# KAPITEL 10 / *CHAPTER 10* [10]
# PRODUCTION OF SUPERHARD AND ULTRAHARD MATERIALS

DOI: 10.30890/2709-2313.2023-22-01-017

## Introduction

Obtaining new materials with a hardness comparable to or even higher than that of diamond is an important goal that has been the focus of research by scientists from different countries in recent years. This is due, firstly, to the theoretical generalization of the accumulated experimental data on the relationship between the structure and properties of materials obtained under various conditions, including high pressures and temperatures, and the prediction on this basis of new phases with a unique combination of physical and mechanical properties. Secondly, it is a consequence of the creation of new structural materials that require special methods of machining, which can be accomplished by using new superhard materials. And finally, it is also due to the fact that the most effective tools today, equipped with mono- or polycrystals of diamond or cubic boron nitride, are very expensive.

As is well known, hardness is one of the defining properties of tool materials, characterizing the ability of a material to resist plastic deformation, i.e., hardness is a characteristic of material strength under a complex stress state that occurs during indentation and is accompanied by large plastic deformations in the test zone, and is related to mechanical properties such as elasticity, tensile strength and yield strength, as well as thermodynamic characteristics of substances and energies. To date, physical theories of solids are unable to describe the hardness of various materials due to the indefinite variety of factors on which it depends. Therefore, the concept of "hardness" without specifying the method and conditions of measurement is indefinite. This concept does not mean a physical constant that characterizes a material, but one of the quantities that is measured by one of the methods and depends not only on the material but also on the conditions and method of measurement [1].

Despite some uncertainty about the physical nature of this property, due to its ease of measurement, ease of reproduction, and high correlation with strength, hardness has become a widely used characteristic of the mechanical properties of materials.

The high rates of development of materials science in the second half of the last century contributed to the creation of a large number of high-hardness materials, which necessitated the classification of these materials. Thus, it is proposed to classify high-hard materials as materials with a hardness of 5–20 GPa, i.e., materials whose hardness

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exceeds the hardness of metals, and superhard materials as materials whose hardness exceeds the hardness of natural corundum (20 GPa) [1].

However, we should pay attention to the following. Although hardness is one of the defining properties of superhard materials, it is not always sufficient. Therefore, when determining the class of tool superhard materials, it is necessary to take into account their other characteristics, in particular, crack resistance, heat resistance, thermal conductivity, and chemical stability.

The experience we have gained, as well as the analysis of literature data, allows us to propose the following definition of superhard materials for tooling purposes: superhard materials should include materials with a hardness of 20-120 GPa, i.e., whose hardness exceeds the hardness of natural corundum and can reach the hardness of the face (111) of single crystals of natural diamond, while their crack resistance $K_{1C}$ should be above 3.5 MPa $m^{1/2}$ . And for a correct comparison of the results obtained by nanoindentation of different samples, it is necessary to compare the results obtained under the same loads, for example, when it is possible to fix an imprint on the diamond surface, in particular, these values should be measured using the Vickers pyramid at a load on the indenter of 9.8 N. And materials with a hardness above 120 GPa should be classified as ultrahard materials.

In recent years, new ideas and approaches to the study of superhard materials have been proposed and experimentally tested, including nanostructuring and special processing of the initial component to produce high-performance superhard materials, the use of alloys or solid solutions to improve complex characteristics (i.e., hardness, fracture toughness, and heat resistance).

In the field of superhard materials research, the relationship between macrohardness and microstructure of superhard materials is being actively studied, which is an important step in creating hardness models with atomic parameters that can be used to guide the design or prediction of new superhard crystals.

## 10.1. Theoretical approaches to the search for new superhard materials

Quantum chemical studies of the electronic structure of molecular complexes and fragments of crystal structures modeling the properties of superhard materials were performed by D. A. Zhogolev and colleagues [2–4]. The calculations were based on a characteristic feature of the electronic structure of diamond, which determined its unique hardness, namely the presence of four electrons in the valence shell of each carbon atom, capable of participating in the formation of four strong, tetrahedral covalent bonds [3].

Thus, one of the possible ways to create new superhard materials is to synthesize multicomponent isoelectronic diamond compounds from small atoms with predominantly covalent interatomic (inter-nodal) bonds. Later, a similar conclusion based on the analysis of semi-empirical dependencies between the bulk compressive modulus (the value of which correlates with the corresponding hardness) and the coordination number for compounds with tetragonal coordination of atomic bonds in a unit cell was made by M. Cohen [5, 6].

One of the results of quantum chemical calculations by D. A. Zhogolev and his colleagues was the prediction of high hardness in such materials as, for example, $C_3N_4$, $B_9N$, $B_4C_5$, $B_5NO_2$.

It should also be noted that while initially the presence of a crystal structure of high symmetry was considered a prerequisite for high material hardness, the results of further studies have shown that this is not always the case [7–9].

In recent decades, progress has been made in theoretical calculations of the mechanical properties of superhard materials. First-principles calculations on modern computers make it possible to determine the elastic characteristics of superhard materials in the linear deformation region, as well as their ideal strength at various deformations, including those outside the linear elastic region, with high accuracy (up to 1–2%) (but with significantly lower accuracy - with an error of several tens of percent) [10, 11].

The generalization of accumulated theoretical calculations and experimental data on the relationship between the structure and properties of materials obtained under various conditions, including high pressures and temperatures, allows us to formulate a concept that defines promising directions for creating new superhard materials for tooling with a unique combination of physical and mechanical properties. The success of the work can be ensured by taking into account the following rules:

1. The Grimm-Somerfeld-Goryunova rule (the rule for the formation of compounds with tetrahedral coordination, which are crystallographic analogues of elementary semiconductors of the fourth group) - elements should belong to groups equidistant from the fourth group; the average number of valence electrons per atom of a compound should be four.

2. Hall-Petch ratio (for hardness growth): $\Delta H_v = \psi \cdot k_y \cdot d^{-1/2}$, where $\psi = H/_v\sigma_s$ ($H_v$ – hardness of the material; $\sigma_s$ – yield strength); $k_y$ – Hall-Petch constant.

3. Taking into account the value of the bulk compressive modulus (the rule formulated by P. Kyslyi and M. Cohen) – substances with a large bulk compressive modulus (the value of which correlates with the corresponding hardness) are formed by small atoms with sufficient electrons to form covalent bonds in three directions.

4. The use of solid solutions such as $B–C_x–N$, $B–O_x–N$, $B–P_x–N$, SiC–C.

 ISBN 978-3-949059-99-5

## 10.2. Experimental production of new superhard materials

One of the experimental results based on the above concept is the production of a new superhard material based on $AlB_{40}C_4$ [12], as well as diamond nanostructured composites for various functional purposes using the high-pressure technique [13].

As a result of studying the peculiarities of forming materials with high physical and mechanical characteristics, applying the latest technologies - ultra-high pressure (> 15 GPa) [13], using materials of the nanostructured range [14], special methods of influencing the material [15] – the list of superhard materials has been significantly expanded, including materials whose hardness exceeds the hardness of natural diamond single crystals (Table 1).

As can be seen from the table, the hardness of polycrystalline diamond obtained by direct transformation from nanographite at a pressure of 25 GPa and a temperature of 2200 K was 140 GPa [23].

It has also been experimentally shown that after heat treatment at high pressure, the hardness of a single crystal of natural diamond type IIa (p = 4 GPa, T > 1800 K) was 130–150 GPa [15], and the hardness of a CVD diamond single crystal was 160-180 GPa (p = 5 GPa, T = 1800–2500 K) [14]. The possibility of achieving such hardness values is assumed from the calculations of the theoretical (ultimate) hardness carried out in [1, 27], according to which the ultimate hardness of a diamond should not exceed 210 GPa. These experimental data became the basis for the development of a hybrid ultrahard polycrystalline material [26].

**Table 1 - New generation of superhard materials**

| No. | Material composition | Hardness, HV0.5, GPa | Developer | Method of preparation |
|---|---|---|---|---|
| 1 | $AlMgB_{14}$ + X [8] | 42 | Ames Lab (USA) | Hot pressing |
| 2 | $AlMgB_{14}$ + X [16] | 42 | ISM (Ukraine) | High pressures |
| 3 | $AlB_{40}C_4$ [11]. | ~ 38 ($K_{1C}$ = 8.5 MPa-$m^{1/2}$ /) | ISM (Ukraine) | High pressures |
| 4 | $B_6O$ [17]. | ~ 38 | | Hot pressing |
| 5 | $B_6O_xN_y$ [18] | ~ 50 | ISM (Ukraine) | High pressures |
| 6 | SiC–C [19]. | 42 | IPM and ISM (Ukraine) | High pressures |
| 7 | $C_{60}$ (fullerite) [20]. | 26–140 | V. Blank et al. Russia | High pressures |

| No. | Material composition | Hardness, HV0.5, GPa | Developer | Method of preparation |
|---|---|---|---|---|
| 8 | $BC_2N$ [21]. | ~ 76 ($K_{1C}$ = 4.5 MPa-$m^{1/2}$ /) | ISM (Ukraine) | High pressures |
| 9 | Diamond nanostructured composite [22]. | 65 ($K_{1C}$ = 14.5 MPa·$m^{1/2}$) | ISM (Ukraine) | High pressures |
| 10 | Diamond nanostructured polycrystal [23] | 100–140 | Japan | High pressures |
| 11 | Composite $B_4$ C+SiC+$C_{алм.}$ [24] | 41 ($K_{1C}$ = 8.1 MPa·$m^{1/2}$) | ISM (Ukraine) | High pressures |
| 12 | γ-$B_{28}$ [25] | 50 | V. Solozhenko et al. France, USA, Italy, China | High pressures |
| 14 | Hybrid ultra-hard polycrystalline composite material [26] | 140 (CVD polycrystalline wafer) 50 (polycrystalline shell) | ISM (Ukraine) IGP (Russia) | High pressures |

## 10.3. Perspective directions of obtaining new polycrystalline superhard materials

Based on the above concept and experimental achievements in the production of superhard materials, a number of promising areas for their production can be identified.

One of the most promising areas for producing new polycrystalline superhard materials is the use of diamond nanopowders and other carbon sources in the nanometer range. The use of high-pressure techniques makes it possible to form a material with a dense, homogeneous, fine-grained structure. The combination of preliminary mechanical activation of the initial charge with the introduction of activating additives can significantly improve the physical and mechanical characteristics. This technology makes it possible to produce composites that can successfully compete with single-crystal diamond tools made of natural diamonds.

Another area that has been actively developing in recent decades is the use of boron compounds (suboxides, rhenium, osmium, and other borides, complex solid solutions of magnesium, aluminum, silicon, carbon, and oxygen in icosahedral boron crystals). The interest in such compounds is primarily due to the possibility of wide variation in the type of chemical bonding in complex boron compounds with other elements when changing their composition, which, accordingly, opens up wide possibilities for changing their structural (creation of heterostructures), physical, and chemical properties and obtaining materials with predetermined performance characteristics on this basis.

In our opinion, the third promising area is the creation of hybrid polycrystalline materials using high-pressure techniques.

As you know, a hybrid is an object that combines the properties of other (two or more) objects. The peculiarity is that the respective elements are complete solutions, and as a result of their combination, new desired properties are created.

In the world scientific and technical literature, there is another definition of a hybrid material: a core-shell material.

Thus, hybrid materials are an integral part of a broader class of materials grouped under the general name of composites.

The following main reasons can be identified that lead to the need to create a hybrid material:

1) the inclusion of another component that is superior to the matrix in some respects helps to eliminate its inherent shortcomings;

2) inclusion of a certain component in composites made of other materials to take advantage of this component.

Thus, in its essence, the method of creating hybrid materials allows us to design materials with predetermined required properties.

Taking into account the above considerations, it is promising to create a hybrid material based on CVD diamond (core) and polycrystal from static synthesis diamond powders (shell) using high-pressure technology, which will combine the unique physical, mechanical and thermal properties of CVD diamonds with high hardness, strength and heat resistance of the polycrystalline diamond shell. Such a technical solution can significantly reduce the impact of the anisotropy of CVD diamond physical properties on the tool performance, increase its strength and thermal stability. The second important problem that is also being solved is the elimination of the possibility of the formation of undesirable impurities in the pores of graphite or amorphous carbon, which significantly reduce the performance characteristics of the material.

This will open up the prospects for equipping tools that operate in particularly difficult conditions, in particular when drilling hard rocks, cutting and grinding stone, concrete, etc.

 ISBN 978-3-949059-99-5

## Conclusion

Based on the generalization of the accumulated experimental data on the relationship between the structure and properties of materials obtained under different conditions, in particular under high pressures and temperatures, a concept is proposed that allows us to determine promising directions for the creation of new superhard materials for tooling with a unique combination of physical and mechanical properties. The experimental result of the proposed concept was the production of a new superhard material based on $AlB_{40}C_4$ , diamond nanostructured composites for various functional purposes, as well as a hybrid material based on CVD diamond and polycrystal from static synthesis diamond powders, using the high-pressure technique, which will combine the unique physical, mechanical and thermal properties of CVD diamonds with the high hardness, strength and thermal stability of the polycrystalline diamond shell.

 ISBN 978-3-949059-99-5