Formation of Iron–Carbon Nanoparticles behind Shock Waves¹

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Abstract—An attempt was made to obtain iron–carbon nanoparticles by two-step pyrolysis of $Fe(CO)_5$ - and C_3O_2 -containing mixtures behind incident and reflected shock waves in a shock tube. The formation of binary particles was monitored by recording the extinction of He–Ne laser radiation and laser-induced incandescence (LII). The LII method provides particle size estimates if the thermal and optical properties of the constituting material are known. Behind an incident shock wave, at temperatures of 700–1500 K, $Fe(CO)_5$ decomposes within a short period of time (~50 µs). The resulting iron atoms combine into particles, which serve as condensation nuclei for carbon vapor resulting from C_3O_2 pyrolysis at 1500–3000 K behind the reflected shock wave. The binary particles thus produced are considerably larger than pure carbon or iron particles. As the mixture temperature behind the reflected shock wave is raised, the diameter of these binary particles decreases.

The formation of carbon nanoparticles by pyrolysis of various carbon-containing substances is of interest for both fundamental science and practice. Of special interest are metal–carbon nanoparticles that can be obtained by pyrolysis of mixtures containing organometallic compounds such as $Fe(CO)_5$, $Mo(CO)_6$, and $Cr(CO)_6$. A handy tool for experimental investigation of the formation of condensed particles via gas-phase reactions is the shock tube, in which the starting reactants can be uniformly heated to a high temperature and the gas temperature and pressure behind the shock wave can easily be controlled and measured with a sufficient degree of accuracy.

Numerous studies have been devoted to the formation of soot and other particulate carbon materials behind shock waves. Furthermore, there have been attempts to study the effect of small additions of $Fe(CO)_5$ (<0.1%) on the pyrolysis of hydrocarbons [1] and tetrachloromethane [2]. No appreciable changes in the soot yield were observed in those studies. Moreover, in spite of the great number of published experimental and theoretical studies, the mechanism of the formation of soot nanoparticles is far from clear. This is largely due to the fact that experimenters have dealt with indirect data such as the extinction of laser radiation due to light absorption and scattering by particles and the intensity of radiation from particles in various spectral regions. From these data, it is very difficult to derive any information as to the properties and structure of the particles formed. More detailed information can be obtained by directly observing nanoparticles under an electron microscope and by structure determination [3]. However, particles sampled from tube walls after a run is complete may differ considerably from the particles observed *in situ* behind the shock wave and may result from the transformation of primary particles cooling in rarefaction waves and boundary layers.

A new method for direct study of primary particles is laser-induced incandescence (LII), which was first suggested by Melton [4] and was developed in later studies [5–9]. This method is based on measuring the radiation of nanoparticles preheated with a laser pulse. Particle size data are derived from the decay time of the radiation signal from the particles cooling down to the temperature of the buffer gas. Obviously, comparison and analysis of data obtained by several observation methods could provide a deeper insight into the formation of nanoparticles under given conditions. This is especially true for binary particles, whose formation has not been adequately studied.

Here, we report a study of the formation of iron–carbon nanoparticles by a combination of methods, specifically, *in situ* LII and laser radiation extinction measurements behind shock waves and *ex situ* electron probe microanalysis of particles. The source of iron atoms was iron pentacarbonyl, Fe(CO)₅. The source of carbon atoms was carbon suboxide, C₃O₂, whose molecule decomposes readily above 1500 K into a carbon atom and two molecules of CO, a rather inert substance. Interaction between iron clusters and hydrogen or chlorine (which could have resulted from the pyrolysis of C₂H₂ [1] and CCl₄ [2]) was thus obviated.

EXPERIMENTAL PROCEDURES

Experiments were carried out in a stainless steel shock tube with an inner diameter of 80 mm (Institute of Gas Dynamics and Combustion, Duisburg University, Germany). The shock tube consisted of a 2.5-m-

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Fig. 1. Setup for measuring the extinction of laser radiation and the laser-induced incandescence of nanoparticles.

long high-pressure chamber and a 6.3-m-long lowpressure chamber separated by a thin aluminum foil diaphragm. The tube was pumped with a diaphragm pump (Edwards Model QDP 80), which tolerated heterogeneous and corrosive media and ensured a rarefaction of 4×10^{-2} mbar. The gas inleakage rate was below 3.5×10^{-4} mbar/s. Mixtures were prepared by the manometric method in a stainless steel cylinder. In mixture preparation, we used high-purity (99.998%) argon. Iron pentacarbonyl (~99.5%), which is liquid at room temperature, was introduced into the cylinder by vacuum evaporation. C₃O₂ was obtained using a standard procedure at a chemical laboratory. It was purified by multistage distillation at different temperatures. The concentration of impurities in the product was determined by IR spectroscopy. The resulting C_3O_2 was 99% pure and contained carbon dioxide (1%) as the main impurity. It was stored at liquid-nitrogen temperature. Prescribed portions of C_3O_2 were also introduced into the mixture cylinder by vacuum evaporation.

The initial gas pressure in the shock tube was 30-150 mbar. Gas parameters behind incident and reflected shock waves were deduced from the initial gas pressure and the observed incident wave velocity using the familiar Rankine-Hugoniot relationships in the onedimensional approximation. Shock velocity was measured with four piezoelectric pressure gages mounted at certain distances from the tube end. Three mixtures were examined: 1%Fe(CO)₅ + 3%C₃O₂ + Ar for formation of binary nanoparticles, 0.5%Fe(CO)₅ + Ar for formation of iron nanoparticles, and $3\%C_3O_2$ + Ar for formation of carbon nanoparticles. In all runs, the mixture was heated in two steps by an incident and a reflected shock wave. The mixture temperature behind the incident and reflected waves was $T_2 = 700-1550$ K and $T_5 =$ 1200-3150 K, respectively. The gas pressure behind these waves was $P_2 = 0.3-0.7$ bar and $P_5 = 1.6-2.7$ bar, respectively. (Gas parameters behind incident and reflected shock waves are given the subscripts 2 and 5, respectively, as is the convention in the shock-tube literature.)

The LII measurement setup is schematized in Fig. 1. Nanoparticles that formed behind shock waves were heated with an Nd : YAG pulsed laser (Spectra-Physics, model LAB 150). The laser beam passed through the measurement section, entering and leaving it through two quartz windows 8 mm in diameter. The pulse energy varied between 50 and 130 mJ. Its value in each particular run was measured with a calorimeter-type radiation energy measurement system. The pulse duration was 9 ns, and the wavelength was 1064 nm. Using a pressure gage mounted in the measurement cross section and a delay generator, the system start-up was timed so that the Nd : YAG laser was activated 1 ms after the reflected wave had arrived at the measurement cross section. The operating time of the shock tube was 1.2-2.0 ms, depending on measurement conditions. This time was determined by recording the radiation from the shock-heated gas in a wide spectral range. Radiation from the particles heated by a pulse of the Nd: YAG laser was measured using an end window 100 mm in diameter and 10 mm in thickness, a cylindrical lens with a focal distance of 75 mm, a plano-convex lens with a focal distance of 70 mm, an interference filter with a transmittance maximum at 492 nm, a set of neutral attenuating filters, and a Hamamatsu R7400 U-4 photomultiplier with a signal amplifier. Signals were recorded using a Tektronix TDS 7104 oscillograph operating at a frequency of 500 MHz. The time resolution limit of the system was ~450 ps.

Nanoparticle formation was monitored by measuring the attenuation of signals from a He–Ne laser of power 20 mW. The beam of this laser passed through the measurement cross section at a right angle to the Nd : YAG laser beam, entering and leaving the tube through two quartz windows. The extinction was measured with an E2VUV active photodiode (Spindler and Hoyer) with a time resolution of $0.5 \,\mu$ s (Fig. 1). To suppress the spurious radiation from the reacting gas mixture, we employed an interference filter with a transmittance maximum at 632 nm. The observed radiation signal and the signals from the piezoelectric pressure gages were recorded with a Krenz-Electronics TRS 4080 PC-based system operating at a frequency of 20 MHz.

After some runs, the resulting nanoparticles were collected on electron microscope grids in order to get information as to their size, shape, and structure. The grids, secured in special-purpose holders, were mounted along or across the particle-containing gas flow in the pumping duct. They were 2 mm in diameter and were made of copper coated with an ultrathin carbon film. The particles collected were photographed under an electron microscope at different magnifications. The highest magnification was 1 : 100000.

As is known from the literature [10], $Fe(CO)_5$ decomposes readily into an iron atom and five CO molecules even at 600 K. Iron nanoparticles of various sizes form in the tube, depending on the initial concentration and temperature and the reaction time [11]. Under our experimental conditions, iron nanoparticles formed behind the incident shock wave, where they were not affected by carbon atoms since the thermal decomposition of C₃O₂ begins at 1400–1500 K [12]. C_3O_2 pyrolysis into a carbon atom and two CO molecules took place after the reflected shock wave had arrived. The arrivals of the incident and reflected waves at the measurement cross section were separated by ~50 µs. This time was sufficiently long for iron nanoparticles to have formed. The basic idea of our experiments was to deposit carbon vapor forming behind the reflected shock wave onto iron particles that had already formed behind the incident wave.

EXPERIMENTAL DATA

Extinction Data

Figure 2 shows how the signal from the helium– neon laser varies with time during the formation of binary nanoparticles under various thermal conditions. The zero point of time in all experiments was the instant the reflected shock wave arrived at the measurement cross section. It is evident from the oscillograms presented that the transmitted laser radiation is markedly attenuated even behind the incident wave, suggesting the formation of condensed particles. Since $Fe(CO)_5$ decomposes at much lower temperatures and at a considerably higher rate than C_3O_2 , it is believed that the extinction behind the incident wave is solely due to iron nanoparticles. This inference is in agreement with earlier data [13]. The attenuation of the laser signal behind the incident wave is >90% at $T_2 = 700$ K and 40% at $T_2 = 1560$ K. Iron nanoparticles form so rapidly that the process is complete before the arrival of the reflected shock wave. The actual time interval between the arrivals of the incident and reflected shock waves is determined by the velocities of these waves and by the distance between the end wall and the measurement cross section. This distance was usually 15 mm. In some runs, we used an insert to lengthen it to 50 mm. This allowed the incident wave observation time to be extended from 50 to 170 µs. We observed no dependence of the formation of binary particles on the time interval separating the incident and reflected shock waves at the measurement cross section.

The arrival of a reflected shock wave causes not only a temperature rise but also an additional compression of the medium. Therefore, provided that the properties of the particles are invariable, extinction must increase abruptly at the wave front in proportion to the ρ_5/ρ_2 ratio. It is clear from the oscillograms presented in Fig. 2 that, if the secondary heating of the mixture by the reflected shock wave results in $T_5 < 2000$ K, the attenuation of the laser signal indeed rises abruptly and then remains constant. For $T_5 < 2800$ K, the extinction changes abruptly and then gradually increases. For $2800 < T_5 < 3150$ K, no extinction step is observed and the extinction signal gradually increases from near the level that was reached behind the incident wave. At the highest temperature examined (3150 K), we observed some decrease in extinction at the front of the reflected wave.

In Fig. 3, the optical density of the medium determined using the Lambert–Beer law is plotted as a function of the mixture temperature behind the reflected shock wave. For convenient comparison of data collected in different runs, the optical density D is normalized to the total concentration of Fe and C atoms (under the assumption that the yield of pyrolysis products is 100%), N (mol/m³), and the optical path l (m):

$$D = -\ln(I/I_0)/(Nl)$$

where *I* is the transmitted intensity of the signal from the He–Ne laser 1000 µs after the arrival of the reflected shock wave and I_0 is the signal intensity in a vacuum. For comparison, we plot optical density data obtained with the same shock tube and measurement procedures for the pyrolysis of $3\%C_3O_2$ + Ar and $1\%Fe(CO)_5$ + Ar mixtures behind reflected shock waves. In the pyrolysis of the mixture containing $Fe(CO)_5$ alone (Fig. 3, curve 2), the optical density falls rapidly from its highest value at T = 900-1100 K as the temperature increases. At some temperature, it stops decreasing to remain virtually constant up to 2000 K. For the mixture containing C_3O_2 alone (curve 1), we observed a familiar two-peak temperature dependence of D [12] between 1500 and 3200 K. In the case of binary particles, D is much higher and shows a quite different temperature dependence: the curve has a plateau slightly sloping down between 1500 and 3200 K [12]. This supports the view that the particles forming in the 1%Fe(CO)₅ + 3%C₃O₂ + 96%Ar mixture differ considerably in properties from pure iron or pure carbon particles. Note that, in the temperature range 1200-1500 K, the optical density of the particles resulting from the binary mixture increases from values characteristic of pure iron particles to its maximum value. In this temperature range, the binary mixture changes from the formation of only iron clusters to the formation of iron-carbon particles owing to the increasing concentration of carbon vapor resulting from C_3O_2 decomposition. This is clear from the behavior of the optical density of the $3\%C_3O_2$ + Ar mixture.

Electron Microscopic Measurements of Particle Size

Additional information as to the ultimate size of the binary particles was obtained by *ex situ* electron microscopy. Particles were sampled after two runs in which the mixture temperature behind the reflected



Fig. 2. Extinction signal intensity (U) at various temperatures behind the incident (T_2) and reflected (T_5) shock waves for the 1%Fe(CO)₅ + 3%C₃O₂ + Ar mixture.

shock wave had been 1524 and 2479 K. In the former case, we observed two kinds of product, specifically, large particles of size 50–70 nm with a well-defined iron core and a thin carbon shell (Fig. 4a) and small (probably iron) particles of size 7–10 nm with an almost homogeneous structure (Fig. 4b). For $T_5 =$

2479 K, we observed only particles of size 5–8 nm, whose structure was difficult to determine (Fig. 4c). For comparison, we show, in Fig. 4d, a micrograph of carbon particles produced from the $3\%C_3O_2$ + Ar mixture at T_5 = 2865 K. The size of the carbon particles in this micrograph is ~25 nm. It is clear from Figs. 4c and 4d that, as

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compared to carbon particles, binary particles are much smaller and have a denser structure, which is likely to be due to the iron core.

LII Data

The theory of the LII method [5, 9, 14] is as follows. Particles are heated up with a nanosecond laser pulse and absorb an integral energy R_0 . Their maximum tem-

perature T_p^0 is almost independent of their size because light absorption is proportional to the total volume of the particles:

$$T_{\rm p}^0 = T_{\rm g} - \frac{6\pi R_0}{\rho_{\rm p} c_{\rm p}} {\rm Im}[(m^2 - 1)/(m^2 + 2)]. \tag{1}$$

Here, *m* is the refraction coefficient, λ is the laser wavelength, T_g is the gas temperature, ρ_p is the density of the particles, and c_p is the heat capacity of the particles. This relationship is valid when there is no evaporation. After being heated with the laser, the particles begin to cool. When the particles are below their evaporation temperature (the evaporation temperature of carbon is ~4000 K at 1 bar), they cool mainly by conductive heat transfer to the surrounding gas, while heat transfer by radiation and evaporation is negligible. The change of particle temperature in this case is described by the heat-transfer equation

$$m_{\rm p}c_{\rm p}\mathrm{d}T_{\rm p}/\mathrm{d}t = -q,\tag{2}$$

where m_p is the mass of the particles and T_p is the current temperature of the particles. The right-hand side of this equation is the heat flux q from a particle to the gas medium. For the free molecular (fm) regime of heat transfer, the conductive heat flux from a compact particle of diameter d_p to the gas medium is

$$q = q_{\rm fm} = \frac{\alpha \pi d_{\rm p}^2 P_{\rm g} v_{\rm t}}{2} (T_{\rm p}/T_{\rm g} - 1), \qquad (3)$$

where T_p is the particle surface temperature, T_g is the gas temperature, α is the thermal energy accommodation coefficient, v_t is the thermal velocity of gas molecules, and P_g is the gas pressure. Formula (3) is obtained by solving the problem of heat transfer between a rarefied gas and a spherical particle in the diffusion approximation [15].

For $d_p = 50$ nm, $P_g = 2$ bar, and $T_g = 1200$ and 3200 K, the Knudsen numbers for a particle are $Kn = 2\lambda/d_p = 10.8$ and 30, respectively. Therefore, our experimental conditions imply free molecular heat transfer. Integration of Eq. (2) yields a particle temperature versus time relationship and a characteristic cooling time.

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Fig. 3. Optical density measured 1000 μ s after the mixture is heated by the reflected shock wave as a function of temperature: (1) $3\%C_3O_2$ + Ar (P = 3.0-4.5 bar), (2) $0.5\%Fe(CO)_5$ + Ar (P = 0.6-1.4 bar), and (3) $1\%Fe(CO)_5 + 3\%C_3O_2 + Ar$ (P = 1.6-2.6 bar).

This time depends on the heat transfer model chosen. For free molecular heat transfer,

$$T_{\rm p}/T_{\rm g} - 1 = (T_{\rm p}^0/T_{\rm g} - 1)\exp(-t/\tau),$$
 (4)

$$\tau = \tau_{\rm fm} = \frac{d_{\rm p}c_{\rm p}\rho_{\rm p}T_{\rm g}}{3\alpha v_{\rm t}P_{\rm g}}.$$
 (5)

The expression for particle diameter derivable from Eq. (5) will include the characteristic cooling time τ . The measurable parameter in this case will be the thermal radiation from the particles at a selected wavelength λ_{detect} rather than the particle temperature. Provided that $d_p \ll \lambda_{detect}$, the emission intensity and the particle temperature are correlated in terms of Planck's law:

$$S = Cd_{p}^{3} \{ [\exp(kT_{g}/T_{p}) - 1]^{-1} - [\exp(k) - 1]^{-1} \}, (6)$$
$$k = hc/\lambda_{detect}kT_{g},$$
(7)

where *C* is a constant, *h* is Planck's constant, *c* is the speed of light, and *k* is the Boltzmann constant. These relationships are valid for an ensemble of particles equal in size. In fact, a particulate product is usually characterized by some size distribution. Therefore, the measurable radiation intensity is an integral signal from particles with various diameters. For the highest energy density of the laser beam and the particle-size distribution function $f(d_p)$, the luminous flux incident on the radiation detector is given by

$$J(t) = n_{\rm p} V_{\rm m} \int_{d_{\rm p_2}}^{d_{\rm p_1}} S(T_{\rm p}(t)) f(d_{\rm p}) \mathrm{d}d_{\rm p}.$$
 (8)





Fig. 4. Electron micrographs of nanoparticles: (a, b) 1%Fe(CO)₅ + 3%C₃O₂ + Ar, T = 1524 K; (c) 1%Fe(CO)₅ + 3%C₃O₂ + Ar, T = 2479 K; (d) 3%C₃O₂ + Ar, T = 2865 K.

Here, $S(T_p(t))$ is equivalent to $S(d_p, t)$ and contains information as to particle size, V_m is the volume lighted by the laser beam, and n_p is the number of particles per lighted cubic centimeter. If the energy density in the beam cross section is not constant, then the radial energy distribution should be taken into account [5].

For estimation of the unknown particle-size distribution function $f(d_p)$ from observed signals, it is necessary to numerically solve the first-kind Fredholm integral equation [5]. However, the problem can be simplified by approximating the observed signals by curves calculated using Eq. (8). To do this, it is necessary to replace the particle-size distribution function with a lognormal distribution function characterized by a mean particle diameter and a geometric standard deviation σ_d . For $\sigma_d < 1.6$, it can be demonstrated that the main contribution to the signal fitted to Eq. (8) is from the particles with the mean diameter.

The above considerations refer to single spherical particles. However, combustion usually yields agglomerates consisting of various numbers of primary spherical particles. These agglomerates vary in size and possess fractal properties. Therefore, particle size data derived from cooling curves obtained by the LII method need a more thorough analysis. The key property of an agglomerate is the accessibility of its surface to the cooling gas. Two limiting cases are possible here: first, the accessible surface area is equal to the total surface area of the primary particles (point contact); second, the accessible surface area is equal to the surface area of the compacted monolith. In the former case, interpretation of observed signals will lead to the size of the constituent primary particles. In the latter case, the particle diameter derived from LII data will be equal to the equivalent heat-transfer diameter, an analogue of aerodynamic diameter. Particles resulting from the process in question are believed to have a compact structure since they form at high temperatures. This view is supported by a large number of other measurements. These particles are certainly nonspherical, yet they can be adequately characterized by the above-mentioned heat-transfer diameter. The error in particle size arising from laser-induced evaporation at the highest temperature examined is analyzed elsewhere [16]. For carbon particles and gas temperatures between 2800 and 3100 K, it does not exceed 50%.

The time dependence of the LII signal observed in one of our experiments is plotted in Fig. 5. The initial LII radiation intensity is taken to be zero since the emission signal from the shock-heated particles was always the same and was subtracted from the overall signal for convenience. The signal from the particles



Fig. 5. Emission signal at $\lambda = 492$ nm from nanoparticles heated with a laser pulse for the $3\%C_3O_2 + 1\%Fe(CO)_5 + Ar$ mixture. $T_5 = 2100$ K; $P_5 = 2.2$ bar.

heated up with a laser pulse grows rapidly, peaks, and then gradually decreases to the initial level as the particles cool down to the temperature of the gas medium. The process parameter measured is the time at which the signal is 1/e of its initial value. The cooling portion of the LII signal is shown in Fig. 6 (curve 1). The free molecular regime of heat transfer was assumed, and LII signals in all runs were processed using the above relationships. Under the assumption that the actual particle sizes deviate only slightly from the mean value, cooling curves were treated in the monodisperse approximation. We did not use any complicated particle-size estimation procedures involving standard deviations.

The properties of the materials making up the particles are presented in the table. They are valid for carbon between 1500 and 4000 K and for iron between 500 and 4000 K. In particle-size calculations for binary particles, we used the properties of pure carbon, assuming that the laser beam primarily heats the carbon shell rather than the iron core. For carbon and iron–carbon particles, the translational energy accommodation coefficient on collision was taken to be unity; for iron particles, it was set at 0.33, as is recommended in [9], where an analysis of the sensitivity of the computational scheme to errors in gas temperature, particle density and heat capacity, radiation absorption coefficient, and laser energy was performed. The sum of these errors can lead to an uncertainty of 50% in particle size.

Figure 7 shows how the particle diameter thus determined depends on the gas temperature behind the reflected shock wave. Clearly, the size of binary particles decreases monotonically in the temperature range 1500-3000 K. Particle size data for the 1%Fe(CO)₅ + Ar and 3%C₃O₂ + Ar mixtures are also plotted here. Note that the size of pure iron clusters also decreases monotonically with increasing temperature, while the temperature dependence of the particle size of pure carbon particles somewhat resembles the two-peak temperature dependence of the optical density (Fig. 3). For comparison, we present size data obtained by electron



Fig. 6. (1) Observed LII signal approximated by (2) a theoretical LII curve for cooling nanoparticles of diameter 19.6 nm for the $3\%C_3O_2 + 1\%Fe(CO)_5 + Ar$ mixture. $T_5 = 2100$ K; P = 2.2 bar.

microscopy (as described above) for binary, pure carbon, and pure iron particles that were produced in several runs. The size of iron particles was reported earlier [9]. As is clear from Fig. 7, for the iron particles that formed at 1100 K, the size determined by ex situ electron microscopy is twice as great as the size determined by LII. This discrepancy is probably due to coagulation taking place as the temperature is lowered. For the binary mixture, electron microscopy revealed two types of particle forming at 1500 K. The particles ~10 nm in diameter were probably iron, and the much larger particles, whose size is in agreement with LII data, are likely to be binary. Note that, at ~1500 K, C₃O₂ pyrolysis was far from complete, while all of the iron pentacarbonyl was decomposed. Therefore, the existence of the two types of particles can be explained by the competition between the pyrolysis products of iron pentacarbonyl and carbon suboxide in nanoparticle formation. At 2500 K, the binary mixture yields one type of particle and the LII and microscopic size data are in good agreement. As to the pure carbon particles produced at 2800 K, the considerable discrepancy between the particle size data obtained by these methods is probably due to the fact that, as the temperature decreases, carbon particles coagulate to a much greater extent than iron or binary particles.

DISCUSSION

We examined rather concentrated mixtures containing 1% Fe(CO)₅ and/or 3% C_3O_2 , for which one might

Properties of the materials constituting the particles

Material	ρ, kg/m ³	m at $\lambda = 1064 \text{ nm}$	$c_{\rm p}$, J kg ⁻¹ K ⁻¹
Carbon	1860 [19]	1.57–i1.4 [20]	2200 [18]
Iron	7700 [17]	3.25–i4.36 [17]	650 [18]

Note: ρ is density, *m* is refractive index, and c_p is heat capacity.



Fig. 7. Particle size versus particle formation temperature as determined by (1-3) the LII method and (4-6) electron microscopy: (1, 4) 3%C₃O₂ + Ar, (2) 0.5%Fe(CO)₅ + Ar, (3) 1%Fe(CO)₅ + 3%C₃O₂ + Ar, (5) 0.5%Fe(CO)₅ + Ar [9], and (6) 1%Fe(CO)₅ + 3%C₃O₂ + Ar.

expect an appreciable heat of reaction and changes in molecular weight. For example, in the pyrolysis of the 3%CCl₄ + Ar mixture, the difference between the observed and calculated mixture temperatures at the highest carbon yield point can be as large as 800 K [21]. However, analysis of the heats of pyrolysis for various mixtures [21] demonstrated that, up to 3% C₃O₂, the actual mixture temperature after the growth of nanoparticles is complete is close to the temperature calculated for the mixture behind the shock front. The same is true for Fe(CO)₅ pyrolysis. This is the reason why we did not take into account the heat of pyrolysis and the pyrolysis-induced changes in the molecular composition of the mixtures. According to our estimates, the error in temperature arising from this neglect is no greater than 10%.

Analysis of the particle size data obtained by LII and electron microscopy together with the optical density data suggests that the two-step heating of the binary mixture to $T_5 = 1500$ K results mainly in iron particles. Heating this mixture to $T_5 = 1500-2000$ K yields large binary particles with a well-defined iron core and a carbon shell. The highest yield of particles in the carboncontaining mixtures is observed in this temperature range. Much smaller binary particles form at $T_5 =$ 2000–3000 K.

In Fig. 8, we demonstrate how the particles change upon secondary heating by a reflected shock wave. Here, the ordinate is the ratio of the optical densities behind the incident (D_2) and reflected (D_5) shock waves normalized to the corresponding density ratio ρ_2/ρ_5 . The abscissa is the mixture temperature behind the reflected shock wave. The fact that the inequality $D_2/D_5 > \rho_2/\rho_5$ is true at $T_5 = 1200-1500$ K apparently suggests that iron particles disintegrate upon secondary heating. At $T_5 = 1500-3000$ K, the optical density



Fig. 8. Ratio of the optical densities behind the incident and reflected shock waves as a function of temperature behind the reflected shock wave in the pyrolysis of the 1%Fe(CO)₅ + 3%C₃O₂ + Ar mixture.

behind the reflected shock wave increases owing to the carbon resulting from C_3O_2 pyrolysis. Starting at 3000 K, binary particles form behind the incident shock wave since Fe(CO)₅ and C₃O₂ decompose almost simultaneously and the $D_2\rho_5/D_5\rho_2$ ratio is close to unity.

From the results of simultaneous measurements of particle size and optical density, we can derive a relationship between the concentration and the formation temperature of particles. Optical density can be expressed as

$$D = f_{\rm v} F,\tag{9}$$

where f_v is the particle volume fraction and F is a function describing the optical properties of the particles.

$$f_{\rm v} = (4/3)\pi N_{\rm p} (d_{\rm p}/2)^3,$$
 (10)

$$F = \{6\pi Im[(m^2 - 1)/(m^2 + 2)]\}/\lambda,$$
(11)

where λ is the wavelength of absorbed light and m = k - in is the refraction coefficient, with

$$Im[(m^2 - 1)/(m^2 + 2)] = 6nk/\{(n^2 - k^2 + 2) + 4n^2k^2\}.$$
 (12)

In view of this, D/d_p^3 is proportional to N_p disregarding the particle refraction coefficient (which can vary, depending on particle structure). In Fig. 9, we plot N_p versus the mixture temperature behind the reflected shock wave for various nanoparticles in the mixtures examined. These data are obtained under the assumption that the refraction coefficient of carbon and binary particles has a constant value of m = 1.57–i1.4. This value was used in the analysis of the properties of particles resulting from the shock-tube pyrolysis of C₃O₂ [20]. For iron particles, we used a value of m =3.25–i4.36 (table). It is clear from Fig. 9 that both iron and iron–carbon particle concentrations increase with

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Fig. 9. Temperature dependence of the concentration of nanoparticles resulting from the pyrolysis of the mixtures (1) $3\%C_3O_2 + Ar$, (2) $0.5\%Fe(CO)_5 + Ar$, and (3) $1\%Fe(CO)_5 + 3\%C_3O_2 + Ar$.

increasing temperature. The concentration of carbon particles shows a more complicated behavior related to the above-mentioned two-peak temperature dependence of optical density. Note the obvious similarity between the behaviors of the iron and binary particle concentrations. The higher value of the iron particle concentration in the temperature range 1700-2500 K is due to the considerable reduction in the size of the iron particles. From the density of iron (7700 kg/m^3) and the LII size of iron particles between 2000 and 2500 K (~0.5 nm), we deduce that, at an iron particle concentration of $\sim 5 \times 10^{15}$ cm⁻³, there may be less than ten atoms in one iron particle. This deduction is consistent with the total number of iron atoms in the mixture. Thus, from the behaviors of the iron and iron-carbon particle concentrations and particle size data (Fig. 7), it follows that the size of the binary particles depends strongly on the size of the iron clusters serving as carbon condensation nuclei.

CONCLUSIONS

The above experimental data suggest the following. Iron nanoparticles form at a high rate behind the incident shock wave starting at 600 K. As the temperature is raised to 1500 K, their radius decreases rapidly from 30 to 1.5 nm, while the optical density of the medium does not fall sharply. This finding probably indicates an increase in the number of fine particles. In considering the formation of carbon particles from C_3O_2 , it is necessary to take into account that the pyrolysis of this compound begins at a much higher temperature of 1400 K. Large soot particles form between 1500 and 1800 K. At higher temperatures, the combination of growing particles into large agglomerates is suppressed; as a consequence, the size of resulting particles decreases with

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increasing temperature. The optical density minimum and the smallest radius deduced from LII data (no LII signal is observed between 2000 and 2300 K) suggest that, above 2000 K, particles are in abundance and their size is ~1 nm or below. After a run carried out above 2000 K, particles as large as 700 nm [3] can be found in the shock tube. Apparently, they result from coagulation at room temperature, which is unrelated to the high-temperature processes in question. The second peak in the temperature dependences of optical density and particle radius is due to the two-step process that includes the formation of condensation nuclei behind the incident shock wave (in the temperature range 1400–1700 K, where the first peak occurs) and the condensation of small carbon particles on these nuclei at 2800–3100 K behind the reflected shock wave. Similar processes take place in the formation of iron-carbon particles. Fe(CO)₅ pyrolysis behind the incident shock wave yields iron particles up to the highest temperature examined (1560 K). Note that, at 1400–1560 K, carbon atoms resulting from C₃O₂ pyrolysis can play some role in particle formation. Next, C₃O₂ pyrolysis behind the reflected shock wave yields carbon vapor up to the highest temperature examined (3150 K). This vapor condenses on iron particles, which are the most favorable condensation nuclei. Here, neither the temperature dependence of optical density nor that of particle size shows an extremum. These quantities gradually decrease with increasing temperature because of the decreasing size of the primary iron particles and the decreasing rate of condensation.

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