

SPECIFIC FEATURES OF THE BEHAVIOR OF SYNTHETIC DIAMOND IN A SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS) COMBUSTION WAVE

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The behavior of synthetic diamond powder in an SHS combustion wave is considered by using the model Ti-B-diamond system as an example. The results presented show that the diamond can retain its properties when exposed to the extreme thermal conditions realized in an SHS combustion wave.

The traditional method for producing hard alloy diamond-containing articles is a combination of complex production operations, including high-temperature sintering under superhigh pressures. This is primarily attributed to the fact that the diamond under normal conditions is a thermodynamically unstable modification of carbon, and diamond graphitization and also reduction of the strength properties of diamond grains occur at high temperatures (no corresponding pressure).

Analysis of the reported data [1-3] shows that heating and exposure of the diamond at temperatures up to 1000°C in vacuum or in an inert gas do not result in somewhat marked graphitization. However, the diamond behavior at high temperatures strongly depends on its nature, admixture composition, and grain size.

By generalizing the graphitization data of different authors it may be noted that despite a sufficiently great scatter in the graphitization values, at temperatures below 2000 K relatively slow surface graphitization takes place, while at higher temperatures the diamond is converted rapidly into graphite. However, in all the above-mentioned cases the heating velocity was not high, and the exposure of the diamond was at a high temperature for no less than several minutes. Hence, the total exposure time of the diamond at a high temperature was not substantial.

The complexity of producing a hard alloy diamond-containing tool with a hard alloy die, especially a large-sized one, by using the traditional technologies has stimulated us to attempt in the present work to fabricate a hard alloy diamond-containing material by the SHS method.

To study the diamond behavior in a combustion wave the synthetic powder AS 20 has been chosen and the model SHS Ti-B (Ti + 2B + 55 wt.% Ti) system as the initial one. The initial exothermal charge was fabricated from PTS titanium powders (particle size less than 100 μm), from amorphous brown boron containing 93% of the main element, and from the synthetic diamond AS 20 (fractions are 160/125 μm in size).

The initial charge mixtures were prepared in ball mills. Mixing was done for 2-8 h with a sphere-to-charge mass ratio of 3:1. The maximum sample temperature under SHS was measured by a tungsten-rhenium thermocouple. The strength of the recovered diamond grains was determined on the PA-4E device according to GOST 9206-80. Diamonds were recovered by dissolving the synthesized samples in a mixture of HNO_3 , HF, and H_2O with a volume ratio of 1:1:2. The degree of graphitization was determined by the weight method when graphite was selectively etched in the recovered diamonds. The process proceeded in a melt of KOH and KNO_3 (mass ratio 8:1).

The experimental data [4] and the thermodynamic calculations made by the methods from [5] show that the combustion temperature of the Ti-2B-55 mass % Ti system lies within 1760-1850°C. If the diamond does not participate in the reaction, then by increasing the diamond powder content in the mixture the combustion temperature decreases. Measurements of the combustion temperature of the Ti-B-diamond mixtures with different diamond content in the charge have supported this assumption (Fig. 1).

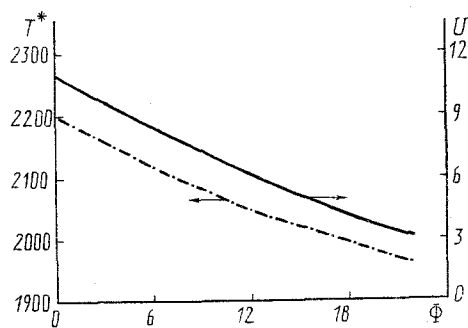


Fig. 1. Combustion temperature T^* (K) and combustion rate U (mm/sec) vs diamond powder concentration φ (vol.%) in a charge.

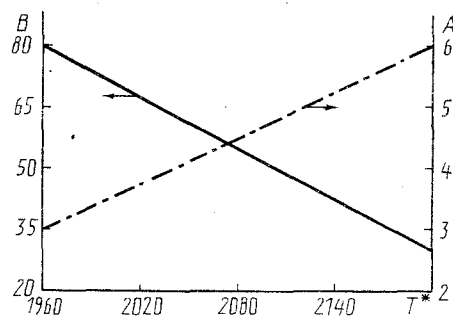


Fig. 2. degree of graphitization of diamond A (mass %) and reduction of diamond grain strength B (rel.%) vs combustion temperature T^* of a mixture.

Figure 2 plots the degree of diamond graphitization in the SHS process and the strength of the recovered diamond grains vs the combustion temperature of the mixture. The observed decrease in the degree of graphitization is consistent with the reported data, according to which the diamond graphitization to a considerable extent depends on the temperature.

However, as is known, the degree of graphitization also depends on the exposure time of the diamond at an assigned temperature. Owing to the specific features of the SHS method, very high heating velocities (10^5 - 10^7 K/sec) are realized in the SHS wave. When combined with substantial cooling velocities, this results in the fact that the diamond placed into the initial exothermal mixture is under unfavorable conditions (at the same temperature shown in Fig. 1) for a short time, and graphitization cannot become substantial despite a sufficiently high temperature (Fig. 2). The initial color reproduced by the diamonds after their recovery and treatment in chemical dissolvents indicates that in this case mainly surface graphitization occurs. For comparison it may be noted that, e.g., according to the data of [6], at heating of the synthetic diamond powder up to 1700°C and its exposure at this temperature for 15 min, the graphitization degree is (depending to the powder trademarks) 13-54 mass %. Heating of the synthetic diamond powder up to 2000°C (at 15 min exposure) completely converts diamond into graphite.

The medium where the diamond is at high temperatures is an additional factor that hinders substantial graphitization of the diamond. It is impossible to speak uniquely about the medium where the diamond is under SHS conditions. However, as studies [7] show, with intense gas evolution (powder-adsorbed gases and soluble admixtures), the air oxygen access to a sample is extremely hindered since the titanium- and boron-adsorbed gases are the basis for the atmosphere. Analysis of the admixtures of the initial Ti and B powders points to a relatively large amount of hydrogen in them. This suggests that the diamond during the synthesis is mostly in reductive atmosphere. The latter also favors the diamond conservation and reduces the degree of graphitization as a whole (irrespective of a specific temperature).

A possible reason for the observed strength of diamond grains vs combustion temperature is that when the combustion temperature decreases with increasing diamond concentration, at the same time the combustion rate of mixtures (Fig. 1) falls, too.

To justify the strength as a function of combustion temperature (Fig. 2), let us estimate the characteristic exposure times of diamond grains in the high-temperature combustion wave zone of a heterophase system.

The effect of the heterophase behavior of a system should be taken into account within the framework of the quasi-homogeneous approach by including the effective heat transfer coefficient between components, which is proportional to a specific contact surface. Such estimates of thermal diffusivity for real SHS systems of the Ti-soot, Ti-boron type, etc. are described in [8, 9]. Estimates have shown that $\kappa \approx 10^{-2} \text{ cm}^2/\text{sec}$.

The approximation of Michelson's (exponential) temperature profile before the combustion front (a widespread approach allowing some calculations to be made) enables one to estimate the thickness of the preheated layer between the combustion temperature and some characteristic temperature as

$$X = \frac{\kappa}{U} \ln \frac{T^* - T_0}{T_x - T_0}.$$

Assume as T_x the initial active diamond oxidation temperature close to 800°C. Then, when the mixture of titanium and boron is not dissolved, it is easy to see that at $T^* = 2000^\circ\text{C}$, $T_0 = 20^\circ\text{C}$, $U = 10 \text{ mm/sec}$ and $\kappa = 10^{-2} \text{ cm}^2/\text{sec}$, the heated layer thickness is $X \approx 10^{-2} \text{ cm} = 100 \mu\text{m}$.

If the particle size of the additionally included component (diamond) has the same order as the heated layer thickness or exceeds it (the latter occurs in reality), then the interaction of this component with the remaining ones may be neglected, in particular, because of the small specific contact surface. Then the mentioned component serves as an inert addition which should be heated by heat transfer from the main reagents. In the heat-conduction equation for steady-state propagation of a combustion wave there appears a heat sink function, and a solution to this equation will be of the following form [10]:

$$T = T_0 + (T^* - T_0) \exp \left[-\tau \frac{U^2}{2\kappa_e} \left(1 + \sqrt{1 + \alpha \left(\frac{2\kappa_1}{Ud} \right)^2} \right) \right]. \quad (1)$$

In Eq. (1) it is easy to separate the exposure time of a diamond particle in the heating zone over the temperature range from T_x to T^* :

$$\tau_x = \frac{2\kappa_e}{U^2 \left[1 + \sqrt{1 + \alpha \left(\frac{2\kappa_1}{Ud} \right)^2} \right]} \ln \frac{T^* - T_0}{T_x - T_0}. \quad (2)$$

We introduce the ratio of the characteristic exposure time of a diamond particle in the heating zone of the combustion wave of a mixture containing an inert addition α_1 to that of a mixture containing α_2 ($\alpha_1 < \alpha_2$). From Eq. (2) we obtain

$$\frac{\tau_{x1}}{\tau_{x2}} = \frac{\kappa_{e1} U_2^2 \left[1 + \sqrt{1 + \alpha_2 \left(\frac{2\kappa_1}{U_2 d} \right)^2} \right] \ln \frac{T_1^* - T_0}{T_x - T_0}}{\kappa_{e2} U_1^2 \left[1 + \sqrt{1 + \alpha_1 \left(\frac{2\kappa_1}{U_1 d} \right)^2} \right] \ln \frac{T_2^* - T_0}{T_x - T_0}}. \quad (3)$$

An expression for the coefficient κ_{ei} is of the form

$$\kappa_{ei} = \frac{\lambda_{ei}}{\rho_{ei} \lambda_{ei}}.$$

In the approximation of not very strongly differing thermal conductivities of the N-component medium, λ_e may be estimated by the following formula from [11]

$$\lambda_e^{1/3} = \sum_{i=1}^N \varphi_i \lambda_i^{1/3}.$$

After the diamond particles with λ_2 amounting to φ_3 have been added to the charge with λ_1 , we have

$$\lambda_e = [(1 - \varphi_2) \lambda_1^{1/3} + \varphi_2 \lambda_2^{1/3}]^3.$$

Values of the density and heat capacity of the diamond-containing charge are determined from the additivity principle [12]:

$$\rho_e = \sum_{i=1}^N \rho_i \varphi_i; \quad C_{pe} = \sum_{i=1}^N \rho_i \varphi_i C_{pi} / \rho_e.$$

Take $\alpha_1 = 0.05$, $\alpha_2 = 0.2$. Then for the remaining parameters based on the experimental dependences (Fig. 1), we have: $U_1 = 1.0$ cm/sec; $U_2 = 0.2$ cm/sec; $T_1^* = 1800^\circ\text{C}$; $T_2^* = 1500^\circ\text{C}$; $T_x = 800^\circ\text{C}$; $T_0 = 20^\circ\text{C}$; $d = 0.015$ cm. The data on density, heat capacity, and thermal conductivity are taken from the handbooks [13, 14].

Substituting the corresponding numerical values into Eq. (3) yields $\tau_{x1}/\tau_{x2} = 0.33$.

Thus, the exposure time of a diamond particle in a heated layer over the temperature range 800°C to a maximum temperature in the combustion front increases with inert component dilution of an exothermal mixture. In particular, τ_{x2} is approximately three times greater than τ_{x1} . The estimates made can account for the strength of diamond grains vs their concentration in a mixture or vs the corresponding combustion temperature (see Fig. 2). Volume disordering of a diamond grain in the SHS process to a greater extent depends on the exposure time in the high-temperature zone than on the absolute value of this temperature. In contrast, graphitization increases with increasing combustion temperature. The latter is possible when heat affects the grain surface alone. The core and greater part of the diamond particle volume retain their strength properties. This very favorable effect has stimulated studies of SHS of diamond-containing composite materials of different purpose.

Thus, in principle, the possibility of conserving a diamond and its strength properties in the SHS process has been supported by the model Ti-B-diamond system used as an example. The obtained dependences of the degree of graphitization and strength of the recovered diamond grains on the combustion temperature enable one to note sufficiently good conservation of the diamond in the SHS process, as well as to consider this method as a promising one for fabricating a hard alloy diamond-containing material.

NOTATION

κ , thermal diffusivity; T^* , combustion temperature; T_x , some characteristic temperature; X , thickness of the heated layer; U , combustion rate of the mixture; T_0 , initial temperature of the mixture; τ , time; κ_e , effective thermal diffusivity of the initial exothermal diamond-containing mixture; α , mass fraction of the added inert component (diamond); κ_1 , thermal diffusivity of diamond; d , diameter of an inert component (diamond) particle; τ_x , exposure time of a diamond particle in the heating zone over the temperature range T_x to T^* ; τ_{x1} , τ_{x2} , exposure time of a diamond particle in the heating zone over the temperature range T_x to T^* at concentrations of an inert component α_1 and α_2 ; κ_{e1} , κ_{e2} , effective thermal diffusivity of an exothermal diamond-containing mixture with a diamond concentration α_1 and α_2 , respectively; U_1 , U_2 , combustion rate of a mixture containing an inert component (diamond), amounting to α_1 and α_2 , respectively; α_1 , α_2 , mass concentrations of an inert component (diamond); T_1^* , T_2^* , combustion temperature of a mixture containing an inert component (diamond), amounting to α_1 and α_2 , respectively; $\alpha_{\text{eff}i}$, effective thermal diffusivity of the i -th exothermal diamond-containing mixture; $\lambda_{\text{eff}i}$, effective thermal conductivity of the i -th exothermal diamond-containing mixture; $\rho_{\text{eff}i}$, effective density of the i -th diamond-containing mixture; λ_{eff} , effective thermal conductivity; φ_i , volume fraction of the i -th component; λ_i , thermal conductivity of the i -th component; λ_1 , λ_2 , thermal conductivities of the exothermal charge containing no diamond and diamond particles, respectively; φ_2 , volume fraction of diamond added to the exothermal charge; ρ_e , effective density of the diamond-containing charge; ρ_i , density of the i -th component; C_{pe} , effective heat capacity of the diamond-containing charge; C_{pi} , heat capacity of the i -th component.

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