Diagnostics of carbon-encapsulated iron nanoparticles by laser heating

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Abstract. In this study the laser-induced incandescence (LII) diagnostics has been applied for sizing of carbon-encapsulated iron nanoparticles (CEINs). The carbon covered iron nanoparticles were synthesized by shock waves pyrolysis of the mixtures of Fe(CO)5 with C2H2 or C6H6 diluted with argon. Iron nanoparticles were formed in the shock tube behind incident shock waves at the temperatures of 700–1000 K. The pyrolysis of hydrocarbons behind reflected shock waves at the temperatures of 1400–2000 K resulted in formation of carbon shell over iron nanoparticles. At the end of the CEINs formation process, particles were heated by one pulse of Nd:YAG laser operated at wavelength 1064 nm with fluences varied in the range 70–800 mJ/cm² to collect LII signals. The LII model, which had been used previously for iron and carbon nanoparticles separately, was updated for carbon-encapsulated iron nanoparticles. Additionally, the nanoparticle samples were investigated by a transmission electron microscope (TEM). The iron core size and carbon shell thickness were measured by statistical treatment of microphotographs. The comparison of TEM and LII particle sizing results is discussed.

1. Introduction
The development of in-situ nanoparticle diagnostics is the important theoretical and practical issue. Different methods of optical in-situ diagnostics are widely used in studying of the nanoparticle formation processes and for environmental pollution monitoring. Conventional optical methods, e.g. laser light extinction and laser light scattering, have limitations in contrast with laser-induced incandescence (LII) technique.

During the last decade the LII method has been extensively used for soot particles size and volume fraction measurements in combustion [1–3]. The advantage of LII over other methods is that it can be successfully applied for time-resolved and spatial measurements of tiny volume concentrations of nanoparticles as well as for measuring the sizes of small nanoparticles (from several nanometers in diameter) in a wide range of environmental parameters.

The LII fundamentals for measuring the soot volume concentration were proposed by Melton [4]. The LII technique is based on rapid nanoparticle heating by a laser pulse and analysis of the detected heat radiation from the particles. The intensity of LII signal is proportional to the volume fraction of condensed phase, while its decay time depends on the size of nanoparticles. Many of the experimental and theoretical studies have been focused on details of the processes of heating, cooling, changes of the structure and properties of nanoparticles caused by the laser heating [1, 3]. Recently, LII model has been improved, making it possible to describe more precisely soot heating and cooling processes [5]. Moreover, the application of LII technique
has been extended for non-soot particles sizing, usually for various metals (e.g. iron [6]). The registration of incandescence signals at two different wavelengths provides the temperature time profile during laser heating of nanoparticles and allows to obtain nanoparticles evaporation temperature [7] and their optical properties [8].

Metal nanoparticles are expected to become the good magnetic materials instead of the oxides because of their high magnetization. However, pure metal nanoparticles are oxidized in the air and can be destroyed by aggressive surroundings, thus, lose their unique properties. The carbon-encapsulated magnetic nanoparticles were previously synthesized in [9, 10]. The carbon shell around nanoparticle allows to protect magnetic core against aggressive media and to bind it with medical drugs for their delivery to diseased organs. For example, high purity iron and iron oxide nanoparticles are used in diagnostics of cancer tumors [11]. The iron nanoparticles promise the essential therapeutic effect in treatment of cancer [12].

The application of LII to binary core-shelled nanoparticle sizing is important from practical point of view. However, the diagnostics of nanoparticles with complex structure, for example, CEINs, is the difficult task due to different properties of iron and carbon parts of nanoparticle. The goal of this study was the development of the LII technique for sizing and properties investigation of CEINs.

2. Shock tube particle synthesis

Shock tube reactor is a powerful tool for nanoparticle synthesis and investigation of their formation process and physical properties. The synthesis of CEINs from the iron pentacarbonyl and different hydrocarbons in the shock tube occurs in two steps. Firstly, Fe(CO)$_5$ decomposes behind incident shock wave (ISW) at the temperatures of 600–1200 K with fast iron nanoparticle formation. Secondly, the pyrolysis of hydrocarbons behind reflected shock wave (RSW) proceeds at the temperatures of 1000–2500 K with formation of CEINs. The carbon-encapsulated iron nanoparticles were synthesized in pyrolysis of 0.25 vol %Fe(CO)$_5$ + 0.25 vol %C$_6$H$_6$ or 0.25 vol %Fe(CO)$_5$ + 0.5 vol %C$_2$H$_2$ mixtures both diluted with argon at the pressures of 4–5 bar.

The scheme of the experimental section of the shock tube and diagnostics used are shown in figure 1. The experiments were performed in the shock tube with an inner diameter of 50 mm. Optical in-situ diagnostics of forming nanoparticles were implemented with the help of four quartz glass windows of shock tube walls of 6 mm in a diameter. Windows were mounted perpendicular to each other at the distance of 45 mm from the end flange. The shock tube was cleaned and evacuated down to the pressure of $2 \times 10^{-2}$ mbar by a fore-vacuum pump before every run.

The temperatures $T_2$, $T_5$ and the pressures $P_2$, $P_5$ behind the incident and reflected shock waves were determined based on the measured incident shock wave velocity by applying one-dimensional gas-dynamic theory with the assumption of “frozen” reaction conditions. An inaccuracy of the temperature $T_5$ calculation affected by an uncertainty of incident shock wave velocity, measured by three pressure transducers, was about 1–1.5% for all range of experiments. In this work we focus on experiments of nanoparticle synthesis at the temperatures behind RSW 1900–2100 K. This temperature range provides the highest soot yield values in shock-wave pyrolysis of benzene and acetylene mixtures [13, 14].

3. TEM measurements

The samples of nanoparticles were collected on copper TEM grids with continuous carbon layer from the shock tube walls after pulse experiment. The samples were analyzed by FEI Osiris transmission electron microscope with 200 kV accelerating voltage at Institute of Crystallography of the Russian Academy of Sciences. Examples of TEM images of nanoparticles
Figure 1. Experimental setup.

Figure 2. Typical microphoto of nanoparticles synthesized in 0.25%Fe(CO)₅ + 0.25%C₆H₆ mixture in Ar at the temperature behind RSW of 1941 K.

synthesized in the mixtures of 0.25%Fe(CO)₅+0.25%C₆H₆ in Ar and 0.25%Fe(CO)₅ + 0.5%C₂H₂ in Ar are presented in figures 2 and 3.

In figure 2 one can see the core-shell structured nanoparticles. The spherical cores are approximately 7–10 nm in sizes and surrounded by 6–8 shell layers. Total diameters of primary nanoparticles with outer layers are 9–13 nm. From figure 2 it can be seen that the primary nanoparticles are aggregated with 8–10 particles per aggregate and its size is around 20–30 nm. While the nanoparticles formed in the mixture of 0.25%Fe(CO)₅ + 0.5%C₂H₂ in Ar presented in
Figure 3. Typical microphoto of nanoparticles synthesized in 0.25%Fe(CO)$_5$ + 0.5%C$_2$H$_2$ mixture in Ar at the temperature behind RSW of 2005 K.

Figure 3 have another structure. They look like dense aggregates of core-shelled primary particles with sizes of 3–5 nm. The particle shells consist of 1–2 carbon layers. The mean aggregate size is about 20–40 nm.

All microphotos were statistically treated to calculate the primary nanoparticle sizes. To analyze the particle-size distribution the log-normal function was used:

$$df = \frac{1}{\sqrt{2\pi}d_p \ln \sigma} \exp \left[ \frac{(\ln d_p - \ln CMD)^2}{2(\ln \sigma)^2} \right] \, dd_p,$$

(1)

where $d_p$ is the current primary particle diameter, CMD is the count median diameter and $\sigma$ is the standard deviation. The histogram of particle size distribution is presented in figure 4 and was approximated by log-normal function (1) to extract the particle count median diameter and standard deviation.

The mean CEINs diameters extracted from particle size distribution formed in the mixture of 0.25%Fe(CO)$_5$ + 0.25%C$_6$H$_6$ in Ar at the temperature behind RSW of 1941 K and in the mixture of 0.25%Fe(CO)$_5$ + 0.5%C$_2$H$_2$ in Ar at the temperature behind RSW of 2005 K were found to be 10.3 and 3.5 nm correspondingly.

4. Electron micro-diffraction measurements

The electron micro-diffraction (MD) analysis of the samples, which had been previously analyzed by TEM, was performed to determine interplanar distances of CEINs in order to find out particle composition. The typical MD patterns are shown in figures 5 and 6. Besides MD analysis, interplanar distances were measured using high resolution TEM microphotos by Fourier analysis.

The interplanar distances extracted from the rings of MD pattern in figure 5 are in good agreement with data for graphite (1.21 Å), $\gamma$-Fe (1.8, 2.11 Å), magnetite Fe$_3$O$_4$ (1.12 Å), hematite Fe$_2$O$_3$ (1.32, 1.46 Å). Some of them could be attributed to carbide Fe$_3$C (1.12, 1.21, and 2.11 Å). However, the brightest rings 2.11 and 1.21 Å we attributed to $\gamma$-Fe and graphite. The interplanar distances in nanoparticles formed in the mixture of 0.25%C$_6$H$_6$ + 0.25%Fe(CO)$_5$
Figure 4. The example of particle size distribution extracted from TEM images statistical treatment and approximation by log-normal function (1) for CEINs synthesized in 0.25%Fe(CO)$_5$ + 0.25%C$_6$H$_6$ mixture in Ar at the temperature behind RSW of 1941 K.

Figure 5. The MD pattern of the nanoparticle samples which were synthesized in 0.25%C$_6$H$_6$ + 0.25%Fe(CO)$_5$ mixture in Ar at the temperature behind RSW of 1941 K.

in Ar extracted from high resolution TEM micrographs using Fourier analysis 1.98, 2.08, 2.13, 2.45 Å resulted in content of Fe$_3$C, Fe$_3$O$_4$, and FeO oxides.

In figure 6 one can see only two rings corresponding to the distances 1.09 Å and 1.97 Å that is a result of loose crystalline structure in comparison with figure 5. The value 1.97 Å could be attributed to carbide Fe$_3$C and 1.09 Å to γ-Fe (1.081 Å) or magnetite Fe$_3$O$_4$ (1.092 Å) or
Figure 6. The MD pattern of the nanoparticle samples which were synthesized in 0.5\%C\textsubscript{2}H\textsubscript{2} + 0.25\%Fe(CO)\textsubscript{5} mixture in Ar at the temperature behind RSW of 2005 K.

hematite Fe\textsubscript{2}O\textsubscript{3} (1.104 Å). The interplanar distances in nanoparticles formed in the mixture of 0.5\%C\textsubscript{2}H\textsubscript{2} + 0.25\%Fe(CO)\textsubscript{5} in Ar extracted from high resolution TEM micrographs using Fourier analysis were found to be 2.12 Å, 2.29 Å, 2.36 Å, 2.48 Å and corresponded to graphite, Fe\textsubscript{3}C, and FeO.

The deviation between measured and reference data can be regarded to the measurement errors and the difference of interplanar distances of nanoparticle from bulk material. Nevertheless, the MD patterns of synthesized nanoparticles showed the presence of \(\gamma\)-Fe, iron oxides, which could be formed when particles were extracted out of the reactor to the air due to imperfection of carbon shell, and iron carbide, which could be formed at elevated temperature during particle formation.

5. EDX and HAADF STEM analyzes of the particles

In addition to above methods of analysis, the elemental analysis by energy-dispersive x-ray spectroscopy (EDX) to reflect elemental composition of nanoparticles was carried out. The examples of the elemental spectra in the nanoparticles obtained in the pyrolysis of the investigated mixtures are presented in figures 7 and 8.

With the help of high angle annular dark field scanning transmission electron microscopy (HAADF STEM) the map of spatial distribution of the main (Fe, O, C) atoms in the samples synthesized in the investigated mixtures are presented in figures 9 and 10.

The main conclusion of these measurements is that the high concentration of iron, carbon, and much less concentration of oxygen in the nanoparticle samples was observed. We supposed the negligible carbide concentration inside the samples because the carbon content in the individual particles was not seen in these maps. As it was noted above the iron oxides occurred in samples because they were kept in air before TEM analysis during several days.

In the both spectra of elements one can found the presence of C, O, Fe, Cu, and Si atoms. The peaks around 1.0, 8.0 and 9.0 keV correspond to Cu \(K\alpha\) and Cu \(K\beta\), which are the result of copper presence in TEM grids. The peak around 1.8 keV, corresponding to Si atoms, is probably the original material from the TEM grid. The presence of C atoms in all samples is presumably
Figure 7. The spectrum of nanoparticle chemical elements formed in pyrolysis of the mixture of $0.25\% C_6H_6 + 0.25\% Fe(CO)_5$ in Ar at the temperature behind RSW of 1941 K.

![Figure 7](image_url)

Figure 8. The spectrum of nanoparticle chemical elements formed in pyrolysis of $0.5\% C_2H_2 + 0.25\% Fe(CO)_5$ mixture in Ar at the temperature behind RSW of 2005 K.

![Figure 8](image_url)

related to carbon cover on TEM grid, and carbon shells over iron/iron oxide nanoparticles, and partially to iron carbides. As we can see, oxygen atoms have the lowest peaks in figures 7 and 8 which can be explained by small concentrations of oxides in the samples. However, oxygen atoms are presented in all samples probably because of nanoparticle iron core oxidation in air.
6. LII particle peak temperature and size measurements

6.1. Particle structure
All previously made analyzes resulted in the confirmation of fact that synthesized particles are carbon-encapsulated iron nanoparticles. Also, MD and HAADF STEM results showed insignificant amount of carbides in the samples. Moreover, one can assume that during the experiments there was no oxygen in the reactor, so no oxides were taken into account in the LII model. Thus, the model of carbon-encapsulated iron nanoparticles was used in the analysis of LII measurements.

6.2. LII setup
The Nd:YAG laser LQ-215 (SOLAR Laser Systems) (see figure 1), operating at a wavelength of 1064 nm with pulse duration of 6 ns FWHM was applied for the particle heating. The laser fluences were varied in the range of 70–800 mJ/cm². The laser fluence, temporal and spatial laser beam profiles were measured and used in the LII model for calculation of the current particle size and the peak particle temperature as described in [8]. The laser beam of 7 mm in diameter was passed through a 4 mm diaphragm to provide the spatial profile close to top-hat, thus, guaranteeing the uniform particles heating inside the beam. The registration of Ti-Re LII signals was performed through a quartz end plate of the shock tube pressed by metal flange and situated at the distance of 45 mm from the laser beam position. The Nd:YAG laser beam was passed through vertically installed pair of quartz windows (see figure 1). The LII signals were detected using two narrow band pass filters, centered at the wavelengths of 450 and 772 nm with a Hamamatsu H6780-20 photomultiplier module (rise time 0.78 ps) coupled with a LeCroy WavePro 7100 oscilloscope (1 GHz bandwidth). The laser pulse shot was triggered by a pressure

Figure 9. The map of chemical elements distribution in the sample of nanoparticles formed in pyrolysis of 0.25%C₆H₆ + 0.25%Fe(CO)₅ mixture in Ar at the temperature behind RSW of 1941 K.

Figure 10. The map of chemical elements distribution in the sample of nanoparticles formed in pyrolysis of 0.5%C₂H₂ + 0.25%Fe(CO)₅ mixture in Ar at the temperature behind RSW of 2005 K.
transducer using a time delay generator at the moment of 700 µs after reflected shock wave arrival to the measurement plane.

6.3. LII model
For application of LII measurements to binary particle sizing the procedure of calculation of theoretical LII signal was changed relatively to [6, 8]. It is evidently quite complicated task to perform the LII particle sizing of binary nanoparticles taking into account the thermophysical properties of two different kinds of nanomaterials. Therefore, some assumptions have been made. The density and heat capacity of bulk iron were used in LII model because the total mass of nanoparticle mostly consists of iron. That was affirmed with TEM results (see figures 2 and 3). A simple linear approximation of data of iron density \( \rho = a + bT \), where \( a = 8200 \text{ kg/m}^3 \), \( b = -0.6 \text{ K}^{-1}\text{kg/m}^3 \) for solid [15] and liquid [16] was adopted and used for iron nanoparticles. The value of thermal energy accommodation coefficient of heat transfer between bath gas molecules and particle surface \( \alpha = 0.44 \) in present study was applied. This value was measured in [17] for carbon nanoparticle conductive heat transfer with argon. Initially, in the present study it was supposed that evaporation process of laser heated CEINs proceeds with outer carbon shell sublimation. Thus, to describe the evaporation process graphitite properties were used. Note, that the proposed model was constructed for isolated particles or for aggregated particles with point contacts between them. It is very difficult to estimate the accuracy of these approximations, one only can postulate that the inaccuracy of present LII particle sizing is not less than ±35% according to evaluated errors of pure iron and carbon nanoparticle LII sizing performed in [8].

6.4. Peak particle temperature measurements
In figures 11 and 12 the peak temperatures \( (T_{\text{max}}) \) of particles, formed in the mixtures of 0.25%C6H6 + 0.25%Fe(CO)5 in Ar and 0.5%C2H2 + 0.25%Fe(CO)5 in Ar, measured by two-color pyrometry [8] are presented versus laser fluence. These are maximum temperatures of particles heated up by laser pulse. Core and shell temperatures were assumed as uniform due to simultaneous volumetric heating of nanoparticle material by laser pulse in Raleigh regime [18] and nearly the same optical properties of nano-iron and nano-carbon [8]. In both figures the peak particle temperatures are stable despite the laser fluence rise and the mean \( T_{\text{max}} \) values were found to be 2852 and 2770 K correspondingly, which are lower than bulk iron boiling temperature—3110 K [19]. In our past study [7], with the same experimental setup, pure iron nanoparticles were heated by laser pulse up to 2200–2600 K depending on particle size, bath gas type and pressure. In [7] the independence of the peak particle temperatures on laser fluence was explained as evaporation of iron nanoparticles which can take place at the temperatures below the boiling point of bulk material. The same situation was observed in present experiments. The absence of maximum temperature dependence on laser fluence means that some phase transition with heat absorption occurs.

6.5. LII particle sizing
In figures 13 and 14 the results of LII CEINs sizing in pyrolysis of the mixtures of 0.25%C6H6 + 0.25%Fe(CO)5 in Ar and 0.5%C2H2 + 0.25%Fe(CO)5 in Ar are presented in dependence on laser fluence used for particle heating. All experimental points in these graphs are related to CEINs synthesized at close temperatures, therefore one can assume that distinctions in size and structure among formed particles were insignificant.

TEM results are shown as horizontal dashed lines. In figure 13 one can see a sharp increase of particle size up to 22 nm in the range of laser fluence of 70–150 mJ/cm². At fluences 250–800 mJ/cm² the particle sizes gradually decrease from 22 down to 7–10 nm. The values of particle sizes measured at high fluences (> 500 mJ/cm²) are in good agreement with TEM
Figure 11. The peak particle temperatures of laser heated CEINs formed at the temperatures of 1889–1995 K in 0.25%C$_6$H$_6$ + 0.25%Fe(CO)$_5$ mixture in Ar in dependence on laser fluence.

Figure 12. The peak particle temperatures of laser heated CEINs formed at the temperatures of 2000–2100 K in 0.5%C$_2$H$_2$ + 0.25%Fe(CO)$_5$ mixture in Ar in dependence on laser fluence.

particle sizing. At laser fluence range 70–500 mJ/cm$^2$ the particle sizes measured by LII show the higher values than TEM results.

The dependence presented in figure 14 for CEINs formed in the mixture with acetylene shows the same trend. This behavior of particle sizes also correlates with the data presented in [20] for LII sizing of CEINs synthesized at room temperature. In figure 14 the particle sizes sharply increase from 25 up to 42 nm at the laser fluence range 70–150 mJ/cm$^2$ and gradually decrease down to 10 nm at fluence rise from 250 to 700 mJ/cm$^2$. For all range of fluences the mean
Figure 13. The mean CEINs sizes measured by LII in 0.25%C₆H₆ + 0.25%Fe(CO)₅ mixture in Ar in dependence on laser fluence. The particle formation temperatures are in the range of 1924–1995 K. The horizontal lines are the results of TEM particle sizing at the temperatures of 1941 and 1995 K.

Figure 14. The mean CEINs sizes measured by LII in 0.5%C₂H₂ + 0.25%Fe(CO)₅ mixture in Ar in dependence on laser fluence. The particle formation temperatures are in the range of 2005–2082 K. The horizontal line is the result of TEM particle sizing at the temperature of 2005 K.

LII-sizes of particles formed in the mixture with acetylene were found to be essentially higher than TEM sizing results. The possible reasons of this behavior of LII size dependence on laser fluence will be given below in discussion section.
7. Extinction measurements

7.1. Extinction setup
To measure the volume fraction of the forming condensed particles the laser light extinction technique was applied. For this purpose, the beam of a conventional 20 mW He-Ne laser (632.8 nm) was passed through two quartz windows of the shock tube (see figure 1) and focused on an active photo-detector PDA10A-ES (THORLABS) with rise time of 10 ns. The detector was optically blocked by an interference filter of $\lambda = 632.8\text{ nm}$ (FWHM 1 nm) to suppress the thermal radiation of the reacting gas-particle mixture. The signal from the detector was recorded on a Tektronix TDS 2014B digital scope with 100 MHz band pass width. The coaxial adjustment of the Nd:YAG and He-Ne laser beams allowed to observe the extinction of heated particles in a moment of Nd:YAG laser pulse.

7.2. Extinction theory
The volume fraction of condensed nanoparticles $f_V$ is determined using Lambert–Beer law:

$$f_V = \ln\left(\frac{I}{I_0}\right)\frac{\lambda}{6\pi E(m)\lambda l}.$$  \hspace{1cm} (2)

In equation (2), $I_0$ and $I$ are the incoming and transmitted laser light intensities respectively, $l$ is the optical path length, $\lambda$ is the diagnostic wavelength, $E(m)\lambda$ is the refractive index function of particle material at the diagnostic wavelength. The value of $E(m)\lambda$ for $f_V$ evaluation was chosen as 0.1 for carbon and iron nanoparticles with sizes less than 10 nm using recommendation [8].

7.3. Extinction measurements results
In figure 15 the typical time dependence of volume fraction of condensed phase in the pyrolysis of the mixture of $0.5\%C_2H_2 + 0.25\%\text{Fe(CO)}_5$ in Ar is presented. At the moment of incident shock wave arrival the volume fraction starts to increase due to fast iron cluster formation [21]. After compression of the gas-particle mixture behind the reflected shock wave the volume fraction of condensed phase increases twice, and starts to grow further, presumably due to carbon shell formation from decomposed hydrocarbons on the iron nanoparticle surface. The delay of LII laser pulse after RSW arrival in the measurement plane was fixed as 700 $\mu$s in all experiments. By this time the particles volume fraction has grown approximately to their final value at investigated ranges of $T_5$ and $P_5$. One can assume that the particle sizes by this time were also close to their final values. Thus, the particle sizes measured by LII and TEM techniques presumably should be the same. The sharp drop of particle volume fraction at the moment of laser pulse, which is clearly seen in figure 15, probably reflects the particle evaporation process at high laser fluence (in this case—380 mJ/cm$^2$). After some delay (about 70 $\mu$s) the volume fraction again grows up due to diffusion of the new portions of gas-particle mixture into the measurement volume. Note that the absolute value of volume fraction measured by laser extinction (equation (2)) can be influenced by the change of particle optical properties ($E(m)\lambda$). However, in [22] the change of iron nanoparticle optical properties was found only at the temperature range 1000–1900 K, that is lower than in the present study (1900–2100 K). Therefore in conditions of present experiments this influence can be neglected.

From the particle volume fraction profile of figure 15 it is clear that the laser extinction measurements can be used not only for observation of CEINs formation, but to study the nanoparticle evaporation process. For this goal the ratio of the reduced value of particle volume fraction after the laser pulse to the maximum value of volume fraction before laser pulse $\Delta f_V/f_{V\text{max}}$ depending on laser fluence has been calculated and presented in figures 16 and 17. One can see that the decrease of the volume fraction of the condensed phase strongly depends on the laser fluence. Up to the laser fluence of 100 mJ/cm$^2$ no noticeable decrease of
Figure 15. The time profile of particles volume fraction in pyrolysis of $0.25\%\text{Fe(CO)}_5 + 0.5\%\text{C}_2\text{H}_2$ diluted with Ar. The pyrolysis temperature is 2043 K, the LII laser fluence is 380 mJ/cm$^2$.

Figure 16. The evaporated part of volume fraction of condensed phase of the particles formed in pyrolysis of $0.25\%\text{C}_6\text{H}_6 + 0.25\%\text{Fe(CO)}_5$ mixture in Ar in dependence on laser fluence. The CEINs formation temperatures are in the range of 1924–1995 K.

$f_V$ was detected. This value of laser fluence was supposed to be an evaporation threshold under investigated conditions. Towards the higher values of laser fluence, the greater part of the CEINs was evaporated. It is notable that the absolute value of evaporated part of volume fraction in acetylene mixtures is higher than in benzene, at laser fluences > 700 mJ/cm$^2$ it exceeds 0.9.
**Figure 17.** The evaporated part of volume fraction of condensed phase of the particles formed in pyrolysis of $0.5\%$C$_2$H$_2 + 0.25\%$Fe(CO)$_5$ mixture in Ar in dependence on laser fluence. The CEINs formation temperatures are in the range of 2005–2082 K.

8. Discussion

Analyzing the micro-diffraction patterns with interplanar distances, and extracted interplanar distances from TEM micrographs, as well as the results of EDX measurements, one can conclude that the particles mainly consist of $\gamma$-Fe. The amount of iron oxides (Fe$_2$O$_3$, Fe$_3$O$_4$) in the particles synthesized in both mixtures is small (see EDX spectra in figures 7 and 8 and low contrast distribution of oxygen in figures 9 and 10). It is likely that iron oxides were formed despite the carbon shielding when the samples were kept in the air waiting for TEM measurements (several days). The amount of carbides in nanoparticles can be neglected because the map of chemical elements distribution did not show any presence of carbon inside the nanoparticles (see figures 9 and 10). In the map of chemical elements the carbon atoms are situated uniformly over the nanoparticles aggregates, which can reflect the existence of carbon shells of nanoparticles. One can compare the carbon maps with the iron ones, which clearly show that iron atoms are situated exactly where the nanoparticles are.

The stable value of peak particle temperatures measured at different laser fluences (see figures 11 and 12) testify that the particle evaporation process really took place. It is important to note that the values of measured evaporation temperatures of 2852 and 2770 K are lower than sublimation temperature of bulk carbon (over 3900 K), and boiling temperature of bulk iron (around 3110 K). Therefore, in the LII model used to analyze present experimental data, neither carbon shell, nor iron core evaporation processes were taken into account. This means that in the considered model the main cooling process of nanoparticles after laser heating is the free molecular heat-transfer with surrounding gas molecules, which mostly are argon atoms. As a result of evaporation under the influence of LII laser pulse, the particle sizes extracted from LII measurements have to be lower than the real particle sizes before LII laser pulse. The extinction measurements of laser heated nanoparticles allowed to evaluate the evaporated part of condensed particles volume fraction (see figures 15-17). Thus, using the data presented in figures 16 and 17, it is possible to reconstruct the initial particle size before the evaporation assuming mono-dispersed spherical particles. The maximum drop of volume fraction of 75%
Figure 18. The mean particle sizes measured by LII in 0.25%C₆H₆ + 0.25%Fe(CO)₅ mixture in Ar in dependence on laser fluence. The particle formation temperatures are in the range 1924–1995 K. The horizontal lines are the results of TEM particle sizing at the temperatures of 1941 and 1995 K. Markers: 1—data from figure 13; 2—corrected mean particle sizes taking into account evaporation process.

observed in pyrolysis of the benzene mixture corresponds to 37.5% decrease of particle size. The maximum decrease of volume fraction of 93% observed in the mixture with C₂H₂ corresponds to 59% decrease of particle size. The results of recalculated nanoparticle sizes with accounted evaporation are presented in figures 18 and 19. In figure 18 the corrected mean particle sizes in the mixture of 0.25%C₆H₆ + 0.25%Fe(CO)₅ in Ar in dependence on laser fluence are shown in comparison with the data from figure 13. It is seen, that the correction resulted in considerable increase of LII particle sizes at high laser fluences, while at lower fluences around 100 mJ/cm² no noticeable correction of sizes was observed. The same results were obtained for the LII particle sizes in the mixture 0.5%C₂H₂ + 0.25%Fe(CO)₅. In figure 19 the corrected sizes of nanoparticles formed in the mixture with acetylene are presented in comparison with the data from figure 14. For both mixtures the corrected sizes measured at high laser fluences lifted up to the values measured at low fluences without evaporation. Thus, the reconstruction of the particle mass loss at high laser fluences > 200 mJ/cm² using volume fraction measurements resulted in satisfactory agreement with sizes obtained at low laser fluences, where the evaporation was not observed. However in both mixtures the LII sizing resulted in much higher values of particle sizes than the sizes of primary particles, observed by TEM. Moreover, in both figure 18 and figure 19 one can see the non-monotonous behavior of nanoparticle sizes in dependence on laser fluence. As it was pointed out above for figures 13 and 14, the particle sizes sharply increase at the laser fluence up to 50 mJ/cm² and gradually decrease at the fluences higher than 250 mJ/cm².

One of the possible explanations of this behavior is the aggregation of primary particles, which is clearly seen in TEM images presented in figures 2 and 3. Note, that in the LII model the particle aggregation was not taken into account, neglecting the contacts (or assuming only point contacts) between the particles. In the mixture with benzene the initial iron nanoparticles formed behind incident shock waves were then covered with carbon shell behind reflected shock waves (see figure 2). As a result, the point contacts between iron particles transformed to
Figure 19. The mean particle size measured by LII in 0.5%C$_2$H$_2$ + 0.25%Fe(CO)$_5$ mixture in Ar in dependence on laser fluence. The particle formation temperatures are in the range 2005–2082 K. The horizontal line is the result of TEM particle sizing at the temperature of 2005 K. Markers: 1—data from figure 14; 2—corrected mean particle sizes taking into account evaporation process.

The second peculiarity of LII sizing results is their non-monotonous dependence on laser fluence. If to try to link this effect also with particles aggregation, it is necessary to assume that extent of aggregation depends on the laser fluence value, and respectively, intensity of particle evaporation. It is possible to assume that on the initial stages of iron vapor emergence under a carbon shell it causes the deformation and more dense aggregation of these shells, and at large intensity of evaporation the process of aggregates fragmentation begins. Thus, the aggregates fragmentation may lead to decrease of the LII sizing results (see figures 18 and 19). Anyway, these observations mean that the particle aggregation must be taken into account at LII sizing of CEINs to avoid overestimation of the particle size. Besides that, the source of additional inaccuracy of LII sizing in these conditions could be the unknown parameters of aggregates size distribution, in particular the standard deviation and non-spherical shape of aggregates. And, finally, to avoid the errors and inaccuracy of the LII particle sizing of core-shelled particles caused by the uncertainty of evaporation process these measurements are recommended to perform at low laser fluences, below the evaporation threshold.
9. Conclusions

The carbon-encapsulated iron nanoparticles (CEINs) with the mean sizes of 3.5 and 10.3 nm were synthesized by two step pyrolysis of iron pentacarbonyl with benzene and acetylene mixtures diluted with argon, respectively. The synthesized particles were analyzed by TEM, MD, EDX, HAADF STEM to understand their structure, size, and composition. The primary nanoparticles formed in the mixture of $0.25\% \text{C}_6\text{H}_6 + 0.25\% \text{Fe(CO)}_5$ in Ar constructed the aggregates of iron cores covered by 6–8 carbon layers 9–13 nm in size. The nanoparticles formed in the pyrolysis of the mixture of $0.5\% \text{C}_2\text{H}_2 + 0.25\% \text{Fe(CO)}_5$ in Ar represent the primary particles (3–5 nm in size) formed the solid aggregates with sizes of 20–40 nm. The LII diagnostics was for the first time applied to CEINs consisted of massive iron core and multilayer carbon shell. The LII model was updated assuming that the main thermophysical properties of such particles are close to iron, and conductive heat exchange is determined by properties of outer carbon shell. Using laser extinction measurements, it was found that strong particle evaporation process under the fluence of LII laser pulse takes place, starting from fluence about 100 mJ/cm$^2$ and reaching 90% decrease of CEINs volume fraction at fluence of 800 mJ/cm$^2$. The particle evaporation temperature (2770–2850 K) measured by two color pyrometry was found to be less than boiling point of iron (3100 K) and carbon sublimation temperature (over 3900 K). The results of LII particle sizing were shown to be laser fluence dependent and were corrected using measured particle volume fraction loss during evaporation. Nevertheless, it turned out that the results of LII particle sizing essentially exceeded the data of TEM sizing of primary particles. This difference was regarded to the strong particles aggregation and corresponding decrease of particle surface area responsible for particle cooling by surrounding gas. And it is likely that the degree of aggregation was dependent on laser fluence. Anyway, it is notable that the mean sizes measured by LII were comparable with the sizes of nanoparticle aggregates observed by TEM.

Thus, particle aggregation of CEINs has a crucial influence on LII sizing results and must be taken into account in LII measurements. Besides that the LII measurements of core-shelled particles are recommended at low laser fluences to avoid uncertainties due to evaporation at high laser fluences.

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