Thermochemical grinding of diamond films in installation for chemical vapor deposition of diamond from the gas phase

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Abstract. The paper studies the process of thermochemical grinding of diamond polycrystalline films in atomic hydrogen, using microwave to generate a plasma discharge, in the temperature range 1000 – 1100 °C. It is established that the increase in temperature leads to an increase in the rate of diamond dissolution due to the formation of eutectic. The study of roughness showed that after thermochemical grinding roughness of the diamond film is about 0,8 µm. The speed of thermochemical grinding varies from 20 µm/h to 3 mm/h. Raman spectroscopy allowed us to establish that thermochemical grinding does not degrade the quality of the diamond film, and atomic hydrogen reduces the possible graphitization caused by heating.

It is suggested that the mechanism of gas bubbles in the process of thermochemical grinding associated with the formation of methane and its subsequent decomposition into a methyl radical and atomic hydrogen in the plasma discharge.

1. Introduction
Diamond is the hardest compound on Earth, its hardness on the Mohs scale is 10 [1], which creates difficulties in its processing. To give the necessary shape to the diamond, mechanical processing with free [2] or fixed abrasive [3], a laser for rough grinding and shaping [4], as well as thermochemical grinding of diamond based on the catalytic dissolution of carbon in iron [5] are used. In [6] proposed installation for thermochemical diamond cutting, grinding speed up to 0.3 mm per hour. One of the disadvantages is the inability to grind diamond polycrystalline films of large diameter, as when scaling the design of the installation will be complicated, due to the need to ensure the rotation of the heated part from 600 °C to 1300 °C in a hydrogen medium.

The method of thermochemical grinding has long been known, and in itself is not new. However, the use of the installation for the growth of diamond from the gas phase for thermochemical grinding can allow grinding diamond films up to 100 mm in diameter, which in turn is promising and will reduce the cost, for example, in the manufacture of diamond output windows for gyrotrons, where mechanical grinding is one of the expensive and long operations.

2. Methods and materials
For the experiments, a device for deposition of diamond from the gas phase in a microwave discharge was used. Hydrogen of high purity gases brand (99.9999%) was used as plasma-forming gas. For dissolve carbon steel grade ST2 was used. To wash the diamond after thermochemical grinding, chemical reagent solution (know-how) was used. The process of thermochemical grinding was carried out in the pressure range of 75–100 torus. A micrometer was used to measure the thickness of the diamond film. Structural studies of the samples were carried out using a scanning electron microscope of the ZEISS series EVO MA10, Raman spectra were obtained using a DXR Raman Microscope spectrometer.

The experimental design is shown in figure 1.
Figure 1. The scheme of the experiment on thermal grinding.

The samples of 10x10 mm in the amount of 4 pieces were placed on a steel plate with a size of 70x70x4 mm. The supports necessary for reducing the heat removal from the plate and the possibility of heating it to the temperatures of the active process of diamond graphitization and its subsequent dissolution were placed under the steel plate.

The plasma discharge heats the samples to activate the process of dissolution of carbon in iron, while the plasma discharge consisting entirely of atomic hydrogen should protect the diamond film from excessive graphitization in the area not in contact with the steel plate. The experiments were carried out at different sample temperatures. The sample temperature was controlled by chamber pressure and microwave power. Three experiments were carried out at 1000 °C, 1050 °C, 1100 °C.

3. Results and discussion

Figure 2 shows the appearance of the samples after the thermochemical grinding process.

Figure 2. Appearance of the sample after the thermochemical grinding experiment.

In the process of iron dissolution, only the angular surface of the diamond film was involved. A gradual transition is visible (figure 2) from a smooth surface to a rough surface, represented by individual crystals with a large number of borders.

Measuring the thickness of the diamond film before and after the process of thermochemical grinding allowed to set that the grinding speed at a temperature of 1000 °C is 20-30 µm/h. Thus, the temperature of 1000 °C is low for the active process of thermochemical grinding.

Figure 3 shows the appearance of diamond films before the thermal grinding process at 1050 °C.
The structure of diamond films is rough, represented by crystals in the form of hexagons or pyramids.

Figure 4 shows the appearance of the samples after thermochemical grinding at 1050 °C.

The surface of all samples after thermochemical processing is almost the same; there are no crystals with faceting. The surface is smooth, represented by small craters.

Figure 5 shows the appearance of the samples before the experiment on thermal grinding at 1100 °C.
Figure 5. Appearance of the original diamond films.

Figure 6 shows the appearance of diamond films after the process of thermochemical grinding at 1100 °C.

After thermal grinding, globules and faceting are practically absent, the entire surface is smoothed to a certain level of roughness. It is worth to note that during the experiment, the samples floated on the surface of the steel plate, which indicates the formation of eutectic. Also under the surface of some diamond films formed bubbles of liquid metal lifting the samples. In the plasma discharge, flashes with a greenish tint were observed when the bubble burst. Figure 7 shows a diagram showing the process described.
The formation of liquid eutectic as a result of metal saturation with carbon occurs at 1100 °C, since the pressure in the working chamber is 100 torus. As a result, atomic hydrogen begins to react with dissolved carbon, resulting in methane bubbles that escape from the liquid eutectic, fall into a plasma discharge, where methane decomposes into methyl radical or atomic hydrogen. However, this theory is hypothetical, since no spectra confirming the nature of this phenomenon has not been obtained.

In the process of thermochemical grinding, the penetration of iron into diamond is possible, as well as the graphitization of diamond. To investigate this assumption, the transverse kink of one of the experimental samples was studied. The result of the study is presented in figure 8.

Elemental analysis did not show any other elements besides carbon, which indicates that iron did not penetrate deep into the sample.
After thermochemical grinding, the samples were washed in chemical reagent solution (know-how). The solution was brought to a boil, and then the samples were dipped in a boiling solution, and then washed with deionized water. Figure 9 shows the result of phase analysis of samples before and after washing.

![Diffractograms](image)

**Figure 9.** Diffractograms.

According to figure 9B, carbon, in the form of diamond and graphite, as well as iron, is present on the surface of the sample after thermochemical grinding. After washing the samples, not only iron is removed, but also graphite, as evidenced by the two peaks in figure 9A, which correspond only to diamond.

In the study, the roughness of the samples was studied, before and after thermochemical grinding. The initial roughness values ranged from 40-60 μm, table 1.

| Sample                      | Roughness, μm |
|-----------------------------|---------------|
| Steel                       | 1.10          |
| Diamond films thermal grinding at a temperature of 1060 °C |
| Sample №2                   | 0.887         |
| Sample №3                   | 0.831         |
| Sample №4                   | 0.785         |
| Diamond films thermal grinding at a temperature of 1100 °C |
| Sample №1                   | 0.548         |
| Sample №2                   | 1.26          |
| Sample №4                   | 0.522         |

The roughness results for the measured samples almost coincide and are equal to an average of 0.8 μm, which is significantly less than the initial roughness of the steel plate. Thus, thermochemical grinding can significantly reduce the level of surface roughness of the original diamond films, tables 2.

Also, the thermal conductivity of samples after thermal grinding was measured. In order to calibrate the instrument, measurements were made on test samples with known thermal conductivity. Copper thickness of 1 mm – 315 W/m·K (table value 394 W/m·K).

Values of test samples:
- Copper thickness of 0.5 mm - 400 W/m·K (table value 394 W/m·K);
- PDF (polycrystalline diamond film) thickness of 0.4 mm growth side - 713 W/m·K;
- PDF thickness of 0.4 mm reverse side – 615 W/m·K.
Table 2. Result of thermal conductivity measurement of diamond films after thermal grinding.

| Sample №1 | Sample №2 | Sample №3 | Sample №4 |
|-----------|-----------|-----------|-----------|
| The growth side of the PDF – 737 W/m·K; | The growth side of the PDF – 975 W/m·K; | The growth side of the PDF – 235 W/m·K; | The growth side of the PDF – 448 W/m·K; |
| The reverse side of the PDF – 656 W/m·K; | The reverse side of the PDF – 985 W/m·K; | The reverse side of the PDF – 280 W/m·K; | The reverse side of the PDF – 736 W/m·K; |
| | | | |
| Sample №1 | Sample №2 | Sample №3 | Sample №4 |
| The growth side of the PDF – 362 W/m·K; | The growth side of the PDF – 817 W/m·K; | The growth side of the PDF – 53 W/m·K; | The growth side of the PDF – 577 W/m·K; |
| The reverse side of the PDF – 616 W/m·K; | The reverse side of the PDF – 915 W/m·K; | The reverse side of the PDF – 174 W/m·K; | The reverse side of the PDF – 895 W/m·K; |

Based on the data in the table, the thermal conductivity of the thermally polished side decreased significantly, which is caused by contamination of the surface with iron, as well as its graphitization according to the data of X-ray diffraction analysis (figure 9B).

After washing the samples, the thermal conductivity was also measured. The results are presented in table 3.

Table 3. The result of measuring the thermal conductivity of diamond films after thermal grinding and washing.

| Sample №1 | Sample №2 | Sample №3 | Sample №4 |
|-----------|-----------|-----------|-----------|
| The growth side of the PDF – 800 W/m·K; | The growth side of the PDF – 980 W/m·K; | The growth side of the PDF – 350 W/m·K; | The growth side of the PDF – 750 W/m·K; |
| The reverse side of the PDF – 690 W/m·K; | The reverse side of the PDF – 918 W/m·K; | The reverse side of the PDF – 270 W/m·K; | The reverse side of the PDF – 700 W/m·K; |
| | | | |
| Sample №1 | Sample №2 | Sample №3 | Sample №4 |
| The growth side of the PDF – 650 W/m·K; | The growth side of the PDF – 950 W/m·K; | The growth side of the PDF – 250 W/m·K; | The growth side of the PDF – 900 W/m·K; |
| The reverse side of the PDF – 620 W/m·K; | The reverse side of the PDF – 900 W/m·K; | The reverse side of the PDF – 165 W/m·K; | The reverse side of the PDF – 850 W/m·K; |

Washing samples allowed to increase the thermal conductivity, while not affecting the thermal conductivity of the reverse side of the diamond polycrystalline film.

The thickness of samples after thermochemical grinding was measured in order to determine the average speed of thermochemical grinding. Figure 10 shows the dependence of the thermochemical grinding speed on the sample temperature.
Figure 10. Graph dependence of the temperature of thermochemical grinding of diamond.

As a result, it was found that the grinding speed in the range from 1000 - 1100 °C varies in the range of 20 μm/h to 3 mm/h. Such a large variation in temperature is caused by the formation of liquid eutectic, in which the process of graphitization and dissolution of carbon is very active.

Separately, a piece of white diamond was selected to assess the visual effect of the influence of thermal grinding on the quality of the diamond film. The appearance of the sample before the experiment is shown in figure 11.

Figure 11. Appearance of the original white diamond film.

Figure 11 shows a diamond film directly subjected to thermochemical grinding. Also, it is worth noting that the diamond film had a bend.

After the process of thermochemical grinding and washing in chemical etchants, the diamond returned to its original transparency and color. The appearance of the sample after washing is shown in figure 12.
After thermochemical grinding, the area of the diamond in contact with the iron became completely black, but after washing it was possible to return the original appearance.

Raman spectroscopy of the area after washing and the area not involved in the grinding process was carried out. The spectra are shown in figure 13.

The area, which was not in direct contact with the steel, was only subjected to heat, which led to the release of a large number of defects on the surface of the diamond, which was expressed on the spectrum by a wide luminescent peak (figure12A). The area subjected to thermo-chemical grinding produces a smaller luminescence (figure12B). Perhaps this is due to the fact that the surface after thermochemical grinding is homogeneous. Thus, thermochemical grinding not only does not degrade the quality of the diamond film, but also allows to obtain uniform surface with uniform roughness and thickness.

4. Conclusion

In the process of studying the process of thermochemical grinding in a plant for the growth of diamond from the gas phase, it was found that in the temperature range 1000 - 1100 °C, the grinding
speed varies from 20 μm/h to 6 mm/h. According to Raman spectra, the process of thermochemical grinding does not lead to graphitization and does not impair the quality of the diamond film.

The method of thermochemical grinding is known for a long time, and in itself is not new. However, the use of the installation for the growth of diamond from the gas phase for grinding can allow grinding diamond films with a diameter of 1 mm to 100 mm, which in turn is promising and will reduce the cost, for example, in the manufacture of output windows for gyrotrons, where mechanical grinding is one of the expensive operations

References
[1] Sergey D 2017 Vickers Hardness of Diamond Crystals Vol 7(369) p 1-13
[2] Burlakov V I 2017 Analysis of methods of processing parts with free abrasive Technical science p 132-137
[3] Avdeev D M, Avdeev D M, Miranchuk A I, Boyko A A, Alekseenko Y A 2000 Diamond grinding elements on a ceramic bond for fine diamond grinding of optical parts Vol 3 p 31-36
[4] Cardoso M S 2005 A valuation model for cut diamonds Intl. Trans. in Op. Res Vol 12 p 417-436
[5] Dongik J Yumkyum K, Minsoo S, Joonho L 2012 Kinetics of carbon dissolution of coke in molten iron Metallurgical and Materials Transactions Vol 43B p1308-14
[6] Shamaev P P, Grigorieva A S, Botvin V V 2002 On thermochemical methods of diamond processing from new positions Science and technology in Yakutia Vol 1 p 27-29