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APPLICATION OF DTA-DTG-TG COMPLEX THERMAL ANALYSIS TO STUDY DIAMOND OXIDATION PROCESSES

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ABSTRACT

The process of synthetic diamond high temperature oxidation in air has been studied by DTA-DTG-TG complex method of thermal analysis. The studies have been carried out on MTB 10-8 thermal microanalyser (SETARAM, France).

Mechanism of diamond oxidation is found to be a multistage process dependent on reaction medium composition, crystals quality and their impurity content.

The interaction of diamond and gas aggressive media has been insufficiently studied, a number of publications available frequently contain inconsistent data. This shows the lack of systematic studies on the point. Kinetics of different diamonds and air oxygen interaction has been studied /1,2/ with various oxidation mechanisms supposed. Detailed review of experimental data available /3/ shows the lack of common opinion on diamond oxidation mechanism.

For more detailed study of diamond and air oxygen interaction the DTA-DTG-TG complex thermal analysis on MTB 10-8 thermal microanalizer has been carried out. AC2 80/63 and AC2 160/125 synthetic diamond powders were the objects to study. The data in Figs.1-3 include typical thermograms for oxidation of the synthetic diamonds. The batch of $3 \cdot 10^{-6}$ kg has been selected for each experiment. A mixture of AC2 80/63 (50%) and AC2 160/125 (50%) synthetic diamond powders (Fig.1) has been studied to reveal the grit size effect on the DTA curve behaviour during diamond oxidation, platinum crucibles being used for the studies. Stabilized Al_2O_3 has been used as a standard. Studies have been carried out at atmospheric pressure of the air. Comparison of Fig.1 (AC2 80/63 and AC2 160/125 mixture) with Fig.2 (AC2 80/63) shows the curve behaviour to remain stable. Initial oxidation temperature is 773 K, here an exothermic effect is initiated attaining its peak at 973 K and accompanied by mass decrease (TG) and reaction rate increase (DTG). With reaching DTA peak, the reaction rate (DTG) also comes to its peak.

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activation energy.

With no limitations for oxygen diffusion to diamond surface, exothermic effect would be retained and the reaction rate would be increased with temperature to a certain measure of oxidation. Figs.1,2 show, however, that exothermic reaction peak is observable even at the initial stages of oxidation, 733-933K and then at 1273K oxidation runs with evident endothermic reaction. Since CO adsorption is practically impossible, with sufficient amount of oxygen available carbon oxide is partially or completely transformed to CO_2 and so with no diffusion limitations the reaction

$C_{diam} + O_2 = 2CO + \Delta T$ (1)

prevails during the initial period. Increased concentration of CO_2 in intergranular pores and over the sample results in oxygen diffusion limitations and in diamond oxidation mechanism variation. Then the reaction

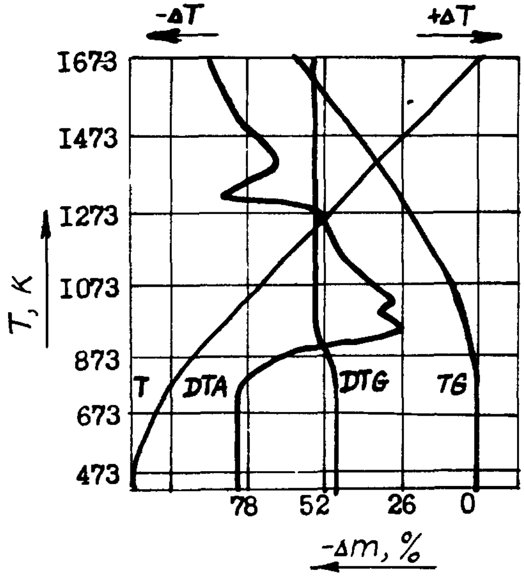

Fig. 2 Thermogram for oxidation of AC2 80/63 (50%) and AC2 160/125 (50%) diamond mixture

$C_{diam} + CO_2 = CO + C - \Delta T$ (2)

starts. Thus, reaction (1) runs in the range of 773-973K(Figs.1,2). The DTA and DTG peaks correspond to the origin of diffusion limitations, and in the range of 973-1273 K the processes between CO and CO_2 run, with enthalpy being decreased and reaction rate being constant. In the range of 1273-1333 K the reaction runs with a deep endothermic effect associated with reaction mechanism variation. The reaction rate decreases with a certain increase on attaining endothermic peak. Endothermic reaction peak results from decreasing diamond reaction power at these temperatures and from increasing the depth of CO_2 layer which inhibits diffusion and reduces the reaction rate. It has been also found that in this temperature range the destruction of crystals occurs accompanied by an endothermic effect, while the absorption processes on restored sur-

From 973 K (Figs.1,2) ΔT value in DTA decreases, with reaction rate being constant up to 1273 K. A sharp endothermic reaction starts at 1273 K, the peak is attained at temperatures of 1313 - 1333 K with the reaction rate being decreased. On attaining endothermic reaction peak the reaction rate increases slightly and further temperature increase results in oxidation with decreasing rate. At 1673 K oxidation is measured 63.3%.

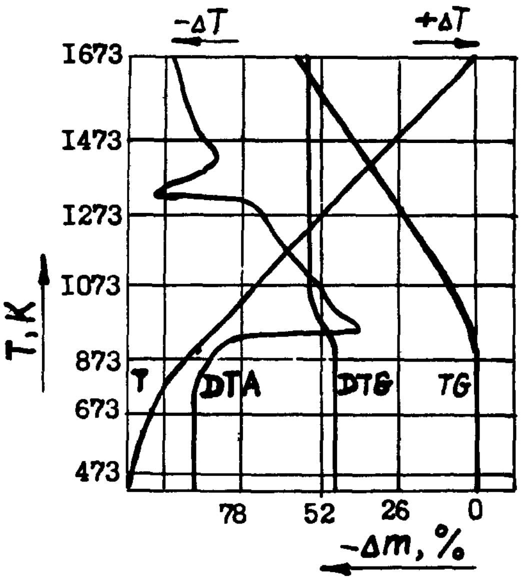

Fig. 1 Thermogram for oxidation of AC2 80/63 diamond

A range of experiments with different grit sizes has not shown the effect of grit size on the curves behaviour. The experiments show, however, that the size and the shape of the crystals as well as the amount and nature of their impurities influence the initial oxidation temperature, reaction rate and measure of oxidation, while the curves behaviour is typical not only for diamonds but for other carbon modifications as well /4,5/.

From numerous experimental data it seems to be possible to interpret a complicated behaviour of the thermal analysis curves in terms of diamond oxidation mechanism.

The surface atoms of carbon in the dimond crystal have free valencies, their number and direction depend on faces orientation relative to the lattice. Under real conditions different atoms and groups are localized on free valencies. First of all, they include O_2, OH, COOH, CHO and other groups introduced by chemical separation of synthetic diamonds forming strong covalent bonds with carbon atoms. At certain temperatures their desorption from the surface is impossible without tearing carbon atoms out of diamond lattice. Therefore, CO molecules are removed during O_2 or OH desorption. The energy required to initiate oxygen desorption with the carbon atom being teared out seems to be a diamond oxidation

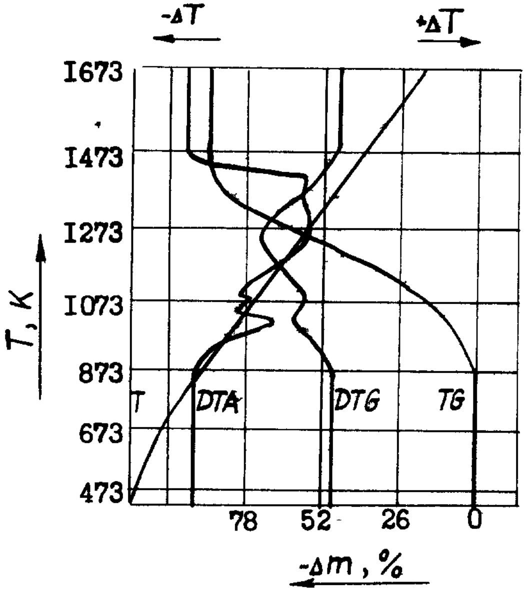

Fig. 3 Thermogram for oxidation of AC2 80/63 (50%) and AC2 160/125 (50%) diamond mixture in air flow

faces result in the reaction inhibition. At temperatures above 1313-1333 K oxidation runs in endothermic region. The oxidation reaction rate (DTG) is being constantly reduced.

To confirm the foregoing, experiments have been carried out intended to exclude diffusion limitations. Thermogram in Fig.3 contains experimental data obtained in air flow of 80.0 l/hr. The process of oxidation runs in the exothermic region. At 1323 K the sample was completely oxidized, $NiMnO_4$ being detected in the incombustible residue. Diffusion limitations were practically absent.

Thus, the DTA-DTG-TG thermal analysis results show the mechanism of diamond oxidation to be a multistage one. Mechanism variation is determined by crystals quality, their impurities content and changes in the reaction mixture composition.

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