Effect of iron pentacarbonyl additives on the nucleation of soot particles during the pyrolysis of ethylene in shock waves

P A Vlasov¹,², V N Smirnov¹, A M Tereza¹, A A Cherepanov², A E Sychev³, A S Shchukin¹, A A Garmash², A N Streletskii¹ and A B Borunova¹

¹ Semenov Institute of Chemical Physics of the Russian Academy of Sciences, Kosygina 4, Moscow 119991, Russia
² National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe Shosse 31, Moscow 115409, Russia
³ Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences, Academician Osipyan 8, Chernogolovka, Moscow Region 142432, Russia

E-mail: iz@chph.ras.ru

Abstract. An experimental-computational study of the formation of pure iron nanoparticles, carbon nanoparticles (soot), and combined nanoparticles composed of an iron core coated with a carbon shell during the pyrolysis of iron pentacarbonyl–argon, ethylene–argon, and iron pentacarbonyl–ethylene–argon mixtures, respectively, behind reflected shock waves is carried out. The shape and size distribution of these nanoparticles are examined on a Zeiss Ultra plus ultrahigh-resolution field-emission scanning electron microscope. Detailed kinetic simulations of the formation of the three types particles are performed, which predict the concentration, average size, and size distribution of such particles.

1. Introduction
Metallic nanoparticles encapsulated in a carbon shell (metal–carbon nanocomposites) are of considerable interest because of their potential applications in technology and medicine [1]. An inert carbon coating of particles makes it possible to use them as nontoxic and biocompatible delivery agents in diagnosis and therapy [2]. A number of studies have revealed a high catalytic activity of metal–carbon nanocomposites [3] and the ability of porous graphite containing encapsulated iron particles to scatter and absorb microwaves [4–6].

There are several publications on various methods of synthesis of carbon-coated transition metal nanoparticles (arc method, decomposition of carbonyls, self-propagating high-temperature synthesis (SHS), detonation method, method of photolytic synthesis etc) [7–15]. Metal nanoparticles composed of nickel and iron are often used as catalysts for carbon nanotube growth [16, 17]. The phase state of catalytic metal nanoparticles (solid or liquid) synthesized in hydrocarbon media is of fundamental importance for understanding the mechanism of the growth of carbon nanotubes, and for clarifying the mechanism of the formation of a carbon coating on nanoparticles. It should be emphasized, however, that the structural and phase state of nanoobjects with a metal core–carbon shell structure has been insufficiently studied,
given the variety of synthesis methods, each of which produces its characteristic impact on the structure of such composites. A deeper understanding of the structural state of carbon-containing nanocomposites can be obtained by comprehensively studying these objects.

One disadvantage of the current methods for synthesis of carbon-encapsulated metal nanoparticles is that such particles are produced mainly in the form of agglomerates; therefore, the major objective in this field is to synthesize isolated carbon-coated nanoparticles.

The authors of [11] successfully synthesized iron nanoparticles encapsulated in a carbon shell by detonating a reaction mixture in a closed reactor. Electron microscopy measurements showed that the size of the resulting particles ranged from 15 to 50 nm and that the shell consisted of ordered graphite plates and amorphous carbonaceous material. Studies of the magnetic properties of the particles on a magnetometer showed that, at a temperature of \( \sim 300 \) K, they exhibit superparamagnetic properties.

In [12], nanoparticles composed of an iron core covered by carbon layers were produced by detonating mixtures of iron pentacarbonyl with various hydrocarbons. X-ray diffraction and electron microscopy showed that the particle core is composed of iron nanocrystals and that the shell thickness can be varied by changing the composition of the explosive mixture. It was also found that the magnetic properties of such particles are strongly dependent on the size of the composite particle core and that the iron-containing core has a bcc crystal lattice or may consist of iron carbide.

In [18], laser-induced incandescence (LII) optical methods was used to monitor the formation of particles in mixtures of iron pentacarbonyl and benzene in shock waves at temperatures of 1750–2600 K and pressures of 1–1.3 atm. In addition, the particles deposited on a substrate mounted at the end face of the shock tube were analyzed with a transmission electron microscope. Specially selected particles showed that they are composed of an iron core and a carbon shell. The main purpose of [18] was to determine the kinetics of the formation of particles behind reflected shock waves. However, the structure of the resulting particles and their size distribution function was not examined.

Synthesis of iron nanoparticles encapsulated in a carbon shell in shock waves enables to clearly separate stages of thermal decomposition of the volatile organometallic precursor followed by the rapid condensation of supersaturated vapor of metal atoms in the incident shock wave and the subsequent slower stage of pyrolysis of the hydrocarbon, followed by the condensation of hydrocarbon fragments on nanosized metal condensation nuclei [19].

The authors of [19] reported data on the two-step formation of iron nanoparticles encapsulated in a carbon shell. Behind the incident shock wave, iron pentacarbonyl decomposes rapidly to form iron particles, which are then coated by carbon-containing fragments from the pyrolysis of \( \text{C}_3\text{O}_2 \) behind the reflected shock wave. The temperature behind the incident wave ranged within 700–1500 K, whereas that behind the reflected wave, within 1500–3000 K. The iron–carbon binary particles produced in this way turned out to be considerably larger than those composed of pure carbon or pure iron, as was demonstrated in control experiments with iron pentacarbonyl–argon and argon \( \text{C}_3\text{O}_2 \)–argon mixtures. Viewing the resulting particles under a transmission electron microscope, the authors concluded that there are three kinds of particles: small-size iron particles completely coated with carbon, average-size particle with a nonspherical iron core partially coated with carbon, and large iron particles only partially coated with carbon. The authors speculated that large particles and nonspherical particles are formed on the surface of the shock tube end face after termination of the experiment, at temperatures much lower than those reached in the reflected shock wave.

The aim of the present work was to produce pure iron nanoparticles, carbon nanoparticles, and iron nanoparticles encapsulated in a carbon shell by shock-heating \( \text{Fe(CO)}_5 \)–\( \text{Ar} \), \( \text{C}_2\text{H}_4 \)–\( \text{Ar} \), and \( \text{Fe(CO)}_5 \)–\( \text{C}_2\text{H}_4 \)–\( \text{Ar} \) mixtures, respectively, and to determine the size and the size distribution of the resulting nanoparticles with an ultrahigh-resolution field-emission scanning
electron microscope. The basic idea of producing iron nanoparticles encapsulated in a carbon shell in shock waves is as follows. Already in the incident shock wave, at temperatures of 700–1000 K, iron pentacarbonyl molecules present in the initial mixture decompose quickly to form iron atoms and various fragments, such as $\text{Fe}_2\text{CO}$, $\text{Fe}(\text{CO})_2$, $\text{Fe}(\text{CO})_3$, and $\text{Fe}(\text{CO})_4$. In this case, the characteristic decay time of $\text{Fe}(\text{CO})_5$ at temperatures above 800 K is not more than a few microseconds. [20] The resulting fragments and iron atoms condense quickly enough to form clusters and pure iron nanoparticles [21]. By contrast, under these conditions, the decomposition of ethylene to hydrocarbon fragments and the subsequent formation of soot particles occur considerably slower [21]. In the reflected shock wave, wherein the temperature is almost twice that behind the incident wave (above 1650 K in our experiments), ethylene disintegration to hydrocarbon fragments proceeds much faster. Under these conditions, in the reaction mixture already containing clusters and iron nanoparticles, ethylene pyrolysis hydrocarbon fragments begin to condense on the surface of these particles [21]. As a result of these consecutive processes in the incident and the reflected shock wave, iron particles in the encapsulated in a carbon shell are formed.

2. Experimental

The experiments were carried out in a stainless steel shock tube with an internal diameter of 75 mm, driver section length of 1.5 m, and a driven section length of 3.2 m. Details of the experimental setup were described in detail in [22, 23]. The test mixtures were prepared manometrically and stored in opaque glass cylinders. The mixtures were prepared from reagent-grade ethylene, reagent-grade iron pentacarbonyl, and 99.998% pure argon (diluent gas). The driver gas was helium. To prepare iron–pentacarbonyl-containing mixtures, liquid $\text{Fe}(\text{CO})_5$ was frozen in a glass trap with liquid nitrogen. Then, the gas communications and the trap were evacuated with a forepump, after which the frozen $\text{Fe}(\text{CO})_5$ was thawed and evaporated. The first fraction of was pumped out, after which $\text{Fe}(\text{CO})_5$ was evaporated into a 10-L mixture storage vessel to the desired pressure of its vapor and diluted with argon so that the mixture pressure in the vessel be 600 Torr. Ultimately, in a dark glass bottle kept a pair of $\text{Fe}(\text{CO})_5$, diluted to the desired level of concentration of argon. Ethylene was used without additional purification. We prepared the following test mixtures:

- mixture 1—0.5%$\text{Fe}(\text{CO})_5$ + 5.0%$\text{C}_2\text{H}_4$ + argon;
- mixture 2—0.5%$\text{Fe}(\text{CO})_5$ in argon;
- mixture 3—5.0%$\text{C}_2\text{H}_4$ in argon.

The experiments were performed at temperatures of 1600 to 2300 K. The pressure behind the reflected wave ranged from 3.0 to 5.5 atm.

Analysis of condensed nanoparticles on a scanning electron microscope (SEM) requires a substrate that would provide the best visualization. Since a priori it is unknown what kinds of surface would provide best physical (and possibly chemical) adsorption of the test particles, we studied particles adsorbed on different substrates, such as quartz, carbon, the surface of a razor blade, and 0.1 mm thick aluminum and copper foils. The surface of the substrates to be tested was carefully cleaned with acetone and purged with a high-pressure argon jet. As a result, it was found 0.1 mm and 0.2 mm thick copper foils are most convenient for obtaining good-quality SEM images. The substrates were attached to the end face of the shock tube by means of clamps which allowed the substrate to be moved over the end face surface.

The size and size distribution of iron nanoparticles, carbon nanoparticles (soot), and iron nanoparticles encapsulated in a carbon shell formed behind the reflected shock wave were examined on a Zeiss Ultra Plus ultrahigh-resolution field-emission scanning electron microscope. The resolution of the microscope reached 1 nm at an accelerating voltage of 15 kV, it could
analyze all elements of from boron (atomic number 5) to plutonium (atomic number 94). A typical SEM images obtained are displayed in figures 1–3.

3. Results and discussion

Since the main purpose of the present work was to explore the possibility of producing iron nanoparticles encapsulated in a carbon shell formed by hydrocarbon pyrolysis, we analyzed the size and shape distribution of iron nanoparticles, carbon nanoparticles (soot), and binary particles composed of an iron core coated with a carbon shell. The use of SEM images taken at the maximum magnification was motivated by the need to obtain well-resolved pictures of the particles and to ensure the possibility of analyzing the particle size distribution. An analysis of images obtained at the highest resolution revealed the presence of extremely small nanoparticles, with sizes close to the detection limit of the scanning electron microscope. This is due to the fact that, with increasing electromagnetic field intensity of the scanning electron microscope, very small nanoparticles begin to move. Such movements of nanoparticles make it impossible to unequivocally determine their size and shape. For example, figure 1 shows that the carbon nanoparticles have a rounded, nearly spherical shape, but not quite clear contour.

Nevertheless, the image is quite suitable for analyzing the particle size distribution, which was carried out using the MicrAN26_INEP software code developed by I O Leipunskii (Institute of Energy Problems of Chemical Physics RAS). The images were processed on the assumption that the particles are spherical. The program is preset to process samples containing no less than 1000 particles; in fact, micrographs featured a fewer number of particles, a factor that worsened the quality of the resultant histograms. However, a higher resolution also somewhat worsened the quality of the histograms. Figures 1–3 display microphotographs and the corresponding histograms of nanoparticles of all three types, namely, iron, carbon, and carbon-coated iron particles, respectively.

As one can see in figure 1, the maximum of the size distribution of carbon particles (soot) particle is located within 18–20 nm. Although particles with sizes from 5 nm to 40 nm are observed, the characteristic half-width of the particle size distribution function is 10–11 nm.

Figure 2 shows an electron micrograph of iron nanoparticles formed during the decomposition of an iron pentacarbonyl–argon mixture and the corresponding particle size distribution histogram. It can be seen that the size of the iron particles ranges from 20 to 90 nm, with the distribution peaking at 40 nm. The half-width of the distribution is 30 nm. As one can
Figure 2. SEM micrograph of carbon nanoparticles formed in the pyrolysis of 0.005Fe(CO)$_5$–Ar mixture behind a reflected shock wave at $T_{50} = 1807$ K and $p_{50} = 4.40$ atm and deposited on a substrate fixed on the end face of the shock tube and the particle size distribution histogram obtained by processing the image.

Figure 3. SEM micrograph of carbon nanoparticles formed in the pyrolysis of 0.005Fe(CO)$_5$ + 0.05C$_2$H$_4$–Ar mixture behind a reflected shock wave at $T_{50} = 1651$ K and $p_{50} = 3.17$ atm and deposited on a substrate fixed on the end face of the shock tube and the particle size distribution histogram obtained by processing the image.

see, iron particles align forming filamentary structures, which assembled larger particles with smaller iron particles being situated at the periphery. Large iron particles probably consist of smaller particles, which, however, are not visible at the given magnification. This is due to the aforementioned blurring of the boundaries of visible particles at a high strength of the electron-accelerating field, which is required to achieve a high magnification of the SEM image. A lower magnification does not make it possible to determine the particle size distribution by means of the MicrAN26,INEP program. A filamentous arrangement of iron nanoparticles may be indicative of their magnetic properties. Figure 2 also shows the results of analysis of a selected iron nanoparticle obtained by using special functions of the scanning electron microscope. In particular, such functions enable to determine the size of an individual particle.

As can be seen, the nanoparticle size distributions displayed in figures 1 and 2, are almost symmetrical with respect to the maximum. By contrast, the size distribution of carbon-coated iron nanoparticles is markedly different (see figure 3).

Figure 3 shows a SEM micrograph of carbon-encapsulated iron nanoparticles and the corresponding particle size distribution histogram. It can be seen that the particle size ranges
within 5–36 nm. The particle size distribution peaks at 12 nm, with the halfwidth being 11 nm. Accordingly, the average size of the nanoparticles is 15 nm, while the number of small particles is considerably higher than that of larger particles. The histogram in figure 3 is very similar to that given in [24], despite the fact that the nanoparticles were prepared under drastically different conditions, at a different experimental facility, and even for a different phase state of the material.

Figure 3 demonstrates the presence of a large ensemble of particles with sizes from 25 to 50 nm and an ensemble of smaller particles with sizes from 5 to 10 nm. Thus, two ensembles of particles are formed. This suggests that, under our experimental conditions, carbon-encapsulated iron nanoparticles can be formed through two different pathways. It is assumed that large particles are formed via the coagulation of smaller particles, a process that begins behind the incident shock wave. The probability of such coagulation is low, but it exists, leading to the formation of a small number of large particles, which, along with numerous small particles, begin to be covered by carbon-containing fragments formed by the pyrolysis of ethylene behind the reflected shock wave. The resolution of the SEM we used was too low to detect the iron core completely covered by carbon layers. Note, however, that, under similar experimental conditions, carbon-encapsulated iron nanoparticles were observed in a number of works, see e.g., [18, 19].

A comparison of our results with those from [19] shows that they are mostly similar, in particular what concerns the existence of two ensembles of particle, large and small, although the hydrocarbons used to produce the carbon coating were essentially different.

4. Conclusions
The above results led us to the following conclusions on the possibility of purposefully producing iron carbon-encapsulated iron particles in shock waves. That the processes of condensation of iron atoms into nanoparticles during the decomposition of iron pentacarbonyl in the incident shock wave and of their coating with carbon fragments formed by the pyrolysis of a hydrocarbon in the reflected wave are separated makes it possible to prepare nanoparticles of preset size, structure, and shape. This can be accomplished by varying the initial concentrations of the starting components, their ratios, and initial temperature and pressure behind the shock waves. Since at temperatures above 1500 K, different hydrocarbons are pyrolyzed at different rates, the use of various hydrocarbons as a source of carbon-containing fragments also makes it possible to change the pattern of formation of the carbon coating on the surface of iron particles. A further research in this area requires a comprehensive approach involving various techniques.

Acknowledgments
This work was supported by program of the Presidium of the Russian Academy of Sciences No. 31P “Basic research of combustion and explosion”.

References
[1] Herrmann I K, Grass R N and Stark W J 2009 Nanomedicine 4 787–98
[2] Xu Y et al 2008 Nanotechnology 19 435102
[3] Ermakov A E, Uimin M A, Lokteva E S, Mysik A A, Kachevskii S A, Turakulova A O, Gaviko V S and Lunin V V 2009 Russ. J. Phys. Chem. A 83 1187–93
[4] Liu Q, Cao B, Feng C, Zhang W, Zhu S and Zhang D 2012 Compos. Sci. Technol. 72 1632–6
[5] Tyagi S, Verma P, Baskey H B, Agarwala R C, Agarwala V and Shami T C 2012 Ceram. Int. 38 4561–71
[6] Zhao D L, Li X and Shen Z M 2009 J. Alloys Compd. 471 457–60
[7] Tsurin V A, Yermakov A Ye, Uimin M A, Mysik A A, Shchegoleva N N, Gaviko V S and Maikov V V 2014 Phys. Solid State 56 287–301
[8] Tokoro H, Fujii S, Muto S and Nasu S 2006 J. Appl. Phys. 99 08Q512
[9] Bystrzejewski M, Pyrzyńska K, Huczko A and Lange H 2009 Carbon 47 1201–4
[10] David B, Pizdívová N, Schneeweiß O, Bezdička P, Morjan I and Alexandrescu R 2004 J. Alloys Compd. 378 112–6
[11] Ning L, Xiaojie L, Xiaohong W, Honghao Y, Fei M and Wei S 2009 *Compos. Sci. Technol.* **69** 2554–8
[12] Luo N, Li X, Wang X, Yan H, Zhang C and Wang H 2010 *Carbon* **48** 3858–63
[13] Fan N, Ma X, Ju Z and Li J 2008 *Mater. Res. Bull.* **43** 1549–54
[14] Atkinson J D, Fortunato M E, Dastgheib S A, Rostam-Abadi M, Rood M J and Suslick K S 2011 *Carbon* **49** 587–98
[15] Gurentsov E V and Eremin A V 2015 *Tech. Phys. Lett.* **41** 547–50
[16] He Z, Maurice J L, Gohier A, Lee C S, Pribat D and Cojocaru C S 2011 *Chem. Mater.* **23** 5379–87
[17] Lee K, Kim M and Kim H 2010 *J. Mater. Chem.* **20** 3791–8
[18] Starke R, Kock B and Roth P 2003 *Shock Waves* **12** 351–60
[19] Gurentsov E V, Eremin A V, Roth P and Starke R 2005 *Kinet. Catal.* **46** 309–18
[20] Smirnov V N 2008 Thermal dissociation of the gas-phase hydrides and organometallic compounds and the reactions of their decomposition products *D.Sc. thesis* (Moscow: Semenov Institute of Chemical Physics)
[21] Agafonov G L, Smirnov V N and Vlasov P A 2012 *Combust. Sci. Technol.* **184** 1838–61
[22] Agafonov G L, Smirnov V N and Vlasov P A 2010 *Combust. Sci. Technol.* **182** 1645–71
[23] Agafonov G L, Smirnov V N and Vlasov P A 2011 *Proc. Combust. Inst.* **33** 625–32
[24] Zhao M and Song H 2010 *Mater. Chem. Phys.* **124** 861–4