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EXPERIMENTAL RESULTS ON RADIATIVE COOLING OF SUBMICRON CARBON-BLACK PARTICLES

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The change in the temperature of the submicron carbon-black particles formed behind the reflected shock wave as a result of the pyrolysis of ethylene was investigated by the photoemission method. It has been established that the temperature of the carbon black substantially differs (by a value of the order of 400–600 K) from the temperature of the gas medium in which it is formed and grown. It is shown with the use of scanning electron microscopy that the average diameter of the carbon nanoclusters forming the carbon black comprises 55–30 nm at a pyrolysis temperatures of 2100–2800 K. The porosity of the primary nanoparticles is equal to 0.95–0.97.

Keywords: *carbon nanoparticles, radiating capacity, thermophoresis, shock tube, ethylene.*

Introduction. The kinetics of formation and growth of different carbon nano- and microparticles (black, fullerenes, nanotubes) has come under the scrutiny of science long ago [1–3]. However, up to now a complete quantitative and qualitative description of the kinetics of these processes in the microsecond scale, which would make it possible to determine the primary and secondary effects in them, has not been made. A knowledge of these effects is of enormous importance because investigation of the short-time processes of growth of carbon structures and of change in the gas medium in which they are formed calls for optical apparatus with a large time resolution. In addition to the problem of time resolution, another problem should be solved. The point is that the kinetics of formation of carbon nanoclusters executing a chaotic motion as a result of their collisions with free atoms is difficult to investigate experimentally.

In this paper we present results of our measurements of the temperature of the submicron carbon-black particles formed as a result of the pyrolysis of an ethylene–argon mixture in a shock tube. It has been established that the submicron carbon-black particles consist of a large number of near-spherical carbon clusters with a characteristic size of about 40 nm. By the microphotograph presented in Fig. 1 we visually estimated the porosity of the carbon-black nanoparticles at 0.95–0.97; some estimates of the influence of this parameter on the processes being considered are given in [4].

The most important result of our investigation is determination of the fact that under certain conditions, the steady-state temperature of the submicron carbon-black particles is substantially lower (by 400–600 K) than the temperature of the gas medium in which they are formed.

We believe that the results obtained by us would be of interest not only for physicists and astrophysicists, but also for specialists in material science, ecology, and aerodynamics.

Experimental Procedure. The investigations were carried out in a shock tube of stainless steel with a length of 7.1 m and a diameter of 50 mm. We used an ethylene–argon mixture (5% C_2H_4–95% Ar) as a working gas and helium as a pushing gas. Carbon clusters were formed as a result of the pyrolysis of the gas mixture behind the reflected shock wave and the subsequent condensation of carbon atoms. The parameters of the gas mixture in the working chamber were calculated by the measured velocity of the incident and reflected shock waves [5, 6] with the use

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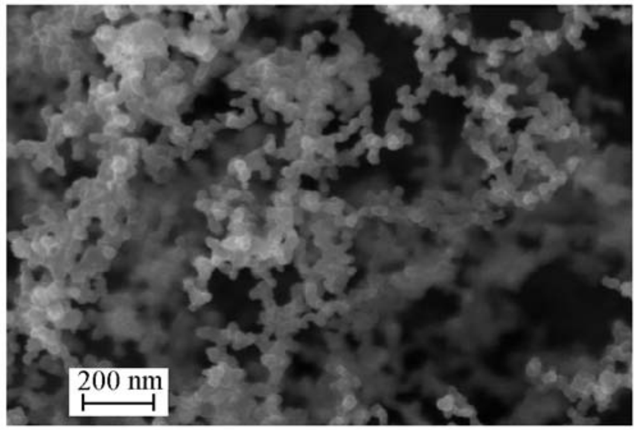

Fig. 1. Microphotograph of the carbon black obtained at a pyrolysis temperature of 2346 K.

of high-accuracy pressure transducers. The temperature of the particles was measured by the method of pulsed photoemission pyrometry [7]; in this case, the electronic work function of the cathode material was equal to 1.46 eV. The carbon black obtained at different pyrolysis temperatures was analyzed with the use of an electron scanning microscope. Carbon-black particles formed in the volume of the working gas were accumulated on stainless-steel plates hard-mounted on the reflecting surface of the shock tube. Carbon microparticles were deposited on these plates as a result of the thermophoresis [8]. The temperature gradient in the channel of the shock tube was about 10^5 K/m. The carbon black was deposited uniformly around the edges of the tube. The investigations were carried out at a working-medium temperature of 2000–3000 K. It was established that the submicron carbon-black particles are cooled very rapidly in the process of their formation (Fig. 2). It is significant that the time of growth of primary carbon clusters and their subsequent coagulation to the radius of ~0.4 μm does not exceed 400 μsec. Clearly, at the initial stage of the process, the temperature of the nanoclusters exceeds the temperature of the gas mixture because of the release of the phase-transition latent heat and the weak radiating capacity of the clusters [9].

The temperature of the carbon-black particles decreases during approximately 100–250 ml μsec long as it differs by no less than 400–600 K from the temperature of the working medium. Then the temperature of these particles remains practically unchanged. It should be noted that the temperature of the submicron carbon-black particles changes fairly rapidly (with a rate of $\sim 4 \cdot 10^6$ K/sec). Such behavior of the temperature of these particles is identical to that predicted in [4] for the case of an optically thin gas layer where the black particles are cooled as a result of the radiative heat exchange between them and the cold walls of the shock tube and are heated as a result of their collisions with argon atoms. In the stationary case, these processes balance each other.

On the basis of the experimental data on the change in the temperature of the submicron carbon-black particles obtained in the volume of a shock tube and solution of the inverse problem with the use of our mathematical model [4], it was established that the diameter of these particles, e.g., in the case illustrated by Fig. 2, is about 0.8 μm. This parameter is independent of the oversaturation of the carbon vapor S changing in the wide range from 1 to 700, which allows us to disregard the kinetics of the pyrolysis. For the particles being considered, the radiating capacity comprises a practically macroscopic value [9]. However, by the microphotograph obtained with the use of the electron scanning microscope (Fig. 1) we were able to estimate the size of the primary carbon clusters entering into the composition of the submicron samples of the high-porosity carbon black. It was established in our experiments that the average diameter of the clusters formed as a result of the condensation of the oversaturated carbon vapor is equal to approximately 30–55 nm. An increase in the temperature of the vapor-gas mixture causes the diameter of the carbon-black clusters to decrease, which correlates well with the results of the processing of the photographs obtained with the use of the electron microscope.

Conclusions. Submicron carbon-black particles were obtained as a result of the pyrolysis of ethylene behind the reflected shock wave in a shock tube. Among other things, the decrease in the temperature of the submicron carbon-black particles consisting of nanodimensional carbon clusters was measured. These clusters are formed as a result

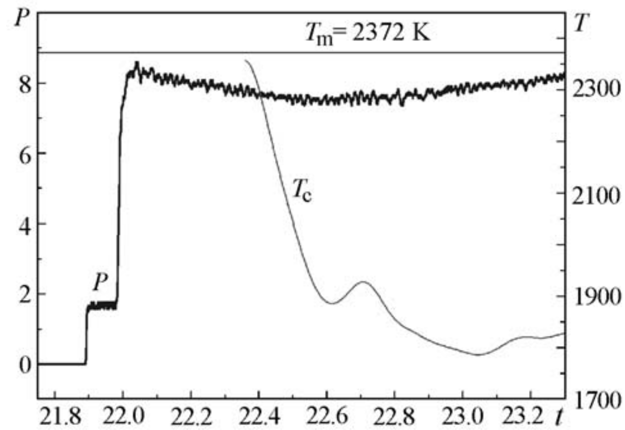

Fig. 2. Dynamics of change in the temperature of the carbon particles (T_c) and the pressure (P) at a cross-section of the shock tube. P, atm; T, K; t, μsec.

of the condensation of the oversaturated carbon vapor. In our opinion, the main mechanism of formation of submicron carbon-black particles is the coagulation of carbon clusters. It has been established that the process of growth and coagulation of primary carbon clusters lasts for no more than 400 μsec (Fig. 2); in this case, the pyrolysis of ethylene takes a longer time. It was shown that the steady-state temperature of the submicron carbon-black particles is much lower (by 400–600 K) than the gas temperature equal to 2000–3000 K. Thus, we experimentally substantiated the effect of radiative cooling of carbon-black particles, predicted by us in [4], to a temperature lower than the temperature of the gas medium in which they grow under the conditions of an optically thin medium. The average diameter of the primary carbon nanoparticles (~30–55 nm), its root-mean-square deviation (~6 nm), and the porosity of the nanoclusters were measured with the use of an electron scanning microscope.

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NOTATION

P, pressure, atm; S, oversaturation of carbon vapor; t, time, μsec; T, temperature, K. Subscripts: m, mixture; c, cluster.

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