

Встановлено вплив швидкості нагрівання 150, 350 і 600 °С/хв, тисків 8 і 18 МПа на процес ущільнення реакційної суміші Cr_2O_3 – $15\text{AlN}_{\text{нано}}$, на твердість і тріщиностійкість щільного матеріалу. Інтенсивність ущільнення шихти Cr_2O_3 – 15AlN залежить від величини тиску і від швидкості нагрівання. Тиск 18 МПа забезпечує повне ущільнення суміші незалежно від вказаних швидкостей нагрівання, а тиск 8 МПа забезпечує повне ущільнення тільки при швидкості нагрівання 600 °С/хв. Для швидкості нагрівання 600 °С/хв. криві ущільнення суміші для тисків 8 і 18 МПа близькі за формою. Встановлено, що при швидкості нагрівання 600 °С/хв процес ущільнення суміші, крім тиску, додатково активується ефектом екзотермічної реакції між її компонентами. Підвищення швидкості з 150 до 600 °С нагрівання дозволяє збільшити твердість і тріщиностійкість щільного матеріалу відповідно на 1,0 ГПа і 1,5 МПа·м^{1/2}. Виявлено, що новоутворена в процесі ГП суміші Cr_2O_3 – $15\text{AlN}_{\text{нано}}$ структура щільного матеріалу є дисперснозміцненого типу: матрична із твердого розчину перемінного складу типу $(\text{Cr}_{1-x}\text{Al}_x)_2\text{O}_3$ ($0 < x < 0,4$) і дисперсних стохастично розподілених в ній включень Cr_2N розміром до 2 мкм, які леговані до 1,8 % Al. Виявлено окремі крупні включення розміром 10–40 мкм з аналогічною, як основна структура, будовою, але з матричною фазою із твердого розчину $(\text{Cr}_{1-x}\text{Al}_x)_2\text{O}_3$ ($0,5 < x < 0,9$). Тріщиностійкість одержаного в процесі досліджень матеріалу, в 1,5 більша, а твердість на 1,2 ГПа менша за аналогічні характеристики найбільш поширеної на сьогодні кераміки «змішаною» типу на основі Al_2O_3 –TiC

Ключові слова: кераміка, Cr_2O_3 , AlN, нано-, мікропорошки, композиційний матеріал, ріжучі пластини, гаряче пресування

EXPLORING THE PROCESS TO OBTAIN A COMPOSITE BASED ON Cr_2O_3 –AlN USING A METHOD OF HOT PRESSING

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1. Introduction

Modern commercially-available types of cutting ceramics largely meet the requirements to the process of high-efficiency dry blade machining of the difficult-to-treat materials based on Fe, Ni, Co, Cr, W, etc. The functional properties of such materials are ensured in the first place by a high level of physical-chemical and mechanical properties of the starting micro-powders. In addition, the powders must be physically and chemically inert to the high-temperature intramolecular interaction with a machined material, and resistant to oxidation in the process of cutting. At present, these criteria are met by a limited number of micro-powders from refractory compounds, in particular, oxides of aluminum and zirconium (partially stabilized), titanium carbide and carbonitride, and silicon nitride. Proof of this is that 20 major companies from Sweden, Japan, the United States, Germany, Russia, China, South Korea, etc. industrially produce those cutting

materials that were designed 30–40 years ago, four kinds of ceramics: white (Al_2O_3), mixed (Al_2O_3 –TiC, TiN), nitride (Si_3N_4 -based), fibrous (Al_2O_3 –SiC_w). The technology of obtaining conventional cutting ceramics employs a costly and low-efficient operation of hot-pressing that involves graphite tooling. High (>1,600 °C) temperature and pressure (30–40 MPa) greatly increase energy intensity and reduce the environmental friendliness of a given technology. Attempts to use much more expensive and non-technological nano-powders from refractory compounds [1–3] based on the conventional production technology of cutting plates failed to enhance their quality though increased the cost [4, 5].

Therefore, in terms of materials science, the base for designing competitive cutting ceramic materials should be the improvement of quality and the reduction of energy intensity of the HP process, specifically by decreasing its temperature and pressure. One of such fields is the technology of reactive synthesis [6].

2. Literature review and problem statement

One of the implemented technologies of reactive synthesis is the development of the material “Bichromit-R” based on a mixture of the micro-powder Cr_2O_3 and 15 (% by weight) of the micro-powder AlN [6]. According to [7], in the process of HP of the mixture $\text{Cr}_2\text{O}_3\text{-15AlN}_{\text{nano}}$ at a temperature of 1 600 °C and a pressure of 18 MPa, as a result of the exothermic reaction among its components, there forms a new matrix phase from the solid solution $\text{Cr}_x\text{Al}_{1-x}\text{O}_3$ of various composition and the phases of CrN, Cr_2N dispersed in it. The peculiarity of a given technology is the use of a cheap commercially-available powder of chromium oxide as a basic component of the resulting mixture.

Study [8] has shown that the stability of Bichromit-R plates under the finishing machining of hardened steel of grade ShKh15 (HRC60) is at the level of stability for plates made from the mixed ceramics of grade CC650 by Sandvik Coromant (Sweden). High operating properties are explained by the authors are due to a higher crack resistance (Mises theory), as compared to pure aluminum oxide in conventional ceramics, of the newly formed matrix phase of solid solution based on Cr_2O_3 and Al_2O_3 . This could be a consequence of the coherence of the newly formed phases – the planes [110], [112] of the disperse phase of the solid solution based on Cr_2N are parallel to planes [110] and [116] of the matrix phase of the solid solution $(\text{Cr}_{1-x}\text{-Al}_x)_2\text{O}_3$ [7, 9]. This structural factor dominates over the presence in it of brittle and non-strong dispersed inclusions from Cr_2N .

The main disadvantage of a given technology is still its high energy intensity due to the temperature and pressure that are similar to the technology of obtaining conventional ceramics. That became one of the main reasons for the absence of Bichromit-R in the market of modern instrumental composite materials. The key issue that was not resolved when designing a given material was the lack of studies into the influence of heating rate, specifically between 1,250–1,500 °C, at which the intense compaction of the material occurs, as well as the chemical interaction between Cr_2O_3 and AlN_{nano} [9].

This factor is very important for the rapid-proceeding, and typically self-emerging, exothermic reactions in powder mixtures, especially when they are compacted under the influence of thermobaric parameters of the HP process.

In addition, when exploring the process of obtaining Bichromit-R, given the lack of necessary instruments, the quantitative content of nitrogen and carbon in its structure was not investigated. That did not make it possible for the authors to define the actual chemical composition of its components.

It is known that CrN forms from elements when heated to 1,200 °C. Therefore, it is of scientific and practical interest to investigate the influence of heating rate and different pressure at HP of the mixture $\text{Cr}_2\text{O}_3\text{-15AlN}_{\text{nano}}$ on the process of its compaction, structure formation, and the properties of the material.

3. The aim and objectives of the study

The aim of this study is to investigate the compaction, structure formation, and the properties of the material at hot

pressing of the mixture Cr_2O_3 with the nanopowder AlN at different pressures and heating rates.

To accomplish the aim, the following tasks have been set:

- to explore the impact of heating rate at HP of the mixture $\text{Cr}_2\text{O}_3\text{-15AlN}_{\text{nano}}$ on the process of compaction, structure formation, and the properties of the material;
- to define the conditions for the formation of the material with maximum hardness and crack resistance;
- to perform the micro-roentgen spectral study of the chemical composition of the components of the structure of the obtained material with maximal mechanical properties.

4. Materials and methods to study the microstructure and properties of a cutting material

The study was carried out using the following powders:

- chromium oxide powder, grade “pure”, GOST 2912-79;
- aluminum nitride, grade “pure”, from furnace synthesis, TU6-09-110-75, made at Donetsk plant “Chemical reagents” (Ukraine);
- the nanopowder AlN, from plasma chemical synthesis (the city of Riga) with specific surface $S=20\text{-}40\text{ m}^2/\text{g}$ (specifications from the manufacturer).

For the study, we prepared mixtures of Cr_2O_3 with 15 AlN (an analog to the mixture Bichromit-R). Hereafter, % by weight.

A mixture of powders with alcohol was stirred in an iron drum by milling bodies made from the alloy BK at a ball mill over 24 hours. The hot pressing of the mixture was carried out in an open air in a graphite mold at the installation with an induction current heating of frequency 2.4 kHz.

Parameters for the process of HP for a billet with a diameter of 20 mm: temperature $T=1,520\text{ °C}$, exposure 10 min, pressure on punches $P=8$ and 18 MPa. We heated the mold to 1,000 °C at a rate of 60–70 °C/min. In the range of 1,000–1,520 °C, the heating of the mixture was performed at a rate of 150, 350, and 600 °C/min in order to determine the maximum influence of the exothermic reaction of the charge components on its compaction, as well as on the properties of the material. The temperature of 1,520 °C for HP was taken based on a condition that it exceeds the temperature (1,450 °C) of the intensive chemical interaction between Cr_2O_3 and AlN_{nano} , and it is close (1,600 °C) to the temperature for obtaining Bichromit-R [6].

One batch of samples was heated under a constant pressure of 8 MPa, then the pressure was increased to 18 MPa. The pressure of 18 MPa corresponds to the pressure that was used in the process of HP of Bichromit-R. The pressure of 8 MPa was taken based on the point of view about the possible additional impact of effect of the reaction on the HP process. A stepwise increase in the pressure from 8 to 18 MPa at 1,100 °C for the second case is due to the insufficient strength of the graphite mold. Cooling of a sample following the isothermal exposure was carried out at a simultaneous decrease in the temperature to 800 °C and the load – to 0 over 15 min.

We explored the microstructure and chemical composition at REM (ZEISS, JENA, Germany). It should be noted that the finely grained, multi-phase structure, especially if obtained from a chemical synthesis, is a difficult object to study the chemical composition of its components.

5. Results of studying the process of hot pressing

Fig. 1 shows the distribution diagrams of dimensions for the micro-powder Cr_2O_3 .

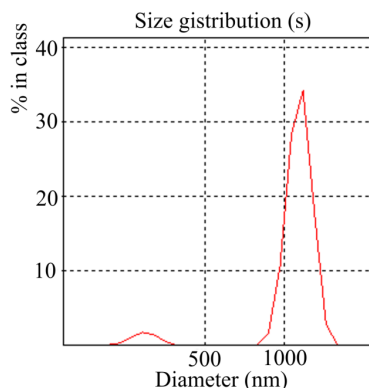


Fig. 1. Distribution diagram of particles' dimensions of the micro-powder Cr_2O_3

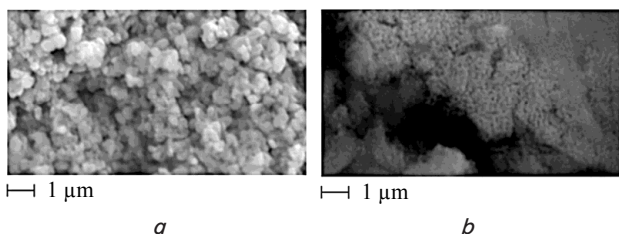


Fig. 2. Starting powders: *a* – Cr_2O_3 , *b* – AlN_{nano}

Images in Fig. 2 show that the size of powders of Cr_2O_3 in the original state (Fig. 2, *a*) are roughly in the range of (0.7–1.5 μm).

Fig. 3 shows compaction diagrams of the mixture 15AlN for different, $p=8$ and 18 MPa, pressure on punches.

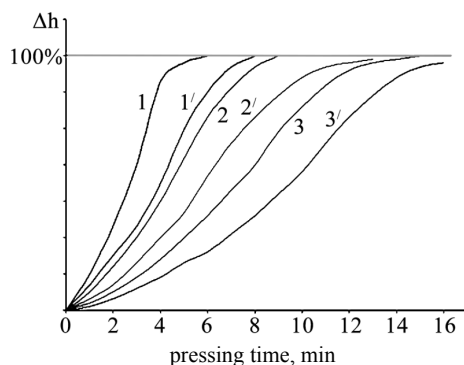


Fig. 3. Compaction diagrams of the mixture $\text{Cr}_2\text{O}_3-15\text{AlN}$ at HP for pressures of 8 and 18 MPa and different heating rates in the range of 800–1,520 °C: 1, 2, 3 – $P=18$ MPa; 1', 2', 3' – $P=8$ MPa; 1, 1' – $v=600$ °C/min.; 2, 2' – $v=350$ degrees/min.; 3, 3' – $v=150$ °C/min.

Fig. 3 shows that the intensity of the charge compaction depends on the magnitude of pressure and the rate of heating. A pressure of 18 MPa ensures the complete compaction of the mixture regardless of the specified heating rates. But a pressure of 8 MPa does not provide for the complete compaction of the mixture at heating rates of 150 °C/min.

For a heating rate of 600 °C/min the compaction curves, regardless of the mixture composition, for pressures of 8 and 18 MPa are similar in shape. This indicates that at a heating rate of 600 °C/min the process of the mixture compaction, in addition to pressure, is additionally activated by the effect of exothermic reaction among its components.

Dependence diagrams of hardness and crack resistance of the material 15AlN_{nano} on heating rate are shown in Fig. 4.

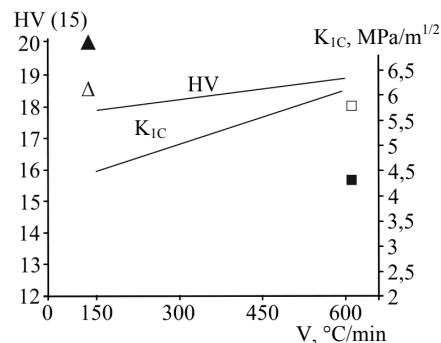


Fig. 4. Dependence diagrams of hardness and crack resistance (of the material 15AlN_{nano} on heating rate at HP under pressure $P=8$ MPa

Fig. 4 shows that the hardness HV and the fracture toughness K_{1C} of the imported ceramics of the “mixed” type is, respectively, 20 GPa, 1 and 4.6 $\text{MPa}\cdot\text{m}^{1/2}$. Similar indicators for Bichromit-R at the level of 18.5 GPa and 5.5 $\text{MPa}\cdot\text{m}^{1/2}$.

Increase the heating rate from 150 to 600 °C/min increases the hardness and crack resistance by, respectively, 1.0 GPa and 1.5 $\text{MPa}\cdot\text{m}^{1/2}$. In this case, the maximum values for hardness and crack resistance of the examined material are by 0.3 and 0.4 units larger than those for its analog Bichromit-R [5].

Fig. 4 shows that this value for crack resistance in diagram 3 is matched with a value for a heating rate of 400 °C/min. That was probably the rate at which they heated the mixture at HP of the material Bichromit-R, which was not registered in [5].

We studied the microstructure (Fig. 5) using samples with the maximum values for hardness and crack resistance, obtained under a pressure of 8 MPa and at the maximum (600 °C/min) heating rate (Fig. 3).

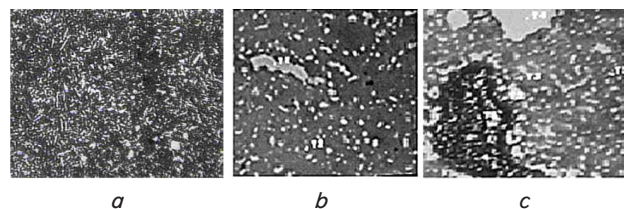


Fig. 5. Images of the microstructure of ceramics samples: *a* – $\text{Al}_2\text{O}_3-\text{TiC}$, *b*, *c* – 15AlN_{nano} , *b* – basic structure; *c* – macro-inclusions to the basic structure

Based on the results from a local chemical analysis, Table 1 gives the share ratios of components in the matrix and disperse phases of the examined samples, as well as the content of impurities in them. Fig. 5 shows that the basic structure of the examined sample is of the dispersed-strengthened type. The matrix phase is the solid solution of variable composition $(\text{Cr}_x\text{Al}_{1-x})_2\text{O}_3$ ($0 < x < 0.5$) newly formed in the process of reaction.

Dispersed inclusions (of light color) are stochastically distributed throughout the matrix phase. By the ratio of N and Cr content, they represent Cr_2N . In addition, they revealed up to 1.8 % of Al. Separate inclusions also demonstrated up to 1.53 % of oxygen.

A feature of the structure of samples (Fig. 5, c) is the presence of individual macro-structural formations of different rounded shapes in it, whose dimensions are in the range of 10–30 μm . In these inclusions, the matrix phase (point T1, Fig. 5, c) is darker in color than the matrix phase (point T2, Fig. 5, c) of the basic structure. Its chemical composition corresponds to the component of the solid solution $\text{Cr}_{1-x}\text{Al}_x)_2\text{O}_3$, ($0.5 < x < 1.0$).

That is, it contains more aluminum and less Cr than in the solid solution of the basic structure.

Table 1

Results from chemical analysis of components of the structure of the material 15AlN, obtained at GP under a pressure of 8 MPa and at a heating rate of 600 °C/min

Material designation	Chemical composition of elements	
	Matrix structure Point number in Fig. 5	dispersed inclusions, points No. 1, 5 in Fig. 5, b, p. 2 in Fig. 5, c
Basic structure	$(\text{Cr}_{1-x}\text{Al}_x)_2\text{O}_3$, $0 < x < 0.4$	Cr_2N , inclusions to 1,8 Al
Macro-inclusions	$\text{Cr}_{1-x}\text{Al}_x)_2\text{O}_3$, $0.5 < x < 1.0$	

The dispersed particles based on Cr_2N in a given macro-inclusion have the same composition of chemical elements, while 2 times smaller size, than the inclusions to the basic structure (Fig. 5, c and Table 1). At the interface between a given inclusion and the basic structure the dispersed particles based on Cr_2N have mostly an elongated shape and the enlarged size (2–10 μm). It is also important to note that the microhardness HV(0.5 H) of the material inside these macro-formations is 1.03 times greater than the microhardness of the material beyond its border.

The disadvantage of a given structure of the material is the presence of separate individual inclusions based on chrome nitride the size of up to 10 μm (point T1 in Fig. 5, a, and point T4, Fig. 5, b).

Fig. 6 shows fractograms of the 15AlN samples. The surface of the samples' fracture (Fig. 6, a) has a clearly expressed relief with rounded ridges, non-characteristic of the conventional ceramics. It is also important to note the presence at the fracture's surface of the micropores of spherical shape smaller

than 1 μm . One can see that the destruction of a given sample occurs mainly in line with the intercrystallite mechanism. A small share of flat facets testifies to the presence of trans-crystallite destruction as well. Similar relief of the fracture's surface is also demonstrated by highly-viscous materials based on complex compounds, such as type of MAX-phase.

6. Discussion of results of studying the process of hot pressing

The structure of the dispersed type, formed in the HP process of the reactive mixture $\text{Cr}_2\text{O}_3\text{--}15\text{AlN}_{\text{nano}}$ is characteristic of the modern ceramic materials for instrumental purposes. The intensification of compaction process of the mixture $\text{Cr}_2\text{O}_3\text{--AlN}$ with an increase in heating rate from 150 to 600 °C in the range of 800–1520 °C with a decrease in pressure from 18 to 8 MPa during HP directly points to the influence of exothermal effect due to the interaction between its components. Formation of solid solutions of alternating composition of the type $(\text{Al}_{2-x}\text{Cr}_x)_2\text{O}_3$ and the disperse phase in it based on Cr_2N that contains up to 1.8 % Al is consistent with the results reported in [10]. The presence of macro-structural formations of the composite type (Fig. 5, a, b) with the chemical composition of the matrix phase, the size and content of dispersed inclusions, different from the base structure, is explained by the agglomerated character of the AlN nanopowder in the starting mixture. The mechanism of their formations is the result of the penetration of gaseous and liquid products from the disintegration of chromium oxide to the pores of aggregates from nanoparticles of aluminum nitride.

The presence of up to 1.5 % of oxygen in separate chromium nitride inclusions (Table 1) is probably the result of that the x-ray beam overlapped the solid solution. The absence of CrN in the structure of a material, compared to the analog Bichromit-R, is due to the high rate of heating at which aluminum nitride cannot form at a temperature of 800–1,100 °C.

It is known that Cr_2N in terms of a set of properties is not included in the group of compounds for instrumental purposes [10]. Therefore, the high fracture toughness of the obtained material is explained as follows:

- formation of the matrix phase of solid solution with complex alternating composition $(\text{Cr}_{1-x}\text{Al}_x)_2\text{O}_3$;
- formation of dispersed inclusions of solid solution up to 1.8 % Al in Cr_2N ;
- formation of individual structural macro-formations of the rounded shape the size of up to 30 μm with a matrix phase of the type $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$.

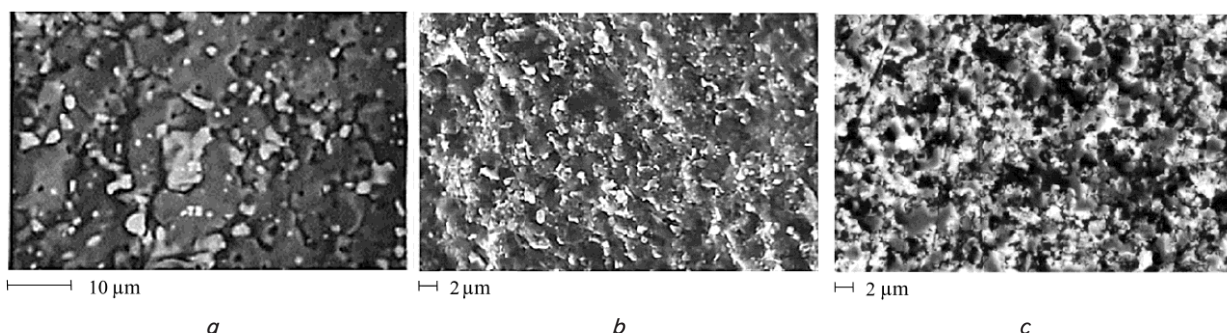


Fig. 6. Fractograms of the sample: a – $\text{Cr}_2\text{O}_3\text{--}15\text{AlN}_{\text{nano}}$ % by weight, b – $\text{Cr}_2\text{O}_3\text{--}35\text{AlN}_{\text{nano}}$ % by weight HP at heating rate $V=600\text{ }^\circ\text{C}/\text{min}$ under pressure $P=8\text{ MPa}$ to temperature $T=1,520\text{ }^\circ\text{C}$, exposure 10 min $\times 3200$

The presence in the structure of the obtained material of separate large (up to 10 μm) inclusions based on Cr_2N , may lead, by analogy with the inclusions of this size to the structure of conventional ceramics, to a decrease in its crack resistance.

7. Conclusions

1. We have established the effect of increasing the heating rate, from 150 to 600 $^{\circ}\text{C}/\text{min}$, on the process at HP of the mixture $\text{Cr}_2\text{O}_3\text{-}15\text{AlN}_{\text{nano}}$, specifically:

– it reduces pressure of the complete compaction of a material from 18 to 8, resulting in lower energy intensity of the technology;

– it improves the hardness and fracture toughness by, respectively, 1.0 GPa and 1.5 $\text{MPa}\cdot\text{m}^{1/2}$.

2. It has been shown that the structure of the obtained material with maximum hardness (HV18.7 GPa) and crack resistance ($K_{\text{IC}} = \text{MPa}\cdot\text{m}^{1/2}$) is a structure of the dispersed type – the matrix phase of solid solution $(\text{Cr}_{1-x}\text{-Al}_x)_2\text{O}_3$ and the particles of Cr_2N , dispersed in it, with inclusions to 1.8 % Al.

3. In terms of structural characteristics, chemical composition, hardness and crack resistance, the material obtained in this work meets modern requirements to instrumental composite material for high-efficiency finishing and semi-finishing machining of difficult-to-treat materials (HRC 65) (carbon, alloyed steels, cast iron, refractory alloys, etc.).

References

1. Panov V. S., Malochkin O. V. Ul'tradispersnyy oksid tsirkoniya kak osnova metallobrabatyvayushchego instrumenta // Porodorzushayushchiy i metallobrabatyvayushchiy instrument tekhnika i tekhnologiya ego izgotovleniya i primeneniya. 2003. Issue 3. P. 245–246.
2. Gleiter H. Nanostructured materials: basic concepts and microstructure // Acta Materialia. 2000. Vol. 48, Issue 1. P. 1–29. doi: [https://doi.org/10.1016/s1359-6454\(99\)00285-2](https://doi.org/10.1016/s1359-6454(99)00285-2)
3. Rahulia A. V. Keramichni nanokompozyty dlia novoho pokolinnia rizhuchykh instrumentiv i vazhkonavantazhenykh znosostiyykh komponentiv // Nauka ta innovatsiyi. 2006. Issue 4. P. 47.
4. Skorohod V. V., Ragulya A. V. Nanostrukturnaya keramika i nanokompozyty: dostizheniya i perspektivy. Vol. 2. Prohresyvnii materialy i tekhnolohiyi. Kyiv: Akademperiodyka, 2003. P. 7–34.
5. Vovk R. V. Investigation of structure and properties of composite material $\text{Al}_2\text{O}_3\text{-SiC}$ obtained by electroconsolidation process // Functional materials. 2018. Vol. 25, Issue 1. P. 43–47. doi: <https://doi.org/10.15407/fm25.01.043>
6. Novi keramichni kompozytsiyni materialy instrumentalnoho pryznachennia: monohrafiya / Vovk R. V., Hevorkian E. S., Nerubatskyi V. P. et. al. Kharkiv, 2017. 248 p.
7. Prokopiv N. M., Gorban' A. E. Strukuroobrazovanie pri goryachem pressovanii shihty $\text{Cr}_2\text{O}_3\text{-AlN}$ // Sverhtv. materialy. 1999. Issue 4. P. 36–39.
8. Volkov A. I., Zharskiy I. M. Bol'shoy himicheskii spravochnik. Minsk: Sovremennaya shkola, 2005. 608 p.
9. Prokopiv M. M., Horban A. Ye. Shykhta dlia vyhotovlennia kompozytsiynoho materialu: Pat. No. 28622. No. 97073869; declared: 21.07.1997; published: 15.05.2002, Bul. No. 5.
10. Guglya A. G. Structure, phase and electronic characteristics of $\text{Cr}_{1-x}\text{-Al}_x\text{-N}$ - and $\text{Cr}_{1-x}\text{-V}_x\text{-N}$ coatings // Voprosy atomnoy nauki i tekhniki. 2008. Issue 2. P. 155–158.