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THE STRUCTURE OF A SUPERHARD COMPOSITE, SYNTHESIZED FROM HEXAGONAL BORON NITRIDE AND ALUMINUM NITRIDE NANOFIBERS

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The paper considers the results of a study of the structure, phase composition, and microhardness of a superhard composite material based on cubic boron nitride. The material under study was obtained from a hexagonal modification of BN modified by nanostructured aluminum nitride AlN. The procedure of an X-ray diffraction study is described that includes a radiography phase analysis at an automated complex based on a diffractometer with recording in scanning. The micromechanical properties of the composite were investigated by the method of nanoindentation. It is shown that obtained under high pressures and temperatures material contains aluminum boride AlB_2 with a hexagonal crystal lattice alongside with the cubic BN and AlN.

***Keywords*:** superhard composite materials, high pressures and temperatures, cubic and hexagonal boron nitride, aluminum nitride nanofibres, modification, nanostructure, nanoindentation, diffractogram, microhardness.

Introduction

At present, superhard composite materials (SHCM) based on micropowders of cubic boron nitride (CBN) for finishing and semi-finishing pieces made of cast iron, hardened steels and other hard-to-machine materials have become widespread instead of traditional hard-alloy tools. As a rule, such materials are made of CBN micropowders with a size of less than 20 microns. Since the initial CBN powders are considerably brittle, when cutting hard-to-machine items, the cutting edge of the tool is chipped. A high level of mechanical properties of SHCM is known to be determined by a highly refined grain structure [1]. Similarly with refractory materials that acquire plastic properties in the nanodispersed state [2], superhard materials obtained on the basis of nanodispersed powders, or on the basis of compositions including nano-, submicro- and micropowders, must also have improved physicomechanical characteristics, including higher fracture toughness. Therefore, the development of methods for obtaining SHCM on the basis of nano- and submicron powders of cubic BN is a very urgent practical problem.

It was shown earlier [3] that for the production of SHCM on the basis of CBN used in metal working, nano- and micropowders of titanium and aluminum nitrides, which are refractory compounds, are sufficiently effective binding substances. The boundaries of the temperature range within which it is advisable to sinter powder compositions for obtaining a cutting tool are determined. It has been found that the obtained material is satisfactory refractory in iron processing, but sufficient quality of the machined surface is not achieved.

At the same time, it is known that SHCM based on CBN, characterized by the most fine-grained structure, are obtained, as a rule, by direct phase transitions from hexagonal boron nitride (HBN) under high pressures and temperatures [4, 5]. However, along with the high hardness approaching the hardness of single crystals of CBN, such materials are characterized by increased brittleness, which limits the field of their practical use.

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The introduction of heat-resistant nanoceramics, in particular of refractory nitrides and borides of titanium, silicon, aluminum [3] facilitates an increase in the plastic properties of such materials and improves sintering of CBN under high temperatures without recrystallization. In addition, metal nitrides, as well as metals themselves, in particular aluminum nitride and aluminum, serve as catalysts for the phase transformation of hexagonal BN to cubic one. It was shown in [6] that under thermobaric treatment of HBN, modified with aluminium, the formation of refractory compounds (AlN, AlB_2, Al_2O_3 corundum and alumina oxide of non-stoichiometric compound $Al_{2,6}O_4$) takes place under high temperature in a high-pressure chamber directly during the synthesis of a superhard material.

In [7, 8], a fundamentally new approach to the creation of nanostructured composite polyfunctional refractory ceramic fillers (NCPRCF) was proposed. The developed physico-chemical principles for the production of NCPRCFs consist in the task-oriented modification of the initial micro- and ultradispersed powders by reaction-active elements of the surface layers that makes for the formation of highly dispersed components on the surface of micropowder particles. According to the developed concept, the initial micro- and ultradispersed powders, when modified with active components, perform, on the one hand, the function of donors for the chemical reactions on their surface leading to the formation of in-situ nanoscale elements and compounds chemically bound by micropowder particles, on the other hand, carriers of nanosized compounds into the reaction medium.

It was established in [7, 8] that the best interaction between the BN and the binder occurs when the nanostructured refractory compounds AlN, AlB_2 are formed directly (in situ) on the surface of the micro-powder particles of the HBN. In this case, the quantitative and phase composition of the nanobinder is specified at the stage of its formation when the HBN is modified. AlN nitride, which forms in this case, is a substance that stimulates the phase transformation of the HBN in CBN and offers a sufficiently high thermal conductivity, which will improve the performance of a metalworking tool.

The purpose of this work is to study the process of obtaining nanostructured SHCM based on CBN by phase conversion from hexagonal BN modified with nanostructured AlN.

1. The research technique

As the source raw material, the micropowder of the HBN from the Zaporozhye Abrasive Plant (TU 2-036-1045-88) with a BN particle size of up to 50 μm was used in the work. The modification of the HBN micro-powder with nanoparticles of refractory compounds was carried out in a reducing medium of ammonia and hydrogen under temperatures of 900-950°C, during which a nanocoating of refractory aluminum compounds was formed on the HBN.

The thermobaric treatment of the charge stock was carried out in an high pressure apparatus (HPA) "anvil with a hollow" under pressures of (4.5-7.7) GPa in the temperature range of 1600-2300°C during (15-45) sec. As a medium transferring pressure, a container made of lithographic stone was used, inside of which a tubular graphite heater with the material under study was placed. To estimate the pressure in the synthesis chamber, a calibration method at room temperature was used, based on the comparison of the press force and the pressure of the polymorphic transformation in the standard substance (Bi and PbSe). Temperature control was carried out by means of chromel-alumel and platinum-platinum-rhodium thermocouples. A controller developed on the basis of a PC-compatible industrial workstation with an installed graphic LCD-display and a keyboard was used to control the specified sintering parameters (duration and heating power, as well as the loading force) [9].

X-ray diffraction studies involving radiography phase analysis (RPA) were performed on an automated X-ray complex based on the DRONE-3M diffractometer in CoKα radiation. The radiographic recording was carried out in the scanning mode (point-source) with the interval of 0.1°. In order to ensure the reliability of the obtained results, the pulse set duration at a point was 20

seconds. A complex AFM analysis was carried out on a scanning NT-206 microscope using triangular cantilevers NSC11 with a resonance frequency of 315 kHz and a radius of curvature of the tip of ~10 nm. The micromechanical properties of the composite were also investigated by the nanoindentation method using a nanoindenter of 750 Ubi brand from Hysitron firm (USA) with a Berkovich indenter with a radius of curvature of 100 nm.

2. Results and discussion

Figure 1 shows fragments of diffractograms of the initial BN micropowder and the synthesis product formed on its basis. It can be seen that there are no impurities in the initial BN powder, as there is no evidence except for reflections belonging to the BN powder in the diffractogram (Fig.1a). It is also seen that the reflections of the HBN powder are sharp, which directly indicates that its particles are sufficiently large, the size of which, as has already been noted, is in the range up to 50 μm. The SEM image of the BN powder is consistent with the X-ray diffraction analysis, from this it follows that the size of its particles is within the specified range and they are of a plate-like shape typical for HBN (Fig. 1a).

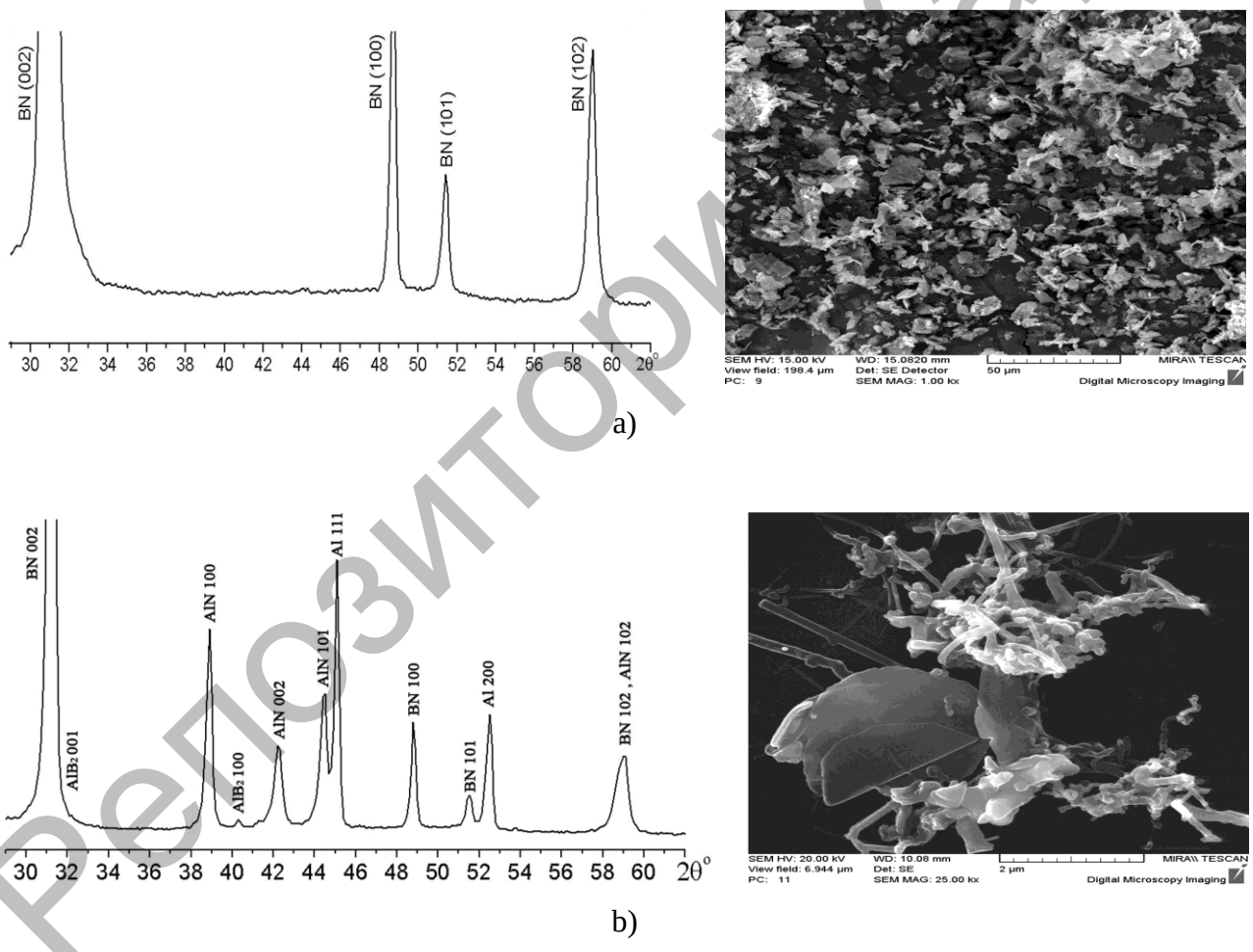

Fig.1. Fragments of diffractograms and the microstructure of the initial powder of hexagonal boron nitride (a) and the product of synthesis (b)

The result of phase transformations and chemical reactions in the modification of BN with aluminum is the formation of BN particles of ceramic compounds of the metal on the surface. An X-ray study of the aluminum-modified BN powder showed that those compounds are AlN and AlB_2 (Fig. 1b). AlN has a form of a hexagonal crystal lattice; the lattice parameters of the unit cell are a=0.3111 nm, c=0.4979 nm. The same syngony is characteristic of aluminum boride. Besides the

synthesis of refractory ceramic compounds, unreacted aluminum is found in the charge mixture (Fig. 1 b). The aluminum nitride in the resulting charge is synthesized in a reducing atmosphere containing ammonia and hydrogen during the processing of the initial mixture at 900-950° C according to the reaction $2Al + 2NH_3 \rightarrow 2AlN + 3H_2$ .. ↑

AlB_2 aluminum boride content in the resulting charge can be explained by partial decomposition of the HBN into components - B and N, and a reaction between aluminum and free boron, a minor amount of which is in the original mixture. Released during decomposition of boron nitride, nitrogen reacts with aluminum to form the additional AlN, the main content of which is synthesized according to the above formula by reaction with ammonia, being in a reducing atmosphere. The obtained data show that in this case the quantitative content of ceramic compounds of AlN and AlB_2 in NCPRCF is 18% and 5% respectively. The particle size of the AlN is 18 nm, and that of AlB_2 is 44 nm. The corresponding share of decomposed hexagonal boron nitride is ~2%.

The study of the structure of the obtained charge by the method of scanning electron microscopy showed that the synthesized aluminum nitride is represented as whiskers and nanofibres, firmly connected with fragments of hexagonal boron nitride (Fig. 1a, b). This character of the structure allows us to conclude that the growth of this nitride is initiated by the partial decomposition of boron nitride, thereby ensuring a strong chemical bond between the nanowhiskers and nanofibres of AlN with the microparticles of the HBN. Thus, in the obtained powder material, a uniform distribution of refractory nanosized ceramic compounds and aluminum serving as catalysts for the phase transition of HBN→CBN and modifying additives for the synthesis of SHCM is observed.

As a result of sintering of the charge modified by nanosized refractory components based on HBN, a solid material was formed under a pressure of 4.5 GPa. The performed X-ray phase analysis showed that under these technological parameters a complete phase transition of HBN→CBN was carried out. This is evidenced by the absence of reflections of lines related to boron nitride of hexagonal modification in the diffractogram of the synthesized material (Fig. 2).

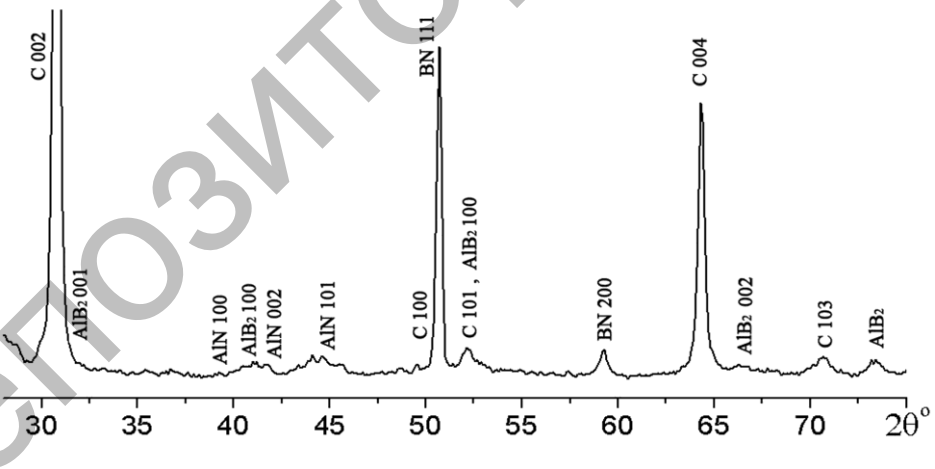

Fig.2. The diffractogram of the composite material obtained as a result of thermobaric treatment of the charge based on BN.

Besides the CBN lines, reflections related to nitride and aluminum boride are recorded in the diffractogram. The low intensity of the corresponding lines indicates that these compounds are present in the tracks. At the same time there are no reflections of aluminum, which indicates its complete transformation during the thermobaric treatment of the material. The presence of intense reflection of graphite refers to the remains of the holder, which is part of the equipment. Such a phase composition of the synthesized material ensures its high microhardness, which reaches (30 - 32) GPa.

Conclusion

Physicochemical principles of in-situ synthesis of AlN in a charge mixture based on the HBN in the form of whiskers and nanofibres, as well as nano-sized aluminum boride AlB_2 serving as catalysts for the phase transition of HBN→CBN and modifying additives in thermobaric sintering of SHCM was developed. As a result of thermobaric sintering of the modified HBN powder, a SHCM based on cubic BN offering a microhardness of 30-32 GPa was obtained, promising for use in cutting tools for finish turning of hardened steels, cast irons, and other hard-to-machine materials.

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