Sublimation Temperature of Soot in Dependence on Particle Size and Formation Conditions

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Abstract
The properties of soot formed at different temperatures in shock tube pyrolysis of benzene diluted in argon were studied. Simultaneous application of the time-resolved laser-induced incandescence and the laser light light extinction techniques allowed investigating the particle sublimation process caused by laser heating. The particle sublimation temperatures were found to be in the range of 3200-4400 K in dependence on particle size and temperature regime of their formation. The surface energy of soot particles was estimated using experimentally found size dependence of sublimation temperature.

Introduction
Soot formation is an eternal topic in combustion science. Modelling of particulate emissions is a challenging task. Soot particles are amorphous carbon nanoparticles formed in combustion process. The soot structure is influenced by condition of particles growth [1, 2]. Size-dependence of nanoparticle properties that can be much different relatively to ones of bulk material are discussed in [3-5]. Moreover the size of carbon particles synthesized in pyrolysis processes is dependent on pyrolysis temperature [6]. Thus the ambiguity in soot properties is assumed to be the result of particle size and conditions of their formation. Another point of this study is the investigation of interaction of carbon particles with nanosecond laser radiation.

Experimental methods
The nanoparticles were synthesized in pyrolysis of 1% of benzene behind the reflected shock waves in the temperature \((T_5)\) range of 1900-2400 K and the pressure \((p_5)\) range of 3-4 bar. The temperature in pyrolysis process can change dramatically due to heat loss in decomposition of initial molecules and heat release of condensation [7]. Therefore the temperature of gas-particle mixture during pyrolysis process in these experiments was controlled by the emission-absorption spectroscopy [7]. The particle sizing was carried out by the time-resolved laser-induced incandescence (LII) starting with different delays relatively to the moment of reflected shock wave arrival to the investigation section of shock tube [8]. Thus, the particle with different lifetime and corresponding size in the range of 3-15 nm were observed by LII. During LII measurements the particle evaporation process could proceed when the laser energy density excess evaporation threshold. The heating of nanoparticles was realized by Nd:YAG laser pulse with the fluences of 0.1-0.5 J/cm² at the wavelength of 1064 nm. Such fluence range allow studying both non-evaporation and evaporation regime. The registration of LII signals was performed at 488 and 760 nm. The main feature of this study is application of the laser light extinction technique at 633 nm for the observation of reduction of volume fraction of condensed phase in evaporation regime. The scheme of described arrangements is presented at fig. 1.

\[
T = \frac{hc}{k_B} \ln \left\{ \frac{\frac{I_{12}}{I_{11}} \frac{e_{12}}{e_{11}}}{\frac{I_{12}}{I_{11}} \frac{e_{12}}{e_{11}}} \right\} + \frac{hc}{k_B} \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)
\]

Here \(h\) – is the Plank constant; \(c\) – is the speed of light; \(k_B\) – is the Boltzmann constant; \(\lambda_2\) and \(\lambda_1\) – are diagnostic wavelengths; \(I_{12}/I_{11}\) – is the ratio of maximum amplitudes of registered LII signals; \(I_{12}/I_{11}\) – is the ratio of radiation intensities of calibration streak tungsten lamp at wavelengths \(\lambda_2\) and \(\lambda_1\); \(e_{12}/e_{11}\) – is the ratio of emissivities of carbon particles at \(\lambda_2\) and \(\lambda_1\); \(e_{12}/e_{11}\) – is the ratio of emissivities of tungsten at \(\lambda_2\) and \(\lambda_1\); \(T_L\) – is the

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temperature of calibration tungsten lamp. The spectral emissivity of particles in Rayleigh limit is:

\[
\varepsilon_{\lambda_i} = \frac{4\pi \cdot d_p \cdot E(m)}{\lambda_i}
\]  

(2)

Here \(d_p\) – is the diameter of particles; \(E(m)\) – is the function of refractive index of carbon particles, \(\lambda_i\) – is the diagnostic wavelength. The ratio of \(\varepsilon_{\lambda_i}/\varepsilon_{\lambda_j}\) equals to the ratio of \(E(m)_{\lambda_i}/E(m)_{\lambda_j}\), that could bring an uncertainty due to probable dependence of \(E(m)\) on the wavelength [9, 10]. The diagnostic wavelengths of 488 and 760 nm are quite close to each other that justifies our assumption of independence of carbon particles optical properties on wavelength.

Results and Discussion

The first series of experiments with varying of laser fluence and keeping constant other experimental parameters: the initial temperature \(T_5 = 2110\pm70\) K, the pressure \(p_5 = 3.65\pm45\) bar in reaction zone and the delay of LII measurements 620 \(\mu\)s relatively to arrival of reflected shock wave, were carried out. Thus, the conditions of particle formation and their size \(d=8\) nm (the error of LII measurements is by an order of 20 \%) were controlled to be the same to study the influence of laser fluence and to observe by laser light extinction the transition from non-sublimation to sublimation regime. In the moment of Nd:YAG laser pulse the considerable decrease in extinction signal was observed (see fig. 2). This drop is the evidence of mass loss due to sublimation in the interaction of particles with the laser radiation. For the fluence up to 0.12 J/cm\(^2\) the sublimation process was not detected. With the further enhancement of energy in the laser pulse the drop of extinction signal increases. At approximately 200 \(\mu\)s after Nd:YAG laser pulse the extinction signal returns to the undistorted level due to diffusion of particles from unheated areas. The fluence dependence of particle maximal temperature - \(T_{\text{max}}\) attained at laser heating measured by two-colour pyrometry is presented at fig. 3.

For the fluence of \(R_0=0.1\) J/cm\(^2\) the registered LII signals were too small for reliable temperature evaluation in our experiments. In the range of \(R_0=0.1-0.12\) J/cm\(^2\) the extinction drop in the moment of Nd:YAG laser was not observed and maximal temperature was increased from 3100 up to 3500 K. With the further increase of fluence \(R_0>0.12\) J/cm\(^2\) the sublimation was observed by the extinction signal drop meanwhile the maximal temperature remained independent of the laser pulse energy and equaled to \(T_{\text{max}}=3500\pm100\)K. Thereby this constant value of maximal temperature was assumed as the sublimation temperature \(T_{\text{sub}}\) of particles formed in our conditions.

The second series of experiments was performed to study the influence of temperature of particle formation on sublimation temperature of formed carbon particles. For this purpose the fluence of \(R_0=0.43-0.45\) J/cm\(^2\) was chosen; the temperature behind the reflected shock wave was varied from 1900 up to 2400 K and the delay of laser pulse relatively the shock wave was varied from 100 up to 750 \(\mu\)s. The sublimation temperature was found to be in the range of 3200-4400 K (see fig. 4) in dependence on particle size and temperature regime of their formation. These results are the evidence of different structure of carbon particles formed at different temperature conditions.
The highest sublimation temperature $T_{sub}$ was obtained for particles formed at highest temperatures of $T_5 = 2337-2386$ K. The measured $T_{sub}$ during laser heating for these particles was found to be 4400 K. The exceeding of particle $T_{sub}$ sublimation temperature over the sublimation temperature of bulk graphite that is equals to 3900 K for pressure around 3.5 bar [11] is questionable. In the case of particles formed at lower pyrolysis temperature of $T_5 < 2200$ K the sublimation temperature did not exceed the value of 3800 K. The determination of sublimation temperature by two-color pyrometry includes the error corresponding to uncertainty of optical properties of particles and accuracy of LII size measurements that decreases for small particles. Besides the uncertainty of used technique of sublimation temperature measurements one should pay the attention to the difference of extracted values of $T_{sub}$ from the peak temperatures observed for soot in flames that are about 4000 K [9]. This distinction is probably caused by the differences in particles structure due to the differences of formation conditions. Firstly, shock tube pyrolysis reactor produces the particles with the mean size less than 15 nm, when in flames the particles grow up to the 30-40 nm. Secondly, the high temperature can change the kinetics of soot formation process [6]. As it generally known [12] the particles formed at high temperatures have the more graphite-like structure. Thus, the shock-tube synthesized particles probably have the different structure from ones formed in flames. The obtained size dependence of sublimation temperature (fig. 4) can be used for determination of size-dependences of other thermodynamic properties in line with the approaches described in [3-5]. The correlation between evaporation temperature of nanoparticles and bulk material taking into account the size-dependence was given in [3]:

$$
\frac{T_{evap}(d)}{T_{evap\_bulk}} = \left[ 1 - \frac{1}{(2d/a)-1} \right] \exp\left[ \frac{2S_{sub\_bulk}}{3R (3d/a)-1} \right]
$$

Here $d$ – is the diameter of nanoparticle, $a$ – is the atomic or molecular diameter, $S_{sub\_bulk}$ – is the bulk solid-vapor transition entropy, $R$ – is the universal gas constant. Such approach is helpful for applying to metallic nanoparticles. In this work for the first time the modest attempt to apply this approach to the carbon nanoparticles was done. The feature of the equation (3) is the absence of adjustable parameters. However in case of carbon particles the uncertainty is appeared with the “molecular diameter”. As it is known the distance between carbon atoms in basal plane in graphite is 0.142 nm. Taking into calculations this value and the enthalpy of sublimation from [13], where averaging of experimental data for clusters C-C, escaping from heated graphite with respect to their concentration was done, the red line at fig. 5 was drawn. The distance between basal planes in graphite is 0.335 nm. Taking into calculations this numerical value, the blue curve at fig. 5 was plotted. In both cases the significant distinction with experimental data is seen (fig. 5).

$$
\frac{T_{evap}(d)}{T_{evap\_bulk}} = 1 - \frac{2\pi a^3}{3E_B d}
$$

In the first variant of evaluations the value of the surface energy of $\gamma=0.13$ J/m$^2$ and the cohesive energy of $E_B=714$ kJ/mol [14] for basal plane of graphite and in the second variant $E_B=16.4$ kJ/mol [15] $\gamma=3.27$ J/m$^2$ [16] in case of direction perpendicular to basal plane were used for calculation by eq. (4). Results of both variants have given even worse agreement with experimental data than estimation made by eq. (3) and do not presented in this paper.

The next step was the evaluation of the value of surface energy of carbon nanoparticles by approximation of experimental data of size dependence of sublimation temperature (fig.6).
Fig. 6. The approximation of experimental data with varying of surface energy of carbon nanoparticles.

The value of surface energy was assumed to be the same for particles of different size. Using the parameters \( \alpha = 0.145 \) nm and \( E_D = 524 \) kJ/mol recommended for carbon clusters in [17] the estimation resulted in \( \gamma = 50 \) J/m\(^2\). However this value for nanoparticles is much greater than that for the bulk material. Taking into calculation the average values for atom in graphite \( \alpha = 0.19 \) nm and \( E_D = 546 \) kJ/mol the value of \( \gamma = 25 \) J/m\(^2\) was obtained. That agrees with the results of study of the surface energy of metallic nanoparticles presented in [4] where the increase in the surface energy for PbS, CdS and Ag nanoparticles comparing to the bulk material amounts up to 7 times.

The evaluated surface energy of nanoparticles could be used for calculation of other thermodynamic parameters according to [5]. The universal equation that gives the correlation between the property of nanoparticle \( P_n \) and property of bulk material \( P_{bulk} \) is presented in [5]:

\[
P_n = P_{bulk} \left( 1 - \frac{k \gamma}{d} \right)
\]

Here \( k \) – is the material constant.

**Conclusions**

The dependence of sublimation temperature of growing carbon nanoparticles was obtained by simultaneous applying the LII and the laser light extinction technique in shock tube experiment. The difference in value of sublimation temperature of particles formed at different temperature conditions is considerable. The greater values of 4400 K were detected for particles formed at higher temperatures. The sublimation temperature is decreasing with the increase of the size of nanoparticles formed at the same temperature regime. The surface energy of carbon nanoparticles synthesized in shock tube reactor was estimated to be around \( \gamma = 25 \) J/m\(^2\).

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**References**