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Application of the dusty plasma method for preparation of diamond ceramics

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ABSTRACT

Diamond particles 3–7 μm in size sustained in plasma in a high-dispersion state were coated with cobalt by magnetron sputtering. The relative concentration of cobalt in obtained powders was 2–3 mass. %. Sintering the diamond powders with the cobalt coating under the pressure of 8 GPa and the temperatures of 2000–2100 K resulted in the production of homogeneous specimens having the density of 3.6 ± 0.1 g cm^{-3}. The produced diamond compacts demonstrated high values of the ultrasonic wave propagation velocity and elastic moduli.

1. Introduction

One of the most widespread industrial methods for producing diamond ceramic materials (compacts) and two-layer plates (a diamond ceramic layer on a substrate from a hard alloy WC–Co) is sintering diamond at high pressure in the presence of an activating admixture (binder) — Co. Omitting the details of the proposed in literature mechanisms for sintering the diamond in the presence of cobalt, we want to note that cobalt can play the role of solvent for carbon and catalyst for transforming graphite to diamond at high pressure and high temperature, which stimulates sintering diamond and forming a hard diamond frame (matrix) [1–6]. However, the presence of cobalt in the final product has rather a negative effect on the diamond thermostability in the process of fabrication and use of diamond cutting tools. The difference in the thermal expansion of the matrix and inclusions leads to the formation of cracks in a diamond material and, finally, to quick wear or destruction of the operation part of the tools. The less the size of cobalt inclusions as well as cobalt content in diamond ceramics, the higher the thermostability of the material is. The cobalt percentage in industrial diamond materials is usually 5–10 vol. % [6]. Cobalt is usually introduced into the diamond powder either by infiltration or by preliminary blending of reagents. Diamond compacts produced by infiltration have an inhomogeneous microstructure and mechanical properties along the direction of the infiltration [7]. Decrease in the size of diamond particles leads to decrease in the infiltration depth [3], which prevents from producing uniform work pieces. It should be noted that the larger the size of diamond grains in a compact, the higher the surface roughness is and the less the accuracy of the material processing with the diamond tool is. In case of preliminary blending of reagents the homogeneous distribution of cobalt fails to be achieved in the sintered samples when the cobalt fraction is decreased down to less than 5 vol. %, especially for the case the size of sintered diamond particles is less than 5 μm [1,8]. In searching for alternative methods of introducing the binder into diamond powders there were experiments carried out on sintering diamond particles having a cobalt coating preliminary deposited by electroless [3] or magnetron sputtering methods [9]. Electroless introduction of the binder made it possible to produce compacts with high mechanical properties with the cobalt content about mass. 5% (3 vol. %). However, deposition of cobalt was only possible upon diamond particles with the size of 12–40 μm [3]. The data on introducing cobalt into diamond powder by the magnetron sputtering and sintering of the produced mixture are of rather fragmentary character [9]. In particular it is noted that in the sintered material containing cobalt within 1.1–1.5 vol. % no formation of cracks was observed after the heat treatment in vacuum under 1370 K for 30 min, whereas the same

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treatment of compacts with vol. 5% of cobalt resulted in numerous cracks. Analysis of the literature data shows that deposition of thin layers of the binder (cobalt) upon micron-sized diamond particles with the cobalt of 1–3 vol. % (2–6 mass. %) in the blend can become a perspective approach for production of thermally stable fine-grained (including submicron or nanometric) diamond compacts for a new generation of tools.

Recently the new dusty plasma methods [10–12] were used for deposition of metal layers upon micron particles. The particles injected in plasma acquire large electric charges, negative in most cases [13]. The like charges prevent the formation of agglomerates in the wide range of experimental conditions. The cloud of the dispersed particles is confined by electric field in plasma in the regions of larger potential. Dusty clouds were irradiated by atomic metal flow from magnetron sputter device [10,11]. Such a method can be useful for deposition of uniform thin Co coatings upon micron diamond particles.

After exposure to ambient air atmosphere, the presence of oxygen impurity in Co-coated diamond powders is inevitable because of the high chemical activity of cobalt in the dispersed state. In the course of high-pressure sintering, interaction of diamond with oxidized cobalt may cause the formation of gas component, the presence of which deteriorates mechanical properties of sintered samples. Influence of gases absorbed on the surface under sintering of nanodiamond powders was studied in [14]. In our case the necessity to remove oxygen out of the reaction area during the sintering process requires an investigation of the thermodynamics of the considered system (Co–C–O).

The main objective of our work is to obtain a uniform Co-coating on the micron-sized diamond particles in the dusty plasma, as well as to clarify prospects of the method for the preparation of fine-grained diamond ceramics at low concentration of Co admixture.

2. Thermodynamics of Co–C–O system

Equilibrium composition of the Co–C–O system was computed by means of the program IVTANTERMO [15] for calculating the thermodynamics of multi-phase multi-component systems. The condensed components of the system were represented by the substances: C, Co, Co_3O_4, CoO, while the gas components were Ar, C, C_2, C_2O, C_3, C_3O_2, C_4, C_5, CO, CO_2, Co, Co_2, CoO, O, O_2, O_3. The calculation was performed for temperature range 400–1500 K and pressure 0.1 MPa for the model in which cobalt and its oxides were components of the same solution. The temperature dependences of mole fractions for the basic components in the considered system are given in Fig. 1.

According to our calculations the reduction of the cobalt oxide by carbon starts at T ~ 500 K with formation of $CO–CO_2$ gas phase; at temperatures above 1000 K the cobalt oxide is almost completely reduced. Thus the calculation shows that the cobalt oxide reduction in a mixture of diamond powder with oxidized cobalt can be solved by the preliminary annealing of the powder at temperature ~1000 K.

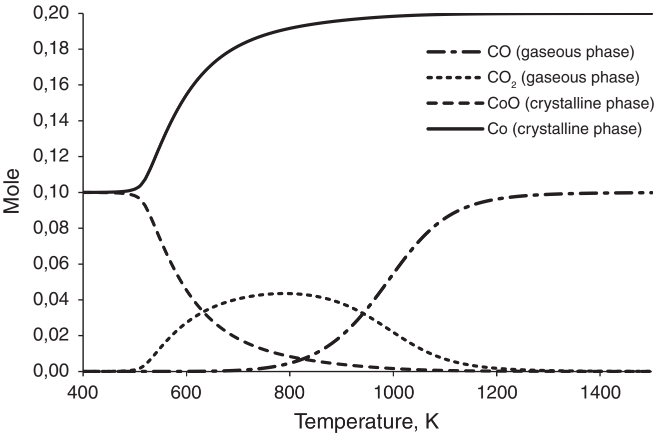

Fig. 1. Temperature dependences of mole fractions for the components of solid and gaseous phases.

3. Methods

3.1. Coating deposition on the diamond particles

The cloud of diamond particles was formed inside the reactor mounted in the vacuum chamber. To obtain the coating, the levitated particles were exposed to the cobalt atomic beam from the magnetron sputter, placed in the chamber near the reactor. A scheme of the reactor is given in Fig. 2.

1 is the reactor shell, 2 is the disperser, 3 is the live RF electrode, 4 is the dusty plasma cloud, 5 is the metal atom beam, 6 is the grid. The arrows in the lower area of the figure indicate the direction of the reactor vibrations in the process of the powder dispersion.

The mechanical shocks of the metallic reactor shell 1 at the frequency of 50 Hz and amplitude of 1.5 mm provided the persistent injection of the particles of the diamond powder from the disperser 2 into the region where the plasma dust cloud 4 was formed. The plasma source was capacitively coupled radio frequency (RF) discharge. The grid 3 was the driven RF electrode and the side and top walls of the reactor shell served as the cold electrode. The injected dispersed particles were confined in RF plasma. A beam of cobalt atoms from magnetron sputter 5 was directed into the vibrating reactor through the metallic grid mounted in the reactor sidewall hole.

We used synthetic diamond powders with the size of particles within 3–7 μm. To remove the adsorbed gas species the reactor containing the powder was heated up to 470 K and simultaneously pumped out for 15 min at the preliminary stage of experiment. Sputtering of the cobalt target was performed in high-purity argon under the pressure 0.4 Pa with the flow rate of 20 sccm. The power of the magnetron sputter discharge was 1 kW. The duration of the deposition process was varied from 40 to 90 min. After the process finished the powder consisting of the coated particles was extracted from the reactor at ambient atmosphere conditions.

3.2. Preparation of diamond compacts

3.2.1. Preliminary annealing of diamond–Co mixture

On the basis of the thermodynamic calculations the conditions for preliminary treatment of the prepared composite material were chosen. The crucial issues are as follows: the duration of the annealing process and the removal of the released carbon oxides out of the reaction area.

The powder was placed into the graphite crucible and then annealed in the quartz reactor in the flowing argon under the temperatures T_a in the range of 770–970 K for 15–30 min. In view of the fact that under the temperatures greater than 940–970 K and the normal pressure there occurs active interaction of cobalt with diamond, which is accompanied by graphitization and etching of diamond [16], the temperature range of the annealing was limited by 970 K. All the operations connected with the production of compacts were carried out in argon (with the purity of 99.998%) that was additionally purified from moisture by special traps.

3.2.2. Sintering of diamond–Co mixture

Sintering the powders was carried out in several sets of experiments in the high pressure “toroid”-type chambers, varying the cobalt concentration in the initial powder, the temperature of the preliminary annealing and the duration of the sintering process t. Heating the reaction chamber up to the given temperature T_s of 2000–2100 K (which is higher than the melting point of cobalt under the pressure of 8 GPa) was performed under the pressure P_s of 8 GPa with the rate of 50–100 K/s. Upon completion of the 5–12 s exposure under the constant pressure