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To cite this article: M L Kuskov *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **558** 012021

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Synthesis of nanopowders of Fe-C system via Flow-Levitation method and study of their properties

M L Kuskov¹, A N Zhigach¹, I O Leipunsky¹, E S Afanasenkova¹, O A Safronova¹, N G Berezkina¹, V V Artemov^{1,2}, O M Zhigalina^{2,3}, D N Khmelenin²

¹ V L Talrose Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences, 38, Bld. 2, Leninsky prospect, Moscow, 119334, Russian Federation

² Federal Scientific Research Centre "Crystallography and Photonics", Russian Academy of Sciences, 59, Leninsky prospect, Moscow, 119333, Russian Federation

³ Bauman Moscow State Technical University, ul. Baumanskaya 2-ya, 5/1, Moscow, 105005, Russian Federation

E-mail: mkuskov72@yandex.ru

Abstract. Nanopowders of Fe-C system are synthesized via modified Guen-Miller Flow-Levitation method by *in situ* reaction of nascent iron nanoparticles with acetylene. Morphology, internal structure, chemical and phase composition are studied by electron microscopy methods, including electron diffraction and element analysis, X-ray phase analysis and CNHS chemical analysis. It is shown that depending on the parameters of the reaction with acetylene (temperature, concentration), particles composition can vary from pure iron with thin carbon coating complex composition consisting predominantly of iron carbide.

1. Introduction.

Nanoparticles with iron-containing core and carbon-containing shell are used widely in biomedical research [1,2], in electrochemical technologies [3], as catalysts for olefin synthesis [4], and as a component of radio-frequency absorbing materials [5]. Plasma chemical methods [6], shock waves pyrolysis of iron carbonyl $\text{Fe}(\text{CO})_5$ [7], mechanochemical synthesis [8], hydrothermal carbonization of iron chloride FeCl_2 [9], and evaporation-condensation Flow-Levitation method where nascent particles react with butane or methane [10,11], are successfully used for synthesis of nanoparticles of Fe-C system.

In the present work synthesis of nanoparticles of Fe-C system via Flow-levitation method, using argon as carrier gas and acetylene as reactant, is described. The aim of this work is to study the influence of acetylene/iron nanoparticles reaction parameters on morphology, structure, element and phase composition of the resulting nanoparticles of Fe-C system.

2. Experimental.

Samples of Fe-C system nanoparticles were synthesized using the modified Guen-Miller Flow-Levitation equipment described in [12,13]. The scheme of the method and operating reactor are presented in Figure 1.

Iron drop is suspended and heated up to the temperature higher than melting point in high-frequency electromagnetic field (440 kHz) of counter-current inductor inside the quartz tube (14-15



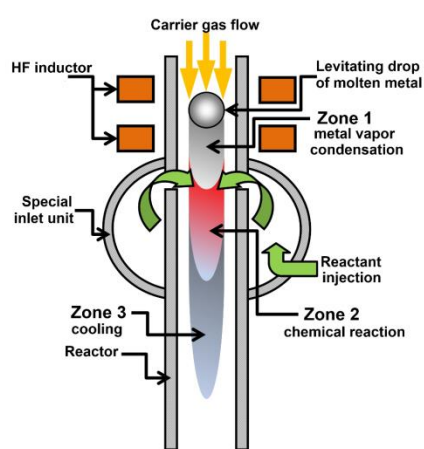
mm inner diameter). The drop evaporates in argon flow blown over it downstream. Iron vapor condenses homogeneously in argon flow thus forming nascent iron nanoparticles. Hot nascent Fe nanoparticles react with acetylene injected into argon flow below the drop. Parameters of reaction of acetylene with Fe nanoparticles are controlled by position of the injector with regard to the drop (determining the reaction temperature) and by acetylene flow rate (determining its concentration in Ar flow carrying nascent nanoparticles).

Iron loss due to evaporation is continuously replenished by Fe wire feeding at constant rate (5.9 g/h in this work).

Synthesized Fe-C nanoparticles are cooled down in the gas path of the equipment, then collected on a fabric filter and subsequently dropped into a special container. After the synthesis process completion, the particles are subjected to a passivation with atmospheric air using at least two cycles “slow inflow followed by pumping out”, for safety.



(a)



(b)

Figure 1. Synthesis of Fe-C system nanoparticles via Flow-Levitation method (a) and scheme of the method with nascent particles chemical treatment (b).

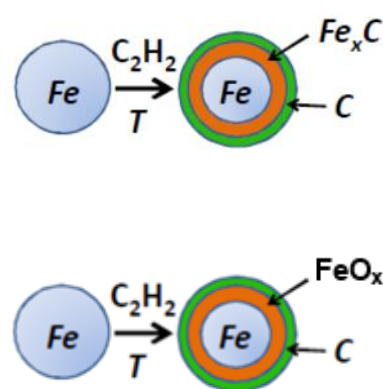


Figure 2. Schematic representation of chemical reactions in Fe + C₂H₂ system.

As a result of the chemical reaction



particles of complex internal structure are formed, containing metallic iron, iron-carbon compounds, elemental carbon, and passivating layer of iron oxide as a result of the reaction of iron in particles with atmospheric air (figure 2).

All experiments are fulfilled at argon pressure of 0,2 ata and the flow rate of 0.18 st. m³/h. To vary the conditions of chemical reaction between acetylene and nascent Fe nanoparticles, the point of acetylene injection was shifted within the range from the hotter zone at 8-10 mm below the drop (synthesis of Fe1) to the colder zone at approximately 30 mm (synthesis of Fe2, Fe3). Acetylene concentration in the reaction zone was varied by more than 2 orders of magnitude: from 5.5 to 0.02 vol. %.

The samples of Fe-C system nanoparticles are studied by scanning (SEM) and transmission (TEM) electron microscopy, including high-resolution microscopy (HRTEM) and scanning transmission electron microscopy (STEM) and electron diffraction analysis (EDA) (FEI Tecnai Osiris, LEO 912 AB OMEGA), energy-dispersive X-ray spectroscopy (EDX) with TEM mapping (JEOL JSM 7401F, FEI Quanta 200 3D FIB). X-Ray diffraction analysis (XRDA) (ADP-1), catalytic burning element CHNS-analysis (Euro Vector EA 3000).

Particle sizes are determined by direct measurements of their TEM images (at least 900 particles per a sample).

3. Results and discussion.

Synthesis parameters, particle sizes and crystalline phase composition of nanopowders of Fe-C system are presented in Table 1.

Table 1. Synthesis parameters and characteristics of nanopowders of Fe-C system.

Sample Fe-C	Acetylene flow rate (st.m ³ /h)	Mean <D> and mass-mean D _m particle sizes	Crystalline phases	
			XRDA	Electron diffraction
			Phase composition (w. %)	Phase
Fe1	1,0*10 ⁻²	<D> = 38 nm D _m = 84 nm	Fe ₃ C (Pnma) - 56.1 %, α-Fe (Im3m) - 16.4 %, Fe _{2.4} C (P63 2 2) - 27.5%	α-Fe, C Fe ₃ C, Fe ₂ C
Fe2	1,6*10 ⁻³	<D> = 38 nm D _m = 78 nm	Fe ₃ C (Pnma) - 55.6 % α-Fe (Im3m) - 44.4 %	α-Fe, C, Fe ₃ C FeO, Fe ₃ O ₄
Fe3	4*10 ⁻⁵	<D> = 45 nm D _m = 109 nm	α-Fe (Im3m) -100 %	α-Fe

Results of XRD analysis are shown in Figure 3.

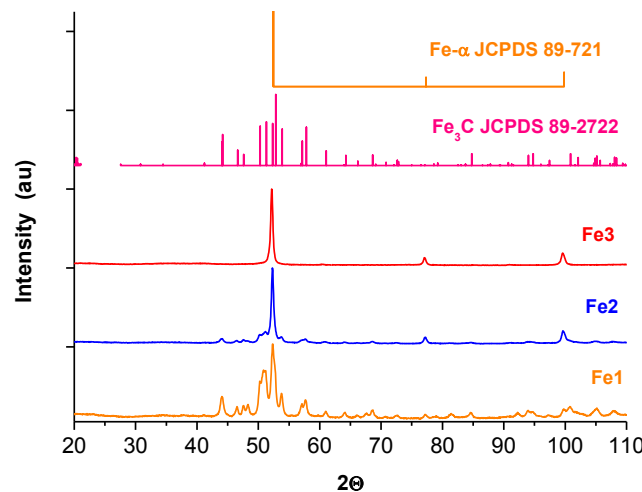


Figure 3. XRDA patterns of the Fe-C samples.

Depending on the synthesis conditions, nanoparticles contain crystalline iron, iron carbides of various compositions (total iron carbides content ranging from 0 to 83.6 w. %) and elemental carbon. The presence of iron oxides can be attributed to chemical reaction of air oxygen with metallic iron in the particles during the powder passivation.

Apparently, the synthesized particles possess a multi-layered core-shell structure. Particles of sample Fe3 shown in figure 4 exhibit spherical shapes and possess a visible core-shell structure. The particles size distribution is presented in figure 4 (c). Since the only crystalline phase revealed in the sample Fe3 by XRDA is metallic iron (Figure 3), it can be assumed safely, that clearly visible outer shells on the particles are amorphous. However, there are crystalline sections of shells revealed on the HR-TEM images due to lattice fringes resolution. The measured magnitude of the inter-planar spacing corresponds to the (111) plane of crystalline phase of Fe₃O₄ (figure 4 (d) and (e)).

Study of Fe3 sample by STEM-EDX method (figure 5) revealed at least triple-layer core-shell structure, where metallic iron core is coated with iron oxide layer 5-7 nm thick and outer elemental carbon shell 4-15 nm thick.

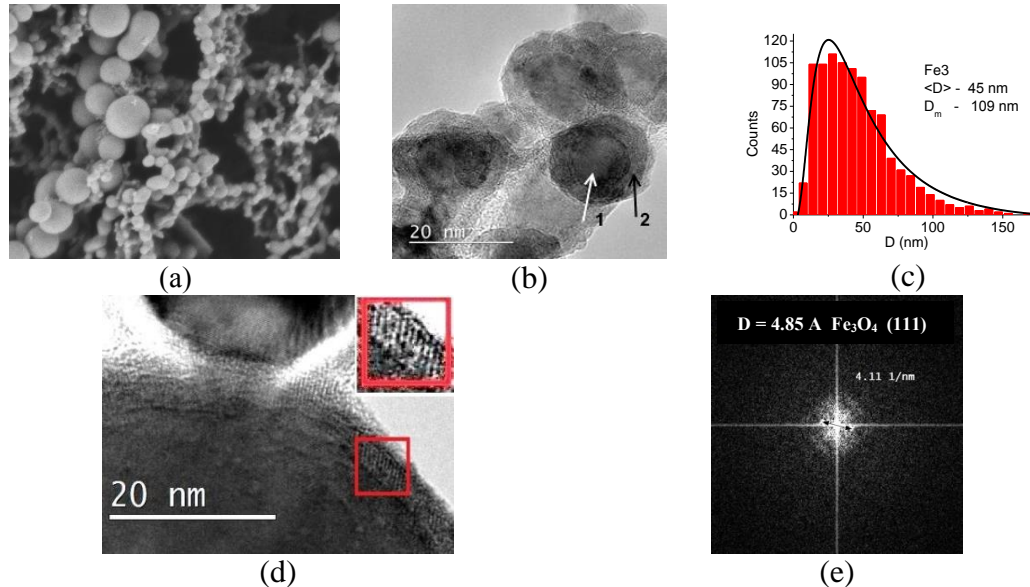


Figure 4. SEM image of sample Fe3 (a); HR-TEM image (b), where 1 is crystalline core, 2 is shell; particles size distribution histogram (c) where black curve is log-normal fit; HR-TEM image with crystalline section of the shell (d) where inset is the enlarged view of the selected area; Fast Fourier transform pattern of the selected area (e) where inter-planar spacing corresponds to Fe_3O_4 (111).

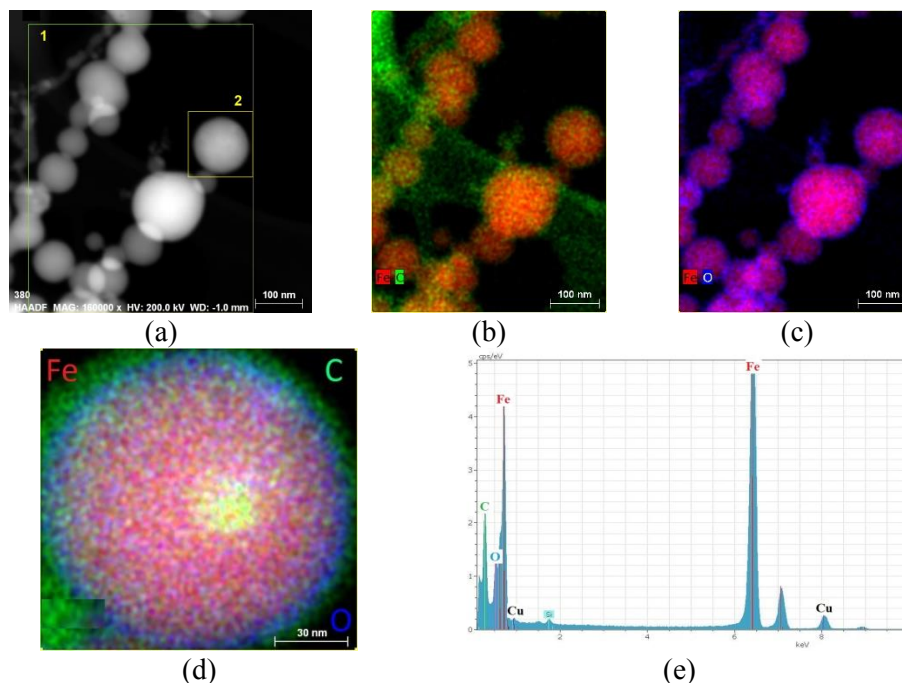


Figure 5. STEM image (a), Fe and C elements distribution map of the particles array within the frame 1 in STEM image (b); Fe and C elements distribution map of the same array (c); Fe, C and O elements distribution map of the particle enclosed within the frame 2 in STEM image (d); EDS spectrum of the particles array (e), where peak of Cu resulted from the copper TEM grid.

Electron diffraction analysis confirms the presence of metallic iron and iron oxides in sample Fe3 (Figure 6).

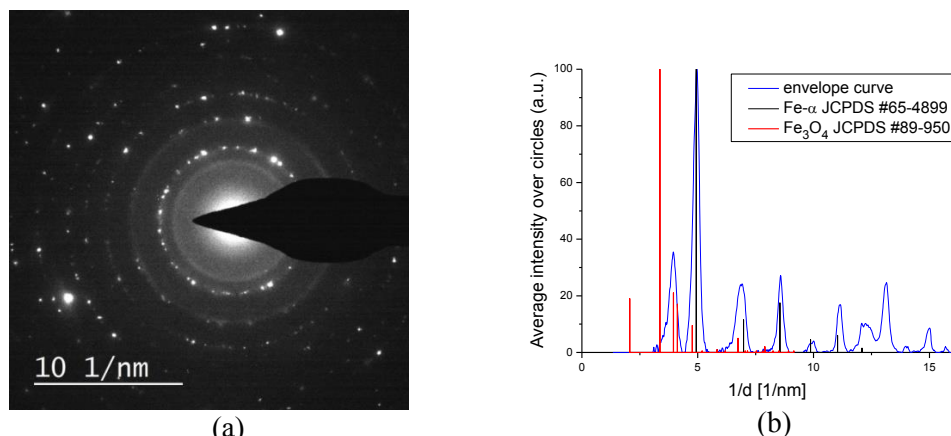


Figure 6. EDA pattern of sample Fe3 (a); EDA net pattern (b)

No differences in morphology of particles of all studied samples were found.

The total carbon content of in the samples Fe2 and Fe3 was obtained using CHNS-analysis method (catalytic sample oxidation in helium flow with oxygen addition).

Weigh content of total carbon in Fe3 sample is 0.4 w. % that corresponds to mean carbon shell thickness of 1.3 nm. Total carbon content in Fe2 sample is 6.7 w. %. Comparison of this value with XRDA data enables to conclude that 3.7 w. % corresponds to Fe_3C , while residual 3 w. % belongs to outer elemental carbon shell with calculated mean thickness of about 10 nm.

Conclusion.

Nanoparticles of Fe-C system with mean size of 38-45 nm are synthesized via Flow-Levitation method using the *in situ* reaction of nascent iron nanoparticles with acetylene. Depending on the acetylene flow rate value, the method enables to synthesize core-shell nanoparticles with high content of iron carbides (about 84 w. %) or iron-core particles ($\alpha\text{-Fe}$) without crystalline iron carbides. Nanoparticles of sample Fe3 have shell with the inner oxide layer of 3-5 nm thick and the outer carbon layer of 4-12 nm thick.

Acknowledgements.

The work was developed within the framework of the Program for Basic Research of the Russian State Academy of Sciences for 2013-2020 and supported by the Ministry of Sciences and Higher Education (agreement GZ №007-00269-18-00), and the Federal Agency for Scientific Organizations (agreement No. 007-GZ / Ch3363 / 26) in terms of electron microscopy

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