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SOLUTION OF THE INVERSE PROBLEM FOR THE PARAMETERS OF PRIMARY CARBON NANOPARTICLES FROM ELECTRON-MICROSCOPY DATA

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From the data on the size of primary carbon particles formed in ethylene pyrolysis in a shock tube in the temperature range 2100–2800 K, calculation of their growth time and temperature is performed. It is shown that the growth time of primary nanosize soot particles does not exceed 7–10 μsec; they are heated up to temperatures hundreds of degrees higher than the gaseous-phase temperature, which is confirmed by the results of measuring the soot temperature.

Keywords: *carbon nanoparticles, shock tube, ethylene, cluster temperature.*

Introduction. A great amount of experimental data on soot formation in flames (diffusion and premixed), reactors, engines, and shock tubes has been accumulated in the past decades. However there has been no comprehensive description of all steps of soot formation to date. This is due to the complexity of the object of investigation (the size of primary nanoparticles and their growth time are small) and to the numerous physicochemical transformations in pyrolysis (burning) of hydrocarbon fuels. Many of these processes are associated with energy release on the surface of a carbon nanoparticle; this gives rise to doubts on the universality of the assumption that the process of formation of primary soot nanoparticles used for many years is isothermal [1].

In connection with the fact that the assumption of the isothermality of the soot formation was abandoned, a great deal of effort has gone recently into measuring the temperature of carbon particles in the process of their growth in the gaseous phase [2–4]. The nonisothermality of the process must in turn have a substantial effect on the kinetics of hydrocarbon pyrolysis in the gaseous phase.

This work seeks to determine the growth time and temperature of primary soot nanoparticles by solution of the inverse problem using experimental data on their final size and the parameters of the working medium. Experimental recording of the dynamics of change in these parameters is impossible at present. Below, we give results of solution of the inverse problem for primary carbon particles which are formed in shock-tube pyrolysis of ethylene diluted with argon. The range of pyrolysis temperatures is 2100–2800 K.

Solution of the Inverse Problem. Figure 1 gives a photograph of primary carbon particles, which has been obtained with an electron microscope. For analysis, we used soot formed in pyrolysis of an ethylene-argon (5% C_2H_4–95% Ar) mixture behind a reflected shock wave in a shock tube [5–7]. Stainless-steel plates were mounted rigidly to the reflecting surface of the shock tube to collect particles formed in the volume. Since the soot was deposited uniformly along the shock-tube's perimeter and the temperature gradient in the tube's channel was $\sim 10^5$ K/m, the deposition may be considered as occurring under the action of a thermopheresis force.

Processing of the photographs has shown that the average size of primary carbon particles decreases from 55 to 28 nm, as the pyrolysis temperature grows from 2100 to 2800 K (Table 1). The standard deviation of the diameter is ~ 6 nm.

To solve the inverse problem we use our own mathematical model of nonisothermal growth of carbon nanoclusters in a free-molecular approximation [8]. Experimental values of the temperature and pressure of the gas mixture behind the reflected shock wave are used as the gaseous-phase parameters in the calculations [5]. The initial radius of a cluster is taken to be one nanometer, and its initial temperature is assumed to be equal to the temperature of the gas medium. Under the assumption of the first stage of decomposition of an ethylene molecule into a stable methane

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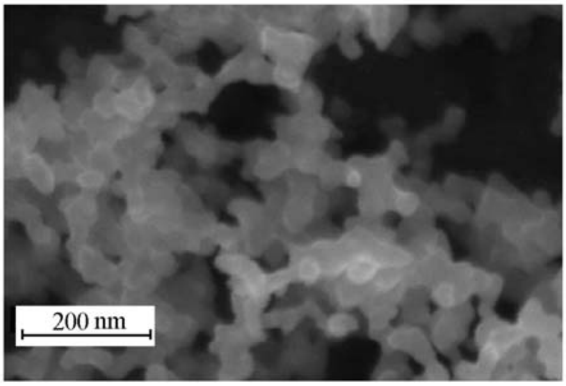


Fig. 1. Carbon soot (pyrolysis temperature 2146 K).

TABLE 1. Diameter of Primary Carbon Particles at Different Pyrolysis Temperatures

Experiment number	T_g, K	D_c, nm
1	2146	53
2	2347	35
3	2510	34
4	2679	28

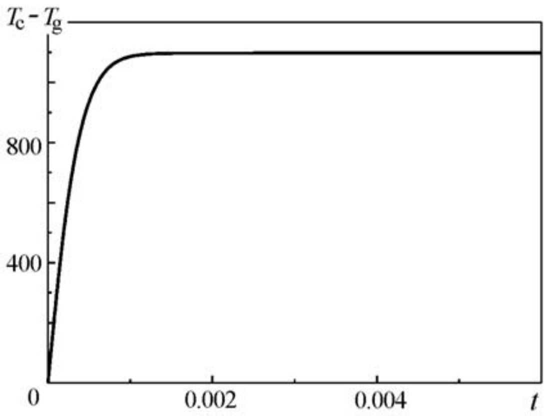
TABLE 2. Results of Evaluation of the Parameters of Primary Carbon Particles

Experiment number	T_g, K	P_{Ar}, Pa	$P_{C_2H_4}$, Pa	t_{gr}, μsec	T_c, K
1	2146	$7.2\cdot10^5$	0.36·105	7.2	4321
2	2347	$8.0\cdot10^5$	$0.39\cdot10^5$	8.2	3653
3	2510	$8.5\cdot10^5$	0.42·105	8.6	3707
4	2679	$9.0\cdot10^5$	0.45·105	6.5	3780

molecule and a carbon atom $C_2H_4 \to C + CH_4$, the degree of supersaturation in experiments can be evaluated by the formula $S \geq 0.5\frac{P_{C_2H_4}T_g}{T_g P_s(T_g)}$, where $P_{C_2H_4}$ is the pressure of ethylene behind the reflected shock wave, P_s is the pressure of the saturated carbon vapor, and T_g is the temperature of the gas behind the reflected shock wave.

Table 2 gives results of calculations from the mathematical model [8] for the experimental data of Table 1. As is seen, in the case of such high supersaturations the growth time of primary carbon particles is ~7–10 μsec. A strong heating of the clusters up to temperatures much higher than the gas-medium temperature is observed. The steady-state value of the temperature on this time interval is held by energy exchange with the atoms of the gaseous-phase argon and evaporation of carbon atoms from the nanoparticles. This is clearly seen in Fig. 2 which gives data on the superheating of a carbon cluster compared to the gaseous-phase temperature for the conditions of experiment 4 from Table 2. As our calculations have shown, a change of ±10% in the degree of supersaturation exerts virtually no influence on the temperature and rate of growth of nanoparticles, all other parameters being constant. The growth time in this case changes by less than 1 μsec, whereas the cluster temperature changes by approximately 50 K. Thus, the accuracy of determination of the degree of supersaturation of the carbon vapor S, which is dependent on the adopted kinetic scheme of pyrolysis, has an insignificant effect on the growth time and steady-state temperature of carbon nanoparticles.

The obtained results on the particle temperature are confirmed by a superheating (recorded with a pulse photoemission pyrometer) of 500–850 K of the soot particles compared to the gaseous-phase temperature [9] (Fig. 3) and in [3, 10]. The data of these works demonstrate that even after the coagulation of nanoparticles, the temperature of



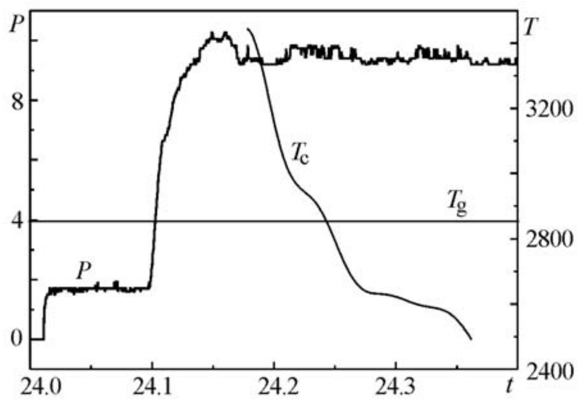


Fig. 2. Calculated difference of the temperatures of the cluster and the gas mixture at T_g = 2679 K, $P_{Ar} = 9.0 \cdot 10^5$ Pa, $P_{C_2H_4} = 0.45 \cdot 10^5$ Pa, and D = 28 nm. $T_c - T_g$, K; t, μsec.

Fig. 3. Particle temperature and pressure in the measuring cross section of the shock tube at T_g = 2854 K. P, atm; T, K; t, μsec.

submicron nanoparticles, when the influence of radiative cooling is substantial now [5], is much higher than the gas temperature.

Conclusions. We have solved the inverse problem on determination of the growth time and temperature of primary carbon nanoparticles from the experimental parameters of the gaseous phase and the data of electron microscopy of the soot produced in shock-tube pyrolysis of ethylene. Calculation of the growth time has shown that it lies within ~7–10 μsec. Over this period, the carbon nanoparticles reach a steady-state temperature 1000–2000 K higher than the gas temperature as a result of the release of the latent phase-transition heat. The residual influence of this heating has been recorded in our experiments (Fig. 3). This conclusion makes changes the concepts on the kinetics of pyrolysis at temperatures of 2100–2800 K.

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NOTATION

D, diameter, nm; P, pressure, Pa; S, degree of supersaturation of the carbon vapor; T, temperature, K; t, time, μsec. Subscripts: Ar, argon; gr, growth; c, cluster; C_2H_4, ethylene; s, supersaturated carbon vapor; g, gas behind the reflected shock wave.

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