Synthesis of diamonds in the C – Mn - Ni - (H) system and the diamond-shaped mechanism

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Abstract. Studying the dependence of the degree (α) and rate (θ) of the phase transformation of graphite into diamond on the synthesis time at different temperatures of the developed synthetic diamonds using the technology of high-pressure high-temperature synthesis in a metal melt (HPHT), we determined the critical mass of diamonds, which indicates the entry of the system into the stability region of graphite, where the graphitization of diamonds occurs. The role of implanted metals and hydrogen in the formation of synthetic diamonds and on its properties was also investigated.

1 Introduction

Natural diamonds have been known since their first finds in the 4th century BC in India. Since then, it has been used mainly as a gem. In the 2nd century BC in China, it began to be used as an industrial stone because of its high hardness. However, the use of diamond in research and development has been limited due to the lack of the required material and high cost. These factors held the researchers back for a long time, although more and more scientists looked towards this crystal because of its outstanding characteristics and unique properties. This fact became the driving force in developing methods for the industrial production of synthetic diamonds [1].

Diamond is one of the allotropic forms of carbon and graphite, another allotropic modification of carbon. At room temperature and atmospheric pressure, the thermodynamically stable form of carbon is graphite. Although graphite and diamond have the same chemical composition, they differ in physical and mechanical properties. This difference is explained by the difference in the shape of the crystal lattice.

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Table 1. Main areas of application of diamonds

Application area	Author	Year
Radiation sensors	Bergonzo and others [2]	2001
Cold cathodes	Baumann and others [3]	2000
Biosensors	Nebel and others [4]	2007
Bionics	Hadjinikolaou and others [5]	2012
Microelectromechanical systems	Auziello and others [6, 7]	2012
Electronic multipliers	Trucci and others [8]	2006
Optical windows	Campos and others [9]	2013
Cutting tool	Ding and others [10]	2012
Electrodes	Zhang and others [11]	2013
Transistors / Superconductors	Takano and others [12]	2009
Quantum computing with room temperature	Markham and others [13]	2011

Diamond inserts can be created with functional physical properties for use in various fields of science and technology. The variety of applications and potential uses in fields of science, where other materials are commonly used, make diamond the material of the present and the future. Table 1 [1] shows the areas of application of diamond.

At the beginning of the 20th century, it was already known that natural diamonds were formed under the influence of high pressures and temperatures, which was described by Bundy and others [14]. At room temperature and atmospheric pressure, diamond is a metastable carbon phase, along with graphite, which is thermodynamically stable under these conditions. Many features made the diamond unique, rare and valuable, which created the need to develop technologies for the formation of synthetic diamonds in laboratory conditions.

The diamond market and the areas of using rough diamonds in technical applications are constantly expanding. It requires constant development of production technologies to obtain diamonds with specified properties that increase the efficiency of their use in high-tech industries related both to electronics and various kinds of optical applications, as well as large volumes of abrasive material, which increasingly used in large volumes in construction technologies and geological exploration. The annual consumption of diamonds in the world is about 5 billion carats [14], but the synthesis of diamond currently reaches about 1000 tons.

Currently, the main methods of mass production of industrial diamonds are high-pressure high-temperature synthesis in a metal melt (HPHT), gas-phase synthesis (CVD), and detonation synthesis of nanodiamonds (DND).

The artificial diamond growth method called HPHT (high pressure, high temperature) was developed by General Electric in the early 1950s. In fact, it was just a reproduction of the conditions under which a diamond was formed in nature but with some peculiarities. In this process, graphite and a metal catalyst, usually Ni, Fe or Co powders, were mixed and subjected to high pressure and temperature ranging from 80 to 300 kbar, and temperatures from 1900°C to 3000°C [15]. HPHT diamonds are formed into crystals, usually several millimeters in size. They are often colored yellow due to the presence of a large number of nitrogen impurities.

2 Methods

In this paper, we consider the possibility of contamination of natural objects with widely used industrial diamonds using HPHT technology, which is more widespread and has huge volumes of use. These diamonds are obtained by a diffusion mechanism from graphite in a metal melt in the region of diamond stability. Synthesis of diamond under such conditions usually is carried out at a temperature of about 1400-1700 ° C and a pressure of about 50-70 kbar.

One of the results of obtaining synthetic diamonds by the above method is the widest range of impurities of various elements used by specific manufacturers to control the quality of the produced diamonds. This requires special attention since the brand and grades of diamonds from different manufacturers can differ significantly from each other precisely in terms of impurity elements, depending on the desired quality of the synthesized crystals. In particular, metals and metalloids - Ti, Al, Si, Mg, Ca, Sr, As, Zr, etc. are added to the charge to neutralize oxygen by forming compounds with it [16], as well as other elements, in particular, Au and Pd, for example, for whitening diamond crystals. The Mg, Ca, Sr added to the system transform into carbides and bind part of the nitrogen into cyanides, reducing the concentration of impurity nitrogen in the diamond.

Several other elements of promoters are known that allow controlling the quality of synthesized diamonds, including their strength characteristics, morphology and size of crystals.

Our studies were carried out at a pressure of 4.5 GPa and a temperature of 1620 K for $t = 60-180$ sec. To study the effect of hydrogen on the technological parameters (P , T) of the synthesis and some properties of the synthesized samples, hydrogen was introduced into the reaction mixture in the form of a hydrocarbon up to 0.5 wt. %. Experiments have shown that the addition of hydrogen to the reaction mixture affects the synthesis parameters. Additions of hydrogen up to 0.2 wt. % lead to a decrease in the minimum synthesis parameters to 0.2–0.4 GPa. An increase in the hydrogen content of more than 0.2 wt. % leads to an increase in the parameters of diamond synthesis and, at the same time, decreases the diamond yield. Further studies were carried out with a content of 0.2 wt% H in the reaction mixture.

3 Results and Discussion

Figure 1 shows the dependence of the degree (α) and rate (θ) of the phase transformation of graphite into diamond on the synthesis time at different temperatures. With an increase in the synthesis time up to 60 sec. degree (α) and conversion rate (θ) change most intensively. Moreover, in the first moments of the synthesis, the conversion rate has the greatest values; apparently, at the beginning of the process, the formation of diamonds occurs at the greatest saturation of the carbon solution in the metal melt [17]. As the temperature rises, the intensity of diamond formation increases, and the incubation period decreases. The resulting critical mass of diamonds reduces the system's saturation and, having reached a certain value, begins to decrease, which indicates the entry of the system into the graphite stability region, where the graphitization of diamonds occurs. With a synthesis time of ~100 sec. and ~130 sec. the conversion rate curves cross the graphite $\leftrightarrow$ diamond thermodynamic equilibrium line and the process is stabilized from the point of view of the system saturation change.

A characteristic feature of the diamond crystallization process is the change in the fractional composition of diamonds with time (Figure 2). Fine and coarse diamonds change oppositely over time. Moreover, the boundary fraction is mainly dominant, which, depending on the synthesis conditions and the type of additives in the manganese-nickel

system, can have one or another grain size of [18]. From a comparison of Figures 1 and 2, it can be concluded that at the beginning of the process, after the incubation period under conditions of increased saturation of the system, there is a predominant formation of fine fractions, which, with the course of the synthesis time, partially or completely dissolve in the melt along the outer, most defective part and due to the dissolving material under conditions of decreasing saturation, there is an increase in larger fractions of diamonds.

Fig. 1. Dependence of the degree (α) and rate (β) of the phase transformation of graphite into diamond on the synthesis time at temperatures: 1-1580; 2-1620, and 3-1670 K

Fig. 2. Dependence of the fractional composition of diamonds on the synthesis time at $T = 1620$ K: 1-50/40; 2-63/ 50; 3-80/63; 4-100/80; 5-125/100; 6-160/125; 7-200/160; 8-250/200; 9-315/250.

The process of diamond crystallization is accompanied by a decrease in the concentration of manganese (C_{Mn}) and nickel (C_{Ni}) in diamonds. Moreover, with an increase in temperature, the level of C_{Mn} and C_{Ni} in diamonds and the rate of their change increase with time. Apparently, the H additive is actively involved in forming manganese and nickel compounds in the crystallization melt and their subsequent displacement from the grains. The lowest concentrations in diamonds C_{Mn} and C_{Ni} correspond to their higher strength, since manganese and nickel, apparently, are the most active centers for the formation of cracks in diamonds, which reduce their strength [18]. The effect of hydrogen on the interaction of carbon materials with metal melts can be explained as follows. The recrystallization of carbon (graphite) into diamond through the metal melt is carried out at the following ratio of chemical potentials: $\mu_C^I > \mu_C^P > \mu_C^A$ (1), where $\mu_C^I, \mu_C^P, \mu_C^A$ are the chemical potentials of carbon in graphite, solution and diamond, respectively.

For P, T conditions close to equilibrium, we can write: $\mu_C^P = \mu_C^I + RT \cdot \ln(\gamma_c) + RT \cdot \ln(X_c)$ (2), where α_c is the coefficient of carbon activity in the metal melt; X_c is the concentration of carbon in the metal melt.

In the presence of the third component, R, the carbon activity coefficient in the melt changes: $\ln(\gamma_c) = \ln(\gamma_c^\infty) + \varepsilon_C^T X_r$ (3), where γ_c^∞ is the carbon activity coefficient at $X_c \rightarrow 0$; ε_C^T - parameter of interaction; X_r is the concentration of the third component.

The introduction of hydrogen into the melt will lead to an increase in the value of $\ln(\gamma_c)$. At the same time, to fulfill condition (3), a corresponding decrease in the concentration of hydrogen in the melt (X_c) is necessary. At certain values of X_c , ε_C^T it becomes impossible not only to recrystallize carbon through the melt but also to dissolve carbon in the metal itself.

The mechanism of diamond formation and crystallization of diamonds in the C-Me system has been researched in several works [19-22], and various mechanisms have been proposed, and methods for studying their properties have been proposed [23-25]. However, the mechanism of diamond formation and crystallization of synthetic diamonds is developed in general terms; the details of the mechanism and the influence of various factors on diamond formation are still debatable. Of the proposed mechanisms, the following three most applicable types of crystallization mechanism for synthetic diamonds can be distinguished:

1. Carbon dissolves in molten metal to saturation concerning graphite. The synthesis conditions are set such that diamond is the thermodynamic stable phase. In this case, the free energy of diamond becomes less than that of graphite, and the solubility in the molten metal will also be lower [19]. Therefore, the solution becomes supersaturated to diamond, and the latter crystallizes out.
2. The activating agent, as a solvent, can catalyze the conversion of a carbonaceous substance into a diamond. The catalytic effect reduces the surface energy at the diamond-metal interface. This reduction is specific to each metal. The authors of [20] note that only those molten substances exhibit a catalytic effect in which carbon is in the form of positively charged ions. Positively charged carbon has a partial molar volume less than the molar volume of graphite but greater than the molar volume of the diamond. Under these conditions, carbon is thermodynamically advantageous to turn into diamond.
3. The layered hexagonal graphite structure can be transformed into a cubic face-centered structure of diamond by shifting one carbon layer in graphite relative to another by a certain distance, bringing the flat layers closer together with their subsequent "corrugation" [21]. Since in the presence of catalysts, the pressure and temperature of

diamond synthesis are greatly reduced, they facilitate the rearrangement of one structure into another.

The process of diamond formation and crystallization of synthetic diamonds, apparently, can be represented in the form of two successive stages: dissolution of carbon material in the melt and the formation of stable growth centers; diffusion of carbon from the graphite-metal interface to the metal-diamond interface; and the process of attaching carbon atoms to the surface of the growing diamond crystal.

At the first stage, when carbon dissolves in a metal - melt and when a certain limiting (critical) for these conditions is reached, carbon saturation spontaneously occurs, stable growth centers (small diamond crystals) are formed, and when the saturation decreases to a certain value, new growth centers do not arise. The number of growth centers depends on P, T, t conditions of the synthesis process, the area of the graphite-metal interface and the chemical composition of the metal-solvent [22].

Small diamond crystals (diamond nuclei) are apparently formed in the following way: at high pressures and temperatures, a metal-graphite layered complex is formed from graphite and a metal-catalyst, where metal atoms are located between carbon networks of graphite. When metal atoms are introduced between carbon layers of graphite, their outer electrons interact with delocalized carbon electrons, which reduces the latter's mobility. Therefore, the stability of the graphite structure is sharply reduced. High pressure brings the carbon nets closer together, and it becomes possible to overlap the electron orbitals of carbon atoms in adjacent nets. This can lead to the formation of covalent bonds between atoms. The flat layers are corrugated, and a diamond structure (diamond nuclei) is formed.

At the second stage, carbon diffuses from the graphite - metal surface to the metal - diamond interface and the process of carbon atoms attaching to the surface of growth centers, i.e. the actual growth of crystals at these centers. At this stage, the value of supersaturation should be noticeably less since the qualitative growth of spontaneously formed crystals occurs at a limited rate. In addition, at the second stage, it is better to have an increased value of the energy barrier to recrystallization of graphite - the diamond to avoid unnecessary growth centers and the formation of aggregates from intergrown crystals.

The nucleation stage should be significantly shorter than the growth stage to obtain sufficiently large single crystals with a minimum number of growth defects. On the other hand, severe limitation of the duration of the first stage can reduce the reproducibility of the formation of crystallization centers. The duration of the nucleation stage is practically commensurate with the thermal inertia of the reaction volume. The duration of the second stage can be limited in the range from ten seconds to ten minutes.

4 Conclusions

Thus, the process of diamond formation and crystallization of synthetic diamonds, apparently, is carried out by the dissolution of carbon material in the melt and the formation of stable growth centers, subsequent diffusion of carbon from the graphite-metal interface to the metal-diamond interface and the process of attaching carbon atoms to the surface of the growing diamond crystal.

It should also be noted that hydrogen introduced into the reaction mixture can significantly affect the dissolution of carbon material in a metal-solvent, up to its complete suppression. All this affects the process of diamond crystallization, i.e. on technological parameters of synthesis and properties of synthesized samples.

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