UDC 539.2: 538.975

MAGNETRON SPUTTERING OF HIGH TEMPERATURE COMPOSITE CERAMICS AlN-TiB_2-$TiSi_2$

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Received 24.09.2013

By means of the magnetron sputtering method using the DC and pulsed voltages applied to the target, the coatings based on AlN-TiB_2-$TiSi_2$ ceramics were obtained. An amorphous-like structure of the obtained coatings was revealed. It had the area of ordering ~ 1 nm and the viscoplasticity coefficient of 0.07. The hardness of the coatings reaches 15.3 GPa, and the modulus of elasticity is 206 GPa. The coatings are characterized by high adhesion strength to the substrate.

Keywords: ceramics, composite coatings, magnetron sputtering method, physical and mechanical properties.

МАГНЕТРОННОЕ РАСПЫЛЕНИЕ ВЫСОКОТЕМПЕРАТУРНОЙ КОМПОЗИЦИОННОЙ КЕРАМИКИ AlN-TiB_2-$TiSi_2$

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Магнетронным методом распыления, с применением постоянного и импульсного напряжений на мишень, получены покрытия на основе керамики AlN-TiB_2-$TiSi_2$. Выявлено аморфноподобную структуру сформированных покрытий с областью упорядочения ~ 1 нм и коэффициентом вязкопластичности 0,07. Твердость покрытий достигает 15,3 ГПа, а модуль упругости составляет 206 ГПа. Покрытия характеризуются высокой адгезионной прочностью по отношению к подложке.

Ключевые слова: керамика, композиционные покрытия, магнетронный метод распыления, физико-механические свойства.

МАГНЕТРОННЕ РОЗПИЛЕННЯ ВИСОКОТЕМПЕРАТУРНОЇ КОМПОЗИЦІЙНОЇ КЕРАМІКИ AlN-TiB_2-$TiSi_2$

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Магнетронним методом розпилення, із застосуванням постійної та імпульсної напруг на мішень, отримані покриття на основі кераміки AlN-TiB_2-$TiSi_2$. Виявлено аморфноподібну структуру сформованих покриттів із областю впорядкування ~1 нм і коефіцієнтом в'язкопластичності 0,07. Твердість покриттів досягає 15,3 ГПа, а модуль пружності складає 206 ГПа. Покриття характеризуються високою адгезійною міцністю по відношенню до підкладинки.

Ключові слова: кераміка, композиційні покриття, магнетронний метод розпилення, фізико-механічні властивості.

INTRODUCTION

Ion-plasma deposition methods by means of sputtering targets, which consist of metals or their nitrides, carbides and borides, can generate a wide range of multi-component coatings. In many papers [1 – 3] various variants of such structures and their properties have been considered.

Prospects for the use of multi-component coatings containing wear-resisting and antifriction components are associated with the possibility of ob-

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taining a new composite structures having the desired physical and mechanical properties. The most common and effective systems of coatings formation are systems based on magnetron sputtering techniques [4, 5]. During the deposition process, the amorphous structure can be formed along with the reduction of the size of the grain and obtaining new chemical compounds. This promotes a significant improve to the physical and mechanical properties of the coatings.

In the current work, the possibility of applying the method of magnetron sputtering of high-temperature composite ceramics and formation of coatings on their basis have been explored. The physical and mechanical properties of the coatings have been studied.

EQUIPMENT AND METHODS OF INVESTIGATION

Operational volume was a vacuum chamber made of stainless steel with a diameter of 75 cm and a volume of ~96 liters. The scheme of the installation is shown in fig. 1.

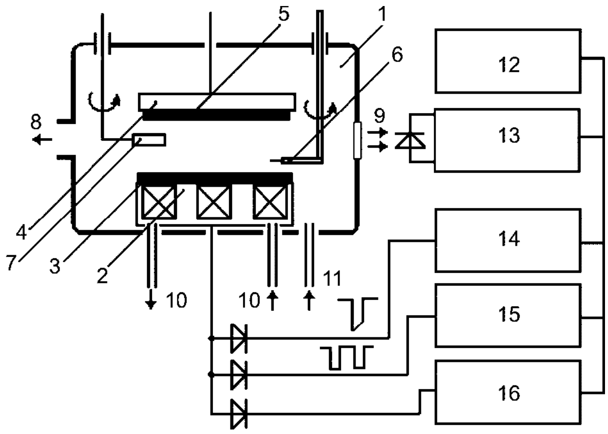


Fig. 1. Scheme of the installation for magnetron sputtering of multicomponent systems: 1 – vacuum chamber, 2 – planar magnetron, 3 – sputtering target, 4 – substrate holder, 5 – substrate, 6 – Langmuir probe, 7 – quartz thickness and the deposition rate measuring instrument, 8 – pumping, 9 – observation window, 10 – water cooling, 11 – operational gas buffing, 12 – system of control and data acquisition, 13 – photometer, 14 – ignition block, 15 – impulse power supply unit, 16 – constant power supply unit.

As the sputtered material we used ceramics (AlN-TiB$_2$-TiSi$_2$) with a diameter ~ 80 mm and thickness of 4 mm.

The coatings were deposited on the polished surface of the samples of steel 45 and on the surface of the silicon samples. Samples were fixed on the substrate, which was located above on a distance of 70 mm from the surface of the sputtering target. For comparison of the results of research, two modes of deposition have been used: at a constant voltage applied to the target and in pulsed mode.

DEPOSITION PARAMETERS

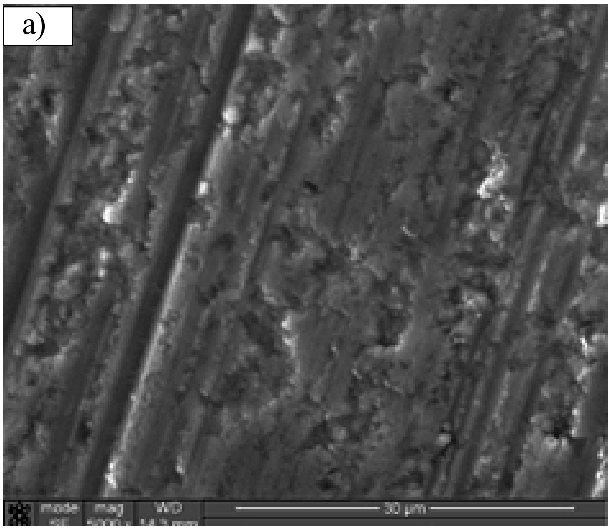
The DC voltage applied to the sputtering target was 400 V, current ~200 mA; deposition time 95 min; bias potential on the substrate was ~200 V. The partial pressure in the chamber during the coating deposition was P_{Ar} = 0.1 Pa. Before the deposition of the coatings, the cleaning of the samples in a glow discharge for 15 minutes at P_{Ar} = 0.08 Pa has been implemented.

The pulse voltage applied to the sputtering target was 700 V, current ~2.0 A; deposition time 35 min; potential bias on the substrate was ~200 V. The partial pressure in the chamber during coating deposition was P_{Ar} = 0.1 Pa. Before the deposition of coatings, the cleaning of the samples in a glow discharge for 15 minutes at P_{Ar} = 0.08 Pa has been implemented.

The surface morphology of the coated samples was studied using a scanning electron microscope FEI Quanta 600 FEG. Nanohardness measurements were carried out using NanoIndenter II (MTS Systems, USA) installation. It was equipped with a three-sided Berkovich pyramid. To study the structural elements, the method of atomic force microscopy (AFM) was used.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 2 and fig. 3 show microphotographs of the surface of the coatings, as well as the fractorgaphy im-



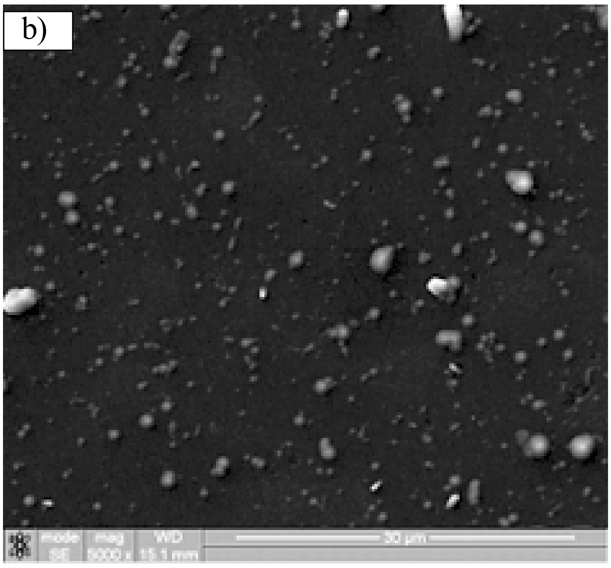


Fig. 2. Image of the surface topography of the AlN-TiB_2-$TiSi_2$ coating: a) – under DC, b) – pulsed magnetron sputtering.

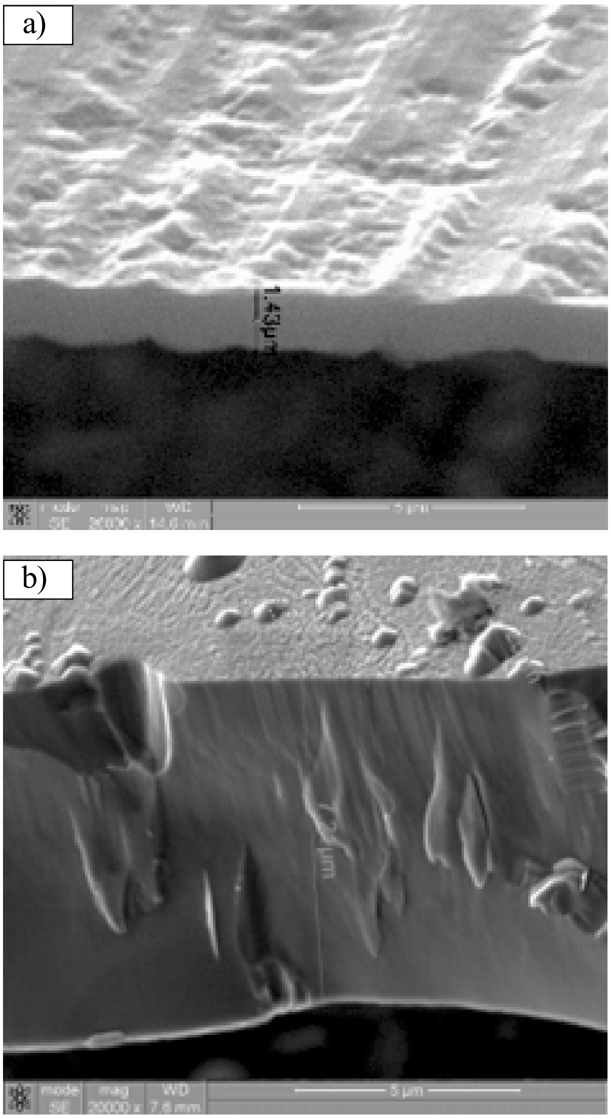


Fig. 3. Fractography images of the fractures of the AlN-TiB_2-$TiSi_2$ coatings: a) – obtained at a DC (t_{dep} = 95 min), b) – impulse magnetron sputtering (t_{dep} = 35 min).

ages of the fracture. The analysis of the images shows that the use of magnetron sputtering for the evaporation of the ceramic targets of compound composition leads to the fact of presence of a drop component in a small amount on the surface. The analysis of the published data suggests that the main factor determining the presence of the drop component is the low thermal conductivity of the vaporized components composing the target [6].

Even with intensive cooling of the target, the temperature of the evaporating surface increases because of the low thermal conductivity of the evaporable components: λ_{AlN}= 160 – 250 W/(m·K) [7]; λ_{TiB2}= 64,4 W/(m·K) [7]; λ_{TiSi2}= 45,9W/(m·K) [8], which leads to the generation of microdrops fraction [9]. Fig. 4 shows the results of energy dispersion microanalysis of the surface of the coatings based on AlN-TiB_2-$TiSi_2$.

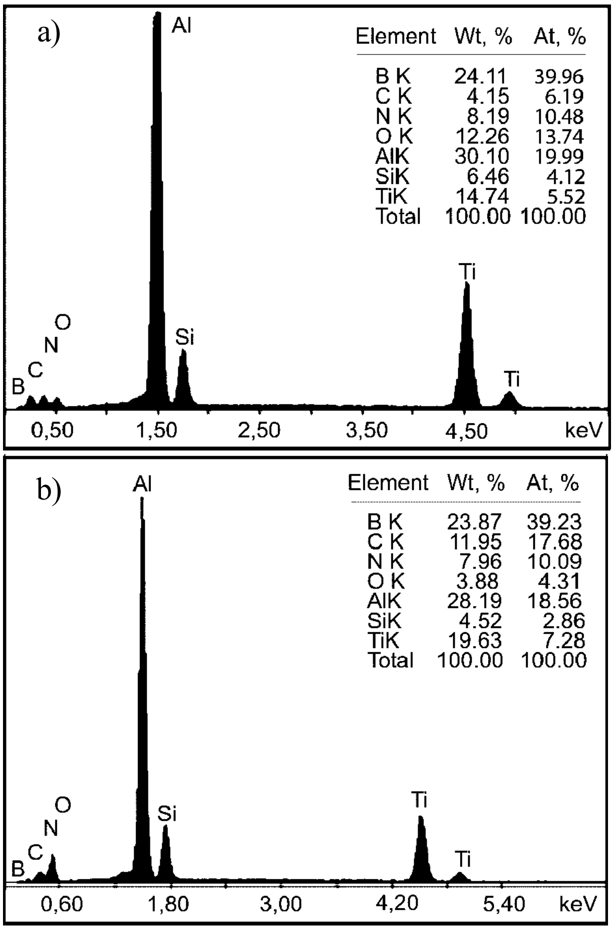


Fig. 4. The elemental composition of coatings based on AlN-TiB_2-$TiSi_2$: a) – in a DC voltage conditions, b) – in a pulsed voltage conditions.

The results of elemental microanalysis of the coating show that when applying a pulsed voltage to the sputtering target, the reduction of content boron, nitrogen, aluminum and silicon takes place (see fig.

5b). As for titanium, the selective sputtering of titanium atoms is less apparent compared with the coatings produced under conditions of DC applied to the target. The presence of oxygen and carbon in the coating is apparently due to the presence of the residual atmosphere in the vacuum system.

$AlN-TiB_2-TiSi_2$ coatings, obtained in this work, had an amorphous structure with a broad "halo" on the XRD spectra after the deposition. It had a center in the area of the diffraction angle $2\theta = 38°$. The size of the ordering area was about $R_m = 10$ Å = 1 nm, i.e., the obtained structure can be attributed to the amorphous cluster class.

Electron microscopy studies of the surface of the coating using reflection and transmission, confirm the presence of the ultrafine structure which is close to amorphous. This is evidenced by the nature of the diffraction pattern (fig. 5).

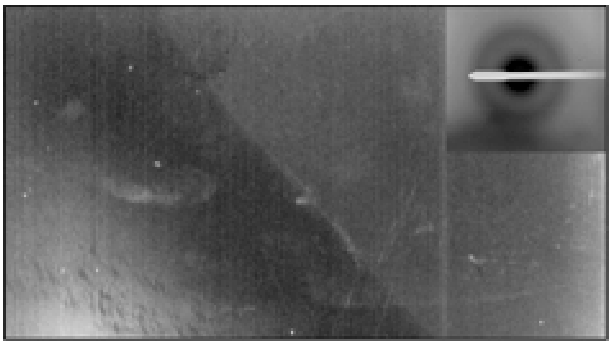


Fig. 5. Electron microscopic image of the coating $AlN-TiB_2-TiSi_2$.

Analysis of the mechanical characteristics, carried out by the nanoindentation method showed that in the initial state the obtained coatings have nanohardness $H = 15.3$ GPa and the elasticity modulus $E = 206$ GPa. The index of viscoplasticity [10] for the system we obtained the system was ~ 0.07, thus striving to the amorphous state of the material.

To obtain a high adhesive strength of the coating to the substrate, according to the literature [11], two factors are required: 1 – mechanical contact between the coating and the substrate, 2 – the chemical interaction on the border of two contacting surfaces. Mechanical interaction is determined by the roughness of the contacting surfaces, and the chemical interaction is determined by the interatomic interaction on the border of the contacting bodies. The high degree of activation can be obtained by surface treatment by the glow discharge and pulse processing before the deposition, which leads to the activation of the atoms interacting at the boundary of the contacting materials.

The adhesion of coatings based on ceramic system $AlN-TiB_2-TiSi_2$, obtained by the pulse magnetron sputtering, to a steel substrate is estimated [12] by the area of the chop which was obtained during the joint local plastic deformation of the coating and its substrate through the penetration of Rockwell indenter at a load of 1470 N. The quality of adhesion determined by this method indicates the presence of chops and peeling around the imprint (see fig. 6).

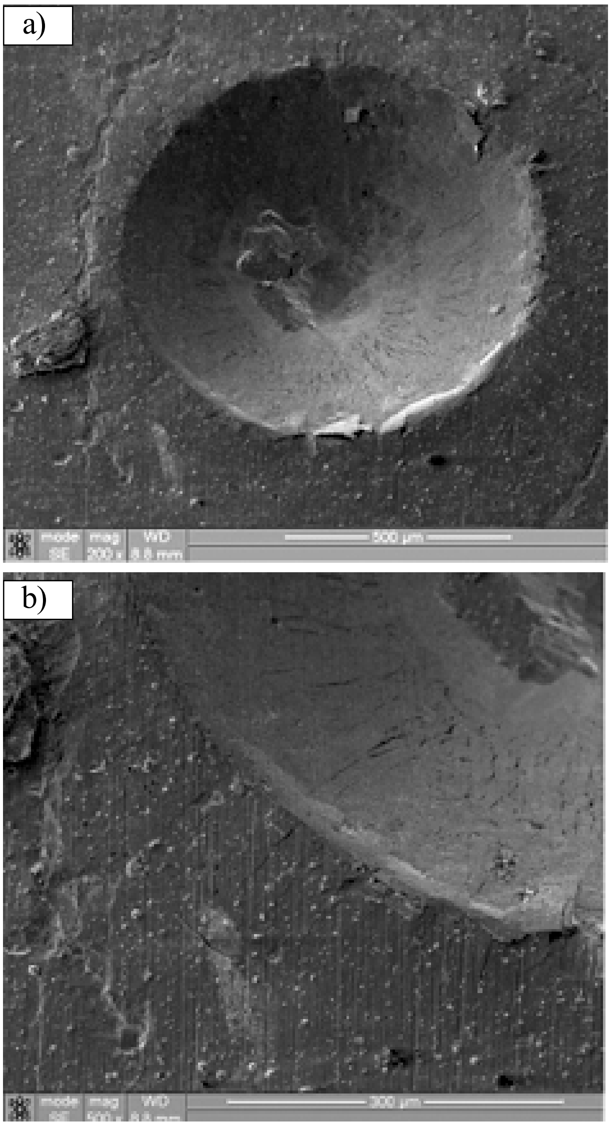


Fig. 6. Image of the area of the indenter imprint on samples of steel with a coating: a) – general view, b) – fragment of the imprint.

Coatings of the system $AlN-TiB_2-TiSi_2$, formed on a steel substrate, are characterized by the sufficient quality (see Fig. 6a) in the area around the imprint after the penetration of the indenter into the deep. Peeling the coating from the substrate was not revealed. The obtained coatings based on ceramics AlN-TiB_2-$TiSi_2$, which have amorphous-like structure [13] can be effectively used to protect the surfaces of the rubbing details from the oxidation wear.

SUMMARY

1. In conditions of applying DC voltage and pulse voltage to the target, the composite coatings based on ceramic compounds AlN-TiB_2-$TiSi_2$ were developed.
2. X-ray diffraction analysis revealed an amorphous-like structure of the coating with the area of ordering about 1 nm and viscoplasticity coefficient of 0.07.
3. The mechanical properties of the coatings are characterized by the hardness of 15.3 GPa, modulus of elasticity of 206 GPa and a high adhesive strength with respect to the substrate.
4. Tribological properties of the obtained amorphous-like coatings based on the ceramic compounds AlN-TiB_2-$TiSi_2$ are promising for using them as protective coatings for the rubbing surfaces of machine details.

1. The work was done by the scientific research topics 0112U006974 and 0113U001079, funded by the Ministry of Education and Science of Ukraine. Part of the work was performed using the diagnostic equipment of the Center of Collective Using of scientific equipment of Belgorod National Research University, “Diagnostics of structure and properties of nanomaterials” under the state contract number 16 55211 7087 with the financial support of the Ministry of Education and Science of the Russian Federation.

REFERENCES

1. Nanostructured Coatings//Editors: Albano Cavaleiro, Jeff Th. M. De Hosson. – M.: Technosphere, 2011. – 792 p. (by Russian).
2. Kelly P.J., Arnell R.D. Magnetron sputtering: a review of recent developments and applications //J. Vacuum. – 2000. – Vol. 56. – P. 159-172.
3. Musil J., Baroch P., Vlиek J. et al. Reactive magnetron sputtering of thin films: present status and trends//Thin Solid Films. – 2005. – Vol. 475. – P. 208-218.
4. Berlin E.V., Seidman L.A. Ion-plasma processes in thin-film technology. – M.: Technosphere, 2010. – 528 p. (by Russian).
5. Azarenkov N.A., Sobol O.V., Pogrebnjak A.D., Beresnev V.M. Engineering of vacuum-plasma coatings. – Kharkiv: Karazin Kharkiv National University, 2011. – 344 p. (by Russian).
6. Lavrov V.N., Orlov I.I., Fedotov A.F. Thermal conductivity and temperature of vacuum-arc evaporation of multilayers of SVS-pressed cathode systems $TiS_{0.5}$-Al and $TiS_{0.5}$-Al-Si//Vestn. Samar. State. Tehn. Univ. Ser. Technical sciences. – 2013. – No. 1 (37). – P. 72-86. (by Russian).
7. Samsonov G.V., Vinnitskiy I.M. Refractory compounds: A handbook. – M.: Metallurgy, 1976. – 560 p. (by Russian).
8. Samsonov G.V., Dvorin L.A. PV Geld Silicide. – M.: Metallurgy, 1979. – 272 p. (by Russian).
9. Andreev A.A., Sabers L.P., Grigoriev S.N. Vacuum-arc coating. – Kharkiv: NSC “KhPTI”, 2010. – 317 p. (by Russian).
10. Firsov S.A., Rogul T.G. Theoretical (limiting) hardness//Add. National Academy of Sciences of Ukraine. – 2007. – No. 4. – P. 110-114.
11. Shautsukov A.G. Contemporary conception about the possible mechanisms of adhesion of metallic films to different films//Applied Physics. – 2006. – No. 5. – P. 16-21. (by Russian).
12. Matsevity V.M. Coatings for cutting tools. – Kharkov: High School, 1987. – 127 p. (by Russian).
13. Musil J. Properties of hard nanocomposite thin films. (In book Nanocomposite Thin Films and Coatings: Processing, Properties and Performance). Ch. 5/Eds. S. Zhang, A. Nasar. – 2007. – London: Imperial College Press. – P. 281-328.