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Thermogravimetric determination of amorphous and crystalline phases in superdispersed diamond

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Amorphous and crystalline phases in superdispersed diamond have been determined by thermogravimetric analysis at a heating rate 1.25 K min^{-1} or lower, and the kinetic parameters of oxidation of different carbon species have been calculated.

Superdispersed diamonds are formed under non-equilibrium conditions of detonation at high temperature gradients and rates of cooling.[1] This process results in the occurrence of several carbon phases in the primary particles of condensed products of detonation[2,3] or detonation carbon.

It is well known[4] that the structure of detonation carbon depends on the conditions of synthesis and, in the general case, can contain several types of primary particles, namely, amorphous, graphite-like and diamond carbon. The following three carbon phases were detected by X-ray diffraction analysis of detonation carbon:[2] diamond (a set of 5 reflections), amorphous carbon and dispersed carbon (a 002 reflection).

The aim of this work was to examine the structure and distribution of carbon phases in the detonation product of a trinitrotoluene–cyclotrimethylenetrinitramine (40:60) mixture.[5] The experimental procedure involved consecutive selective oxidation of carbon phases under special conditions. The detonation carbon was oxidised by oxygen of the air and by nitric acid solutions.

The kinetics of oxidation of detonation carbon by oxygen of the air was investigated by dynamic thermogravimetry on a Q-derivatograph (F. Paulik, J. Paulik and I. Erdey, Hungary) in the temperature range 603–89 3 K. The experimental conditions provided selective oxidation of the carbon phases. The DTA and TGA curves measured at a heating rate of 10 K min^{-1} exhibited only two stages of oxidation:[6] one of them refers to the oxidation of dispersed carbon with nondiamond structure and the other, to the oxidation of superdispersed diamonds. The DTA and TGA curves of superdispersed diamond measured under the same conditions exhibited one stage of oxidation.[6] A decrease in the heating rate down to 1.25 K min^{-1} resulted in the appearance of three and two stages of oxidation in the cases of detonation carbon and superdispersed diamond, respectively (Figure 1). A sample of superdispersed diamond was separated from detonation carbon by thermal liquid-phase oxidation.[7]

The kinetic parameters of oxidation for detonation carbon and superdispersed diamond were calculated by the Freeman and Carroll method.[8] Table 1 summarises the results.

The mass fractions of each individual phases in a number of the detonation carbon samples were determined from the thermogravimetric data. These data indicate that 40–45 , 20–25, and 30–3 5% dispersed carbon was oxidised at stages I, II and III, respectively.

While the loss of mass at the first stage in superdispersed diamond prepared by the treatment with a mixture of sulfuric and nitric acids varied from 3 to 7%, the residual carbon was oxidised as a structurally homogeneous material.

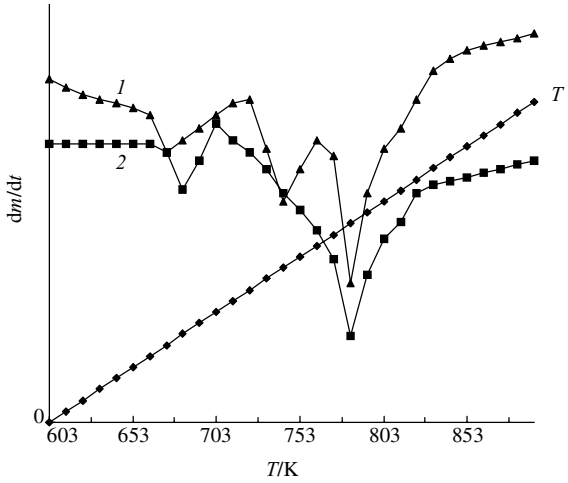

Figure 1 DTG curves for (*1*) detonation carbon and (*2*) superdispersed diamond oxidation by oxygen of the air at a heating rate of 1.25 K min^{-1} (sample mass of 5.0 mg).

Note that the E_a and A_0 values are similar for the last two stages of oxidation of detonation carbon and superdispersed diamond. Thus, we can assume that the phase that is oxidised immediately before the diamond phase is an amorphous phase of diamond.

Next, using thermogravimetry at a heating rate of 1.25 K min^{-1} , it is possible to determine a loss of the amorphous diamond phase in the course of oxidation of a nondiamond carbon phase. Thus, for the cited example, these data indicate that approximately 2/3 of the amorphous diamond phase was lost in the course of purification.

An analysis of the kinetics of the liquid-phase oxidation of detonation carbon by nitric acid solutions at 366 K has also shown the occurrence of three stages in the oxidation.

The first stage corresponds to the removal of the easiest oxidisable carbon. The degree of oxidation depends on the oxidation potential of the system and on the duration of exposure; however, it is characterised by a limiting value of the conversion of a nondiamond phase. The first-order rate constant of this reaction in the oxidation by 65% HNO_3 solution is 2.5×10^{-9} s^{-1} .

The second stage differs from the first by a lower rate of reaction. For 65% HNO_3, the first-order rate constant of this stage is 0.5×10^{-9} s^{-1} .

The third stage occurs in systems with high oxidation potentials (mixtures of Cr^{VI} compounds, sulfuric and nitric acids *etc*.)

Table 1 Kinetic parameters of gas-phase oxidation for detonation carbon and superdispersed diamond.

Stage	Detonation carbon			Superdispersed diamonds		
	Temperature/K	Activation energy E_a/KJ mol^{-1}	Preexponential factor A_0/s^{-1}	Temperature/K	Activation energy E_a/KJ mol^{-1}	Preexponential factor A_0/s^{-1}
I	633–69 8	114.1	0.04×10^{4}	—	—	—
II	698–72 3	73.5	0.34	693–803	115.4	0.28
III	>723	193.5	5.5×10^{8}	>803	194.4	0.51×10^{8}

under long exposures and corresponds to the conditions of etching diamond structures.

A comparison of these results with each other and with the published data[5,7,10] allowed us to suggest that stages I, II and III in both gas-phase and liquid-phase oxidation of detonation carbon characterise the structural inhomogeneity of this material and are responsible for the step-by-step removal of amorphous nondiamond carbon, the amorphous surface structure of diamond particles and then the diamond phase of carbon.

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