carried out according to Vegard rule from period values of solid solution (the influence of macrostresses on the change of diffraction lines was not taken into account).

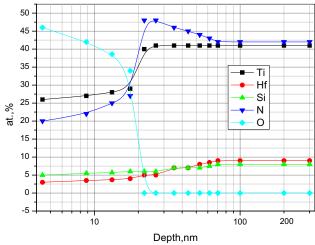


Fig. 4. The depth profiles in the Ti-Hf-Si-N coating obtained from spectrums (2) on Fig. 2 (mode 2).

It is well known that RBS method is a reference for the determination of concentration of the elements with high atomic number and films thickness; also RBS is a nondestructive method. Whereas SIMS is more sensitive method (threshold of sensitivity is about 10⁻⁶ at.%). Therefore comparison of results obtained by the RBS, SIMS and GT-MS methods allows obtaining of more reliable data of the chemical composition and depth distribution of the concentration of compound components. This joint analysis let us to study the chemical composition along the films cross-section from the surface to the films-substrates interfaces. Analysis of samples chemical composition also includes measurement of the concentration of uncontrolled oxygen from the residual chamber atmosphere.

As a result we have determined chemical composition $(Ti_{40}\text{-Hf}_9\text{-}Si_8)N_{46}$ of the coatings (films) with thickness about $1\mu\text{m}\pm0.012~\mu\text{m}$. The second set of Ti-Hf-Si-N samples was obtained at increased bias potential (200 V) under the pressure of 0.3~Pa.

Joint analysis of the films chemical composition by the RBS (Fig. 2 curves 2), EDXS and SIMS methods allowed determining of stoichiometry of films as $(Ti_{28}\text{-H}f_{18}\text{-}Si_9)$ N₄₅. Considering that atomic density of layer is close to atomic density of titanium nitride. Taking into account the results of SIMS analysis, obtained for this coating and represented on Fig. 5 a, b (mode 1).

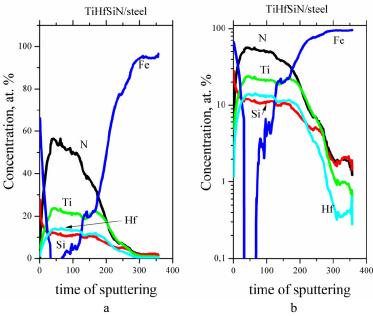


Fig. 5. SIMS depth profile analysis obtained under assumption that atomic concentrations in the TiHfSiN layer are Ti – 25%, Hf – 12,5%, Si – 12,5%, N – 50% (first series): in linear and a – at.%, standard scale of concentration; b – Logarithmic scale of concentration.

The measuring of nanohardness by the triangular Berkovich pyramid (Fig.6) showed that the nanohardness of the samples from the first set is H=42.7 GPa and elastic modulus is E=390 \pm 17 GPa (Fig. 6, Fig. 3), and for the Ti-Hf-Si-N samples from the second set, the nanohardness is H=48.4 \pm 1.4 GPa and elastic modulus is E = 520 \pm 12 GPa.

The XRD-analysis of the phase composition and calculation of the lattice parameter allow us to consider that

the two-phase system based on substitutional solution (Ti, Hf)N and α-Si₃N₄ is formed in films.

It was determined that lattice parameter of the solid solution increased with pressure and does not depend on substrate potential. The minimal lattice parameter of the (Ti, Hf)N solid solution was observed in samples from the 23 set.

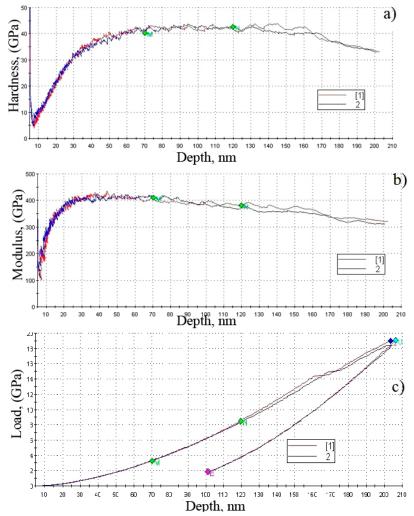


Fig. 6. The dependence of hardness H(GPa) (a) on the depth of indentation, (b) dependence of elastic modulus E(GPa) on the depth of indentation (the regions of H, E measurements are marked with points), (c) loading and unloading curves for nanoindentation of Ti-Hf-Si-N coatings.

The calculation by the Debye-Scherrer method showed that the size of nanograins of the $(Ti_{28}-Hf_{18}-Si_9)$ N₄₅ samples from the second set is 4 nm, and it is approximately 1.5 times less than for the first set of the samples. Moreover size (thickness) of amorphous (or quasiamorphous) interlayer was also less than for the first set of the samples (Table).

The preliminary results of the HRTEM analysis of samples with nanostructured superhard films revealed that size of nanograined phase is about 2-5 nm, this result is in correlation with XRD data. In addition it was determined that size of α -Si₃N₄ interlayer, which envelops the (Ti, Hf)N nanograin, is about (0.8-1.2) nm.

The properties (hardness, elastic modulus) of Ti-Hf-Si-N samples from the first set were not changed during the storage time from 6 to 12 month.

An analysis of thermal and oxidation resistance was not performed. Therefore it is difficult to conclude that the process of spinodal segregation at the grain boundaries is fully completed. In addition the substrate temperature during the deposition was not more than $350 \div 400$ °C, and it is substantially less than full segregation temperature ($550 \div 620$ °C) [2, 5, 8].

CONCLUSIONS

The Ti-Hf-Si-N-based superhard nanostructured coating with different chemical composition was obtained under different growth conditions. An analysis of properties and structure of the coatings was carried out.

It was determined that size of nanograins of solid solution changed from 3.8 to 10.6 nm, at the same time the size of α -Si₃N₄ interlayer, which is envelop the (Ti, Hf)N nanograin, is about $(0.8 \div 1.2)$ nm.

The nanohardness varied from 36.4 to 48.6 GPa depending on bias potential on substrate and pressure in chamber.

Preliminary measurements of the friction coefficient showed that samples with high hardness and good surface morphology have low friction coefficient (about 0.2), which is stable along the whole wear length. The adhesion of film to steel also changes almost in 2.5 times (39.5 MPa).

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REFERENCES

- 1. Pogrebnjak A.D., Shpak A.P., Azarenkov N.A., Beresnev V.M. Structures and properties of hard and superhard nanocomposite coatings. // Usp. Phys., 2009. Vol. 179. P. 35-64.
- 2. Veprek S., Veprek-Hejiman M.G.L., Karvankova P., Prohazka J. Different approaches to superhard coatings and nanocomposites// Thin Solid Films. 2005. Vol. 476. P. 1-29.
- 3. Nanostructured Coatings. (Edit. A Cavaleiro, De Hosson) 2006. Shringer Verlag 661 p.
- 4. Veprek S., Argon A.S., Zhang R.F. Origin of the hardness enhancement in superhard nc-TiN/α- Si₃N₄ and ultrahard nc-TiN/α-Si₃N₄/TiSi₂ nanocomposites // Philosophical Magazine Letters. 2007. Vol.87. P. 955-966.
- 5. Pogrebnjak A.D., Sobol O.V., Beresnev V.M. et. al. Features of the Structural State and Mechanical Properties of ZrN and Zr(Ti)–Si–N Coatings Obtained by Ion–Plasma Deposition Technique // Tech. Phys. Lett. 2009. Vol. 35. P. 103-110.
- 6. Pogrebnjak A.D., Danilionok M.M., Drobyshevskaya A.A., Beresnev V.M. et.al. Nanocomposite Protective Coating Based on Ti-N-Cr/Ni- Cr-B-Si-Mo, their Structure and Properties // 9Th International conference on modification of materials with particle beams and plasma flows. 2008. Tomsk, Russia, 21-26 September. P.604- 608.
- 7. Pogrebnjak A.D., Danilionok M.M., .Drobyshevskaya A.A., Beresnev V.M. et. al. Investigation of the structure and physicochemical properties of combined nanocomposite coatings based on Ti−N−Cr/Ni−Cr−B−Si−Fe // Russ. Phys. J. − 2009. − №12. − P. 1317-1324.
- 8. Uglov V.V., Anischnik V.M., Zlotskij S.V. et. al. Structural and mechanical stability upon annealing of arc-deposited Ti–Zr–N coatings // Surf. and Coat. Tech. 2008. Vol.202. P.2394-2398.
- 9. Pogrebnjak A.D., .Sobol O.V., Beresnev V.M. et. al. Phase composition thermal stability, physical and mechanical properties of superhard on base Zr-Ti-Si-N nanocomposite coatings //Nanostructured Materials and Nanotechnology IV: Ceramic Engineering and Science Proceedings. −2010. − Vol.31, № 7. − P. 127-139.
- 10. Smitls K.J. Metals (Enquiery Book) (Metallurgija, Moscow, 1980), 287 p. (in Russian).
- 11. Korotaev A.D., Borisov D.P., Moshkov V.Yu. et.al. Elastic stress state in superhard multielement coatings // Physical Mezomechanica. 2009. №12. P.79-91.