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SYNERGISTIC INFLUENCE OF FLUORINE AND HYDROGEN ON PROCESSES OF THERMAL TRANSFORMATIONS OF CARBON-CONTAINING SYSTEMS UNDER HIGH PRESSURES

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Thermal transformations of naphthalene ($C_{10}H_8$), octafluoronaphthalene ($C_{10}F_8$) and their binary mixtures at 8.0 GPa have been investigated by X-ray diffraction, Raman spectroscopy, scanning and transmission microscopies. As a result, the pronounced synergistic effect of fluorine and hydrogen on mechanisms, p, T parameters and products of pressure-temperature-induced transformations of carbon-containing systems has been established. Simultaneous presence of fluorine and hydrogen gives rise to significant reduction of the temperature thresholds (TT) for carbonization, graphitization and diamond formation in $C_{10}H_8$ – $C_{10}F_8$ mixtures in comparison with the TT values for pure $C_{10}H_8$ and $C_{10}F_8$ at the same pressure. This synergistic effect manifests itself also in the simultaneous presence in the products of transformation of both nano- and micrometer-sized diamond fractions. The reasons of formation of different diamond fractions in the products of binary mixture treatment are discussed in this work.

Keywords: High pressure, High temperature, Transformations, Nanocarbon materials.

1. Introduction

Comparative studies of pressure-temperature-induced transformations of naphthalene ($C_{10}H_8$), fluorographite ($CF_{1.1}$), and their binary mixtures have led to the observation of a synergistic effect for fluorine and hydrogen on the mechanisms, p, T parameters and products of the transformations of binary mixtures of hydrocarbons and fluorocarbon compounds relatively to transformations of pure compounds [1]. Along with a significant decrease in the p, T parameters for the initiation of carbonization, graphitization and diamond formation in binary mixtures relatively to transformations of pure hydrocarbon and fluorocarbon compounds, a synergistic effect results in a considerable increase in the content of nanosize graphite and diamond phases in the products of binary mixture transformations. This finding is particularly attractive from an application standpoint, since it presents additional opportunities for the synthesis of pure and doped nanosize modifications of graphite and diamond with fine-tuned properties. However, the mechanistic nature of the nanosize carbon phase formation remains a subject for discussion. In the present work, we have attempted a more detailed investigation of the synergistic effect on processes of nanosize carbon phase formation in the products of reactions using hydrocarbon-fluorocarbon mixtures, which has been exemplified by two structural analogs, naphthalene and octafluoronaphthalene.

2. Experimental section

Naphthalene (Chemapol) and octafluoronaphthalene (Alfa Aesar) have been used as starting hydrocarbon and fluorocarbon materials, respectively. Homogeneous 1:1 mixtures of $C_{10}H_8$ – $C_{10}F_8$ were prepared by thorough grinding of weighed amounts of powdered starting materials in an agate mortar. Samples of heterogeneous $C_{10}H_8$ – $C_{10}F_8$ mixtures appeared as two-layer compacts made from two separately compacted pellets of pure naphthalene and octafluoronaphthalene.

Tablet-shaped samples (5 mm diameter, 4 mm height) of starting materials were placed into a graphite heater and then treated in the 'Toroid' high pressure apparatus under a pressure of 8.0 GPa and different temperatures up to 1500 °C. Isothermal exposure times were kept at 20 seconds. Samples of high pressure states were quenched under pressure and recovered at ambient conditions, and then characterized by X-Ray diffraction, Raman spectroscopy, scanning (SEM) and transmission (TEM) electron microscopies. X-ray diffraction patterns of powder samples were recorded on an INEL CPS 120 diffractometer using Co $K_{\alpha 1}$ radiation source. Microscopy characterization of the samples was carried out on SEM Ultra plus (Carl Zeiss) and TEM JEOL JEM-1230 microscopes.

3. Results and discussion

XRD patterns for the starting $C_{10}H_8$, $C_{10}F_8$ and products of their treatment under 8.0 GPa pressure and different temperatures are shown in Fig. 1. This figure also presents XRD patterns of the samples produced by pressure – temperature treatment of the homogeneous $C_{10}H_8$ – $C_{10}F_8$ binary mixture.

XRD data show that active stages of octafluoronaphthalene carbonization at 8.0 GPa proceeded at considerably lower temperatures than naphthalene, which maintained its thermal stability up to ~ 600 °C. According to Fig. 1, two broad peaks at 30.5 and 50.5 °, which

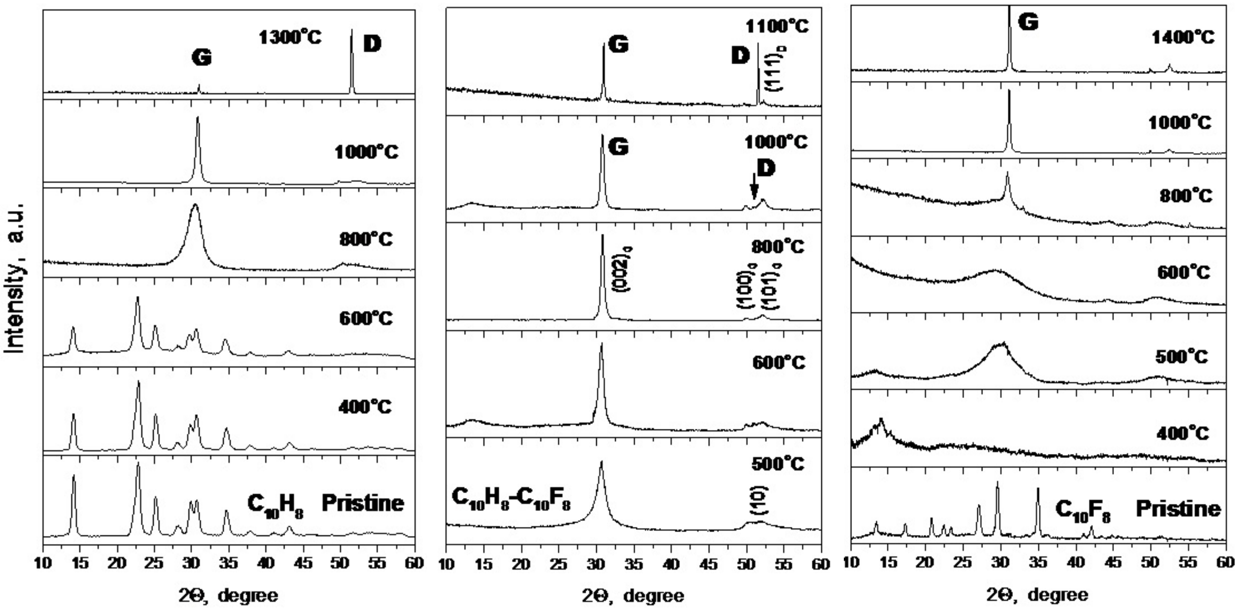

FIG. 1. XRD patterns of pristine $C_{10}H_8$, $C_{10}F_8$ and products of their treatment under pressure 8.0 GPa and different temperatures in the form of individual compounds (left and right panels) and homogeneous binary mixture (middle panel) (G – graphite, D – diamond)

are related to three-dimensional (002) and two-dimensional (10) reflexes of weakly-ordered graphite-like materials, already appeared in the diffractogram of the $C_{10}F_8$ transformation products at a temperature of 500 °C. These peaks indicate the formation of small fragment packings of graphene planes. In the case of naphthalene, similar states of carbon are formed at temperatures of 700 – 800 °C. Further increasing treatment temperature resulted in an acceleration of the graphitization processes, which caused growth in the linear sizes and the three-dimensional ordering of graphene layers. This was shown on the diffractogram by an intensity increase and narrowing of the (002) main reflex and splitting of the two-dimensional (10) reflex into two three-dimensional (100) and (101) graphite reflexes. In the case of $C_{10}F_8$, the formation of fairly crystalline graphite was noted at a temperature of $\sim$ 900 °C, while for naphthalene, this occurred at $\sim$ 1000 °C.

According to SEM data, graphite particles produced from $C_{10}H_8$ exhibit an oval shape, while those produced from $C_{10}F_8$ show a mostly polygonal form. Another special feature of the $C_{10}F_8$-produced material, is that besides the micron size graphite particles, which are the main product of naphthalene treatment, some amount of weakly-ordered nanosize carbon phase, not observed in the products of $C_{10}H_8$ transformations, was present.

X-Ray data shown on Fig. 1 indicate that the temperature threshold for initial diamond formation in the pure naphthalene-based system is 1300 °C. For $C_{10}F_8$, the formation of diamond was not observed at all within the studied temperature range (up to 1500 °C).

In the case of homogeneous binary mixtures of $C_{10}H_8$ and $C_{10}F_8$, the mechanisms for thermal transformations of these compounds are essentially modified by the combined influence of volatile fluorine-containing destruction products of $C_{10}F_8$ on the processes of naphthalene carbonization and hydrogen-containing decomposition products of $C_{10}H_8$ on the processes of octafluoronaphthalene carbonization, respectively. This resulted in a significant reduction of the temperature thresholds for main transformation stages, observed for individual $C_{10}H_8$ and $C_{10}F_8$. So, according to Fig. 1, the formation of graphite in the binary system at 8.0 GPa was already observed at 800 °C, while diamond was formed at 1000 °C.

SEM images of diamonds, produced by the treatment of naphthalene and homogeneous $C_{10}H_8$ – $C_{10}F_8$ binary mixture (Fig. 2), show that diamonds obtained from pure $C_{10}H_8$ (Fig. 2a), appear as 5 – 40 micron monocrystals. The distinctive feature of the diamonds produced from a homogeneous $C_{10}H_8$ – $C_{10}F_8$ mixture, is that along with the micron size diamond fraction typical for naphthalene transformation, it also contains a considerable amount of nanosize diamonds appearing on Fig. 2b,c as shapeless agglomerates of nanoparticles.

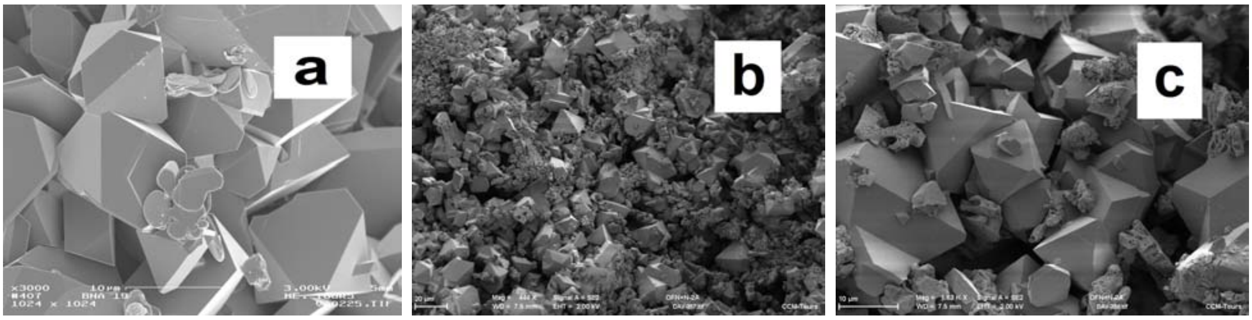

FIG. 2. SEM images of diamond materials obtained by treatment of naphthalene at 8.0 GPa and 1300 °C (a) and homogeneous mixture of $C_{10}H_8$ – $C_{10}F_8$ at 8.0 GPa and 1100 °C (b, c), taken at low magnification (b) and high magnification (c)

At first glance, the formation of two different size diamond fractions via the thermobaric treatment of organic compounds may have a purely thermodynamic explanation, according to which, the nano- and micron-size fractions of diamond can be considered as primary and secondary fractions during diamond formation. Indeed, according to p, T diagram of carbon [2], the formation of diamond from graphitization products at 8.0 GPa from 1000 – 1300 °C occurs within the p, T region of diamond stability, at a significant distance from the graphite-diamond equilibrium line. It is worth noting that the temperature of graphite-diamond phase equilibrium at 8.0 GPa is equal to $\sim$ 2500 °C. That is, it can formally be said that in this case, diamond formation takes place at high degrees of overcooling. The realization of phase transition under such conditions enables the emergence of a large number of seeds for the new phase, and accordingly, the formation of a significant amount of nanodiamonds during the first stage of graphite-diamond phase transformation. However, since diamond is a higher density material than graphite, the formation of the primary diamond fraction is accompanied by a pressure drop in the reaction zone. As a result, the coordinates of the phase transition point on the p, T diagram become shifted towards the phase equilibrium line. Accordingly, the final stages of diamond formation occur under p, T parameters being much closer to the graphite-diamond phase equilibrium line. This matches the conditions favorable for the growth of a larger, micron size diamonds which can be considered as a ‘secondary’ transformation product. By taking into account that the degree of overcooling for the system during diamond formation from a binary $C_{10}H_8$ – $C_{10}F_8$ mixture is 300 °C higher than for the case of pure naphthalene, this can be suggested as a possible explanation for the elevated content of the nanosize diamond fraction present in the products of reactions using hydrocarbon and fluorocarbon mixtures as compared to pure hydrocarbons.

However, no notable quantities of nanodiamond have been detected among the products of $C_{10}H_8$ transformations, for which the degree of overcooling of the system relative to the temperature of the graphite-diamond phase equilibrium at 8.0 GPa was also quite high ($\sim$ 1200 °C). This allows one to assume that the formation of nanodiamonds from binary mixtures can be related to the difference in fractional composition of intermediate carbon states formed during carbonization and acting as direct precursors for diamond formation from $C_{10}H_8$ and $C_{10}H_8$ – $C_{10}F_8$ mixtures.

Since the relationship of the carbonization product to a particular starting component of the mixture cannot unambiguously be established for samples made from homogeneous mixtures, studies of the structure-morphology differences of $C_{10}H_8$ and $C_{10}F_8$ carbonization products have been carried out using samples of their heterogeneous mixtures, which consisted of two individual pellets of naphthalene and octafluoronaphthalene.

SEM images taken of the contact region in the sample of heterogeneous mixture (Fig. 3), treated at 8.0 GPa and 950 °C, clearly show differences in the morphology of the carbonization products of naphthalene and octafluoronaphthalene formed during thermal transformations of these compounds in a joint fluorine-hydrogen-containing environment. Flat-shaped graphite particles with lateral sizes of 0.5 – 1.0 microns (Fig. 3a,b) are major reaction products of $C_{10}H_8$. Unlike $C_{10}H_8$, the ultradispersed 10 – 20 nm nanoparticles (Fig. 3b,c), built from two-dimensional states of carbon, become a major component of $C_{10}F_8$ reactions under the considered conditions. The obtained data show that thermal transformations of the binary $C_{10}H_8$ – $C_{10}F_8$ mixture under high pressures and temperatures of $\sim$ 900 – 1000 °C are indeed accompanied by the formation of nano- and micron-size fractions of carbon which can serve as precursors for the formation of nano- and micron-size diamond fractions. It is interesting

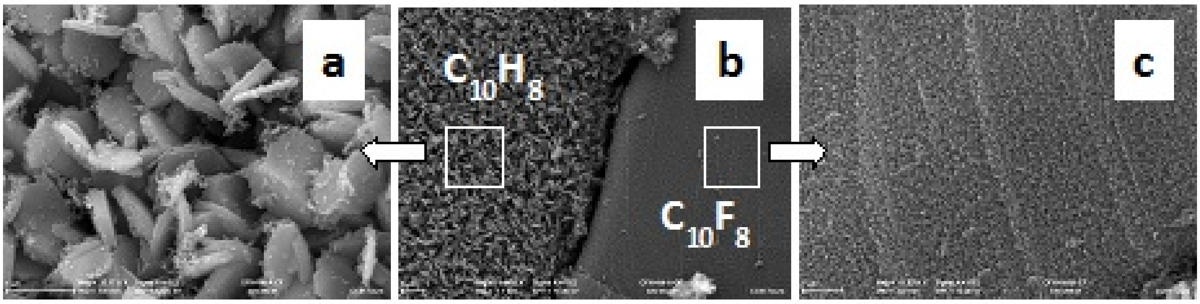

FIG. 3. SEM images of the products of thermal transformations of $C_{10}H_8$ (a,b) and $C_{10}F_8$ (b,c) taken from the region of contact area in the $C_{10}H_8$ – $C_{10}F_8$ heterogeneous mixture treated at 8.0 GP and temperature of 950 °C

to note that the micron-sized graphite and diamond fractions mainly originate from naphthalene carbonization products, while nano-size fractions were formed from octafluoronaphthalene carbonization products.

Thus, these results lead one to conclude that the main reason for the simultaneous formation of nano- and micron-size fractions of carbon materials in thermal transformations of different hydrocarbon-fluorocarbon mixtures at high pressures is the difference in the fractional compositions of the hydrocarbon- and fluorocarbon-based carbonization products under conditions of binary mixtures.

Acknowledgments

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