THE PREPARATION OF SUPERHARD MATERIALS (SHMs) BY DIRECT SYNTHESIS OF THE
NANODISPERSED DETONATION DIAMOND, CARBON AND BORON NITRIDE POWDERS AT
VERY HIGH PRESSURE AND TEMPERATURES

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Abstract

The modernization of high-pressure apparatus (HPA) “double toroid-15”, which is used for the preparation of superhard materials (SHMs) by direct synthesis at very high pressures (12-13 GPa) and temperatures of from1000 to 2000 °C for from several seconds to several minutes, was performed. The calibration for temperature was performed using chromel-alumel (600-1200 °C) and tungsten-rhenium (1200-2000 °C) thermocouples. A purification procedure of nanopowders with respect to water and absorbed gases was developed. The initial powders placed in specific ampoules were purified by holding at 350 °C for 15 min and then – 450 °C for 30 min in argon using a specific autoclave. Optimum conditions were determined; these are the 12-13 GPa pressure, 1300-1700 °C temperature, and 10-15 s time. Preliminary experiments of the sintering of purified nanodispersed detonation diamond, carbon and boron nitride powders (10-100 nm in size) were performed. Polycrystalline samples of SHMs were prepared in the form of cylinders 5 mm in diameter and 3 - 5 mm in height. The sintered SHMs are characterized by a microhardness of 30-60 GPa and a density of 3.0-3.4 g/cm³. The grain size in sintered specimens and initial nanopowders is virtually the same. The composition and structure of SHMs specimens are presented. This method may be used for sintering of metallic nanopowder.

The synthesized SHMs may be effectively used as high durable cutting tool characterized by very high wear-resistance in high speed machining of pieces.

1. INTRODUCTION

All existing methods of compacting and sintering of nanopowders offer to prepare the high dense complex shape products [1]. But in sintered materials it is impossible to save the same grain nanosize as in initial powders. On many occasions the sintered materials are characterized by 200-300 nm grain size that is 5-10 times as many as in initial nanopowders. For saving initial grain size it is necessary to prepare the SHMs at lower temperature and more short time of sintering and in high dynamic and static pressure regime [2, 3].

For this purpose the high pressure apparatus (HPA) «double toroid - 15 » can be used. The HPA is known already some tens years [4]. It has been used basically for synthesis of diamonds [5]. For the compacting and sintering of SHM nanopowders (1-100 nm) it was not used earlier.

The aim of this work is to prepare the superhard materials (SHMs) (Hv=30-60 GPA) by compacting and
2. EXPERIMENTAL

For this purpose we have modernized a reactor cell. Their heat insulation has been improved. Figure 1 shows the scheme of HPA (the Bridgman anvils and fastening rings) (a) and the scheme of equipment for the reactor cell (b).

![Figure 1](image1.png)

**Fig. 1:** (a) Scheme of the HPA «double toroid-15»: 1 - hard-alloy plunger with crater, 2 - lens, 3-reactive volume, 4 and 5 – sealing rings, 6, 7, 8 and 9 – set of steel supporting rings, 10-teflone ring; (b) Scheme of equipment for reactor cell: 1 – specimen, 2 – graphite heater (exterior and interior diameters are 7 mm and 5mm, respectively), 3 – graphite disk of 1 mm in thickness, 4 – Ta or Mo disk of 0,3 mm in thickness, 5 – container (lithographic stone, Algeti, Georgia)

In this investigation we have been carried out the pressure and temperature calibration of HPA for ensuring of accurate thermobarical parameters during the sintering [6, 7]. The calibration on pressure has been carried out using the chemically pure metals Bi and Ba. This metals are characterized by phase transitions: Bi I-II (2,55 GPa), Bi VI-VII (7,7 GPa), Ba I-II (5,53 GPa) and Ba III-IV (12 GPa). Thus we have the enough number of points for comparison of our data and the calibration data [6].

The calibration for the temperature in a range of 600-1200 °C was carried out using the chromel-alumel – thermocouples. The chromel-alumel- thermocouples have been chosen due to their temperature ranges which are satisfying to demand of our experimental condition. According to our experience and the standard opinion of the acknowledged experts the chromel-alumel - thermocouples indications do not depend on pressure.

The calibration for the temperature in a range of 1200-2000 °C was carried out using the–W-Re (5/20) thermocouples. Such careful approach to questions of the HPA «double toroid - 15 » calibration are explained by the need for careful control of the thermobarical parameters during the sintering of such slightly studied substances, as nanodispersed phases of carbon and boron nitride prepared by explosion method.

A purification procedure of nanopowders with respect to water and absorbed gases [8] was developed. The initial powders placed in specific ampoules were purified by holding at 350 °C for 15 min and than – 450 °C for 30 min in high purity argon using a specific autoclave (fig.2). The ampoule restrictions are made for the subsequent sealing after finishing of purification process. The argon flow velocity is 2-3 ml/sec and pressure...
is 50 mm water-column above atmospheric. Such conditions are maintained for using of the bubbler. The ampoules containing the purified powders are opened before compacting and sintering immediately.

Detonation diamonds and amorphous carbon, wurzitic boron nitride and silicon nitride were used as initial powders with nanocrystalline structure. Powders were prepared at the Institute of Materials Science Problems, National Academy of Sciences of Ukraine. The grain sizes are 10-300 nanometers. Sintering was carried out at pressure of 12-13 GPa and temperatures of 1300-2000 °C. The time of sintering is 30-60 seconds.

**Fig. 2.** Scheme of powder purification

### 3. RESULTS

Polycrystalline cylindrical samples of 5.0 mm in diameter and 3 - 5 mm in height have been prepared. Such SHMs are characterized by the microhardness Hv of 30-60 GPa and the density of 3.0-3.4 g/sm³. Method of hydrostatic weighing was used for density measuring.

Figure 3 shows typical X-ray pattern for the polycrystalline specimen prepared by sintering of nanodispersed powders containing the amorphous carbon (90 wt %) and detonation diamonds (10 wt%). Sintering was carried out at a pressure of 13 GPa and a temperature of 1700 °C.

According to a calculated X-ray pattern, the carbon (90%) was transformed into diamond (lonsdeilit), and initial detonation diamond was not changed. The grain sizes of detonation diamonds (100 nm) and lonsdeilit diamond (10 nm) are identical to those in both sintered specimens and initial powders.

**Fig. 3.** X-ray pattern for the polycrystalline specimen prepared by sintering at the pressure of 13 GPa and the temperature of 1700°C (10% - detonation diamond, 90% - lonsdeilit diamond). Initial powders are mixture of 10%-detonation diamonds and 90% - amorphous carbon
Fig. 4. TEM images of SHMs specimen sintered at 1700 °C (10% - detonation diamond, 90% - lonsdeilit diamond). Initial powders are mixture of 10%-detonation diamonds and 90% - amorphous carbon: (a) - the grains of nontransformed detonation diamond (100 nm) and lonsdeilit diamond (10 nm) transformed from amorphous carbon (bright field); (b) - lonsdeilit diamond (10 nm) transformed from amorphous carbon (dark field); (c) - electronogram.

Figure 4 shows TEM images of SHMs-specimens prepared by sintering of detonation diamond and amorphous carbon powder mixture at 1700 °C.

The microhardness of such specimens is tabulated in Table 1.

**Table 1.** The microhardness of SHMs specimens prepared by sintering of detonation diamond (C_{DD}) and amorphous carbon (C_{AM}) powder mixture at 1300, 1500 и 1700 °C

<table>
<thead>
<tr>
<th>№</th>
<th>Composition of initial powders, wt.%</th>
<th>Temperature of sintering, °C</th>
<th>Microhardness of SHMs (H_{200}), GPa</th>
<th>Shape and integrity of specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C_{AM} 65  C_{DD} 35</td>
<td>1300</td>
<td>20 ±6</td>
<td>Entire cylinder</td>
</tr>
<tr>
<td>2</td>
<td>C_{AM} 65  C_{DD} 35</td>
<td>1700</td>
<td>74 ±16</td>
<td>Entire cylinder</td>
</tr>
<tr>
<td>3</td>
<td>C_{AM} 90  C_{DD} 10</td>
<td>1500</td>
<td>63 ±20</td>
<td>Cracked cylinder,</td>
</tr>
<tr>
<td>4</td>
<td>C_{AM} 90  C_{DD} 10</td>
<td>1700</td>
<td>60 ±20</td>
<td>Failure cylinder,</td>
</tr>
</tbody>
</table>

*Fig. 5. TEM images of SHMs specimen sintered at 1700°С: (a) bright field; (b) dark field; (c) c-Si₃N₄ and BN₈ (partial) – reflections (dark field); (d) – electronogram*
Figure 5 shows TEM images of SHMs-specimens prepared by sintering of BN$_6$ + c-Si$_3$N$_4$ powder mixture at 1700 °C. The BN$_6$ grains are characterized by stratified structure. C-Si$_3$N$_4$ grains are isometric. The BN$_6$ and c-Si$_3$N$_4$ grains are firmly grown together.

The microhardness of such specimens is tabulated in Table 2.

**Table 2.** The microhardness of SHMs specimens prepared by sintering of BN$_6$ + c-Si$_3$N$_4$ powder mixture

<table>
<thead>
<tr>
<th>№</th>
<th>Composition of initial powders</th>
<th>Temperature of sintering, °C</th>
<th>Microhardness of SHMs ($H_{200}$), GPa</th>
<th>Integrity and thickness (t) of specimens,</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BN$_6$ + c-Si$_3$N$_4$</td>
<td>1700</td>
<td>52</td>
<td>cylinder, segregation into layers, t ≈ 1 mm</td>
</tr>
<tr>
<td>3</td>
<td>BN$_6$ + c-Si$_3$N$_4$</td>
<td>1300</td>
<td>13</td>
<td>cylinder, segregation into layers, t ≈ 1 mm</td>
</tr>
<tr>
<td>4</td>
<td>BN$_6$ + c-Si$_3$N$_4$</td>
<td>1270</td>
<td>8</td>
<td>cylinder, t ≈ 3 mm</td>
</tr>
<tr>
<td>5</td>
<td>BN$_6$ + c-Si$_3$N$_4$</td>
<td>1230</td>
<td>13</td>
<td>cylinder, t ≈ 3 mm</td>
</tr>
<tr>
<td>6</td>
<td>BN$_6$ (without wetting)</td>
<td>1700</td>
<td>63</td>
<td>cylinder, t ≈ 3 mm</td>
</tr>
<tr>
<td>7</td>
<td>BN$_6$ (without wetting)</td>
<td>1300</td>
<td>10</td>
<td>cylinder, t ≈ 3 mm</td>
</tr>
</tbody>
</table>

Note: BN$_6$-wurzitic boron nitride; c-Si$_3$N$_4$-sfaleritic (cubic) silicon nitride.

It is necessary to note that our sintering temperature for preparing of high quality SHMs from nanodispersed powder is lower (by ~ 300°C) in comparison with that used in standard methods [9-10]. All existing standard methods for compacting of nanodispersed carbon and nitride in low-pressure regime (7-8 GPa) and the same temperatures allow us to prepare the SHM characterized by 25-30 GPa microhardness; that is a upper limit. Just as SHMs prepared by our method are characterized by ≥ 60 GPa microhardness.

4. **CONCLUSIONS**

1. For the first time, SHMs are prepared by sintering of detonation diamond and amorphous carbon ($\rho = 2, 95$ g/sm$^3$) nanopowders (10-100 nm) in the very high-pressure regime (12-13 GPa) at temperatures (1300-2000 °C) and times (30-60 sec) using modernized HPA «double toroid - 15 ». The grain size in sintered blanks and initial nanopowders is virtually the same (in according to TEM-investigations), i.e. the sintering followed without the recrystallization process.

2. A purification procedure of nanopowders with respect to water and absorbed gases was developed for preparing of high quality SHMs-specimens.

3. Polycrystalline cylindrical samples 5,0 mm in diameter and 3 - 5 mm in height have been prepared. The samples are characterized by the diamond-Ionsdeilite structure, microhardness of 30-60 GPa and density of 3, 0-3, 4 g/cm$^3$.

4. SHMs prepared by proposed method are characterized by ≥ 60 GPa microhardness, i.e. twice as many as SHMs prepared by all existing standard methods for compacting of nanodispersed carbon and nitride in low-pressure regime (7-8 GPa). Moreover, the proposed temperature of sintering is lower (by ~ 300°C).

5. The synthesized SHMs - specimens may be effectively used not only for investigation of physical and mechanical properties of SHMs but for making of the high durable cutting tool characterized by very high wear-resistance in high speed machining of pieces.
ACKNOWLEDGMENTS

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LITERATURE


