Study on the Structure and Morphology of Iron Nanopowders Obtained by the Method of Electric Explosion of Wires

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Abstract

This article presents the results of comprehensive study on the structure and morphology of iron nanopowders synthesized by electric explosive evaporation of metal wire. The results of scanning and transmission electron microscopy showed that nanoclusters have a spherical shape with an average diameter of 65 nm. It was revealed based on the analysis of the diffraction patterns that nanoparticles of nanopowders obtained in electric explosion have a crystal lattice with a parameter less than a standard cell. The results of computer experiments are in good agreement with the findings of X-ray analysis. However, the question about the reasons of distortion of the crystal lattice of nanoclusters remains controversial.

1. Introduction

Over the last decade, metal nanoclusters which are close to monodisperse metal particles are of great interest. Nanopowders (NPs) have unique properties related to their intermediate position between the bulk phase and individual atomic or molecular particles.

The iron nanoparticles have great potential for various applications, including their use as catalysts for formation of carbon nanofibers and nanotubes [1-3], contrast agents for magnetic resonance imaging [4], fillers of iron-nickel battery [5] and as adsorbents and catalysts for purification of exhaust gases [6]. Different sizes of iron nanoparticles are required depending on the application.

Numerous methods for production of nano-dispersed particles are classified according to the type of dispersant effects. Electric explosion of wire (EEW) is one of the methods for obtaining metal nanoparticles. The EEW is implemented with a pulse current which passes through the metal wire. The EEW method is environmentally friendly and produces nanoparticles with high performance on inexpensive equipment with a relatively low energy consumption.

The results of studies on the morphology and structure of nickel NPs obtained by EEW by scanning and transmission electron microscopy, X-ray analysis and computer experiments carried out in ChemBio3D program are presented in this work.

2. Experimental

Iron NPs were obtained at the Tomsk Polytechnic University (Russia) by the group of Professor A.P. Ilyin by electro-explosive evaporation of metal wire in argon atmosphere. The procedure and experimental details are described in detail in works [7, 8]. NPs were purchased from Tomsk Polytechnic University to be used as catalysts in the synthesis of carbon nanostructures [2, 3].

The structure and morphology of the samples were studied by scanning, transmission electron microscopy and X-ray analysis. The morphology of the samples was investigated by scanning electron microscopy at the Department of surface and technology of new materials at the Institute of Materials Science of the University of Siegen (Germany). The field emission scanning electron microscope with ultra-high resolution of model Gemini Ultra 55 of the company Zeiss, with a device for X-ray microanalysis of the company (Thermo Scientific) was used.

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Studies by transmission electron microscopy (TEM) were performed at the Institute of Nuclear Physics (Almaty, Kazakhstan) with transmission electron microscope JEM-2100 JEOL. NPs were suspended in ethanol with purity of 99.9% for preparation of the samples. Further sonication was carried out in the solution for 5 minutes, after which the droplets of suspension were deposited on a copper grid.

Investigation of the structure of electro-explosive Ni NPs was carried out using X-ray diffractometer Philips X'Pert PRO MRD at the University of Siegen (Germany) using copper radiation (λ(CuKα1) ~ 0.15405 nm). The spectral and angular monochromatization of probe beam was carried out using asymmetrical 4-crystal monochromator Ge (220). Processing of X-ray spectra to determine the angular position and intensity of the reflection was performed in program OriginPro 8.1. PCPDFWIN program with the base of diffractometric data PDF-2 was used for the phase analysis.

The computer experiments on minimization of energy at different temperatures to estimate changes of cell parameter in nanoclusters were conducted using program ChemBio3D Ultra.

3. Results and Discussion

3.1. SEM-studies

Figure 1 shows SEM image of iron NPs and the separated samples. NPs samples were suspended in hexane for separation. Further sonication of solution was carried out (volume of suspension 30 ml, frequency of ultrasound waves 27 kHz, the power of generator 120 W, exposure was carried out for 30 min) and then drops of suspension of metal particles were deposited on a silicon substrate.

SEM images of Fe powders show that agglomeration of metal particles with a smaller size (from 10 to 50 nm) around the clusters with the size from 100 to 200 nm is present. Thus, the formation of chain-like structures from small clusters (10 to 30 nm is observed. The shape of Fe particles is close to spherical. Figure 2b presents energy dispersive spectrum (EDX) of EEW Fe NP. The agglomerates of particles with a large diameter usually coagulated with smaller clusters. Hexane allows to separate the individual iron nanoclusters as shown in Figs. 1b and 1c. The diameter of the clusters ranges from 50 to 100 nm.

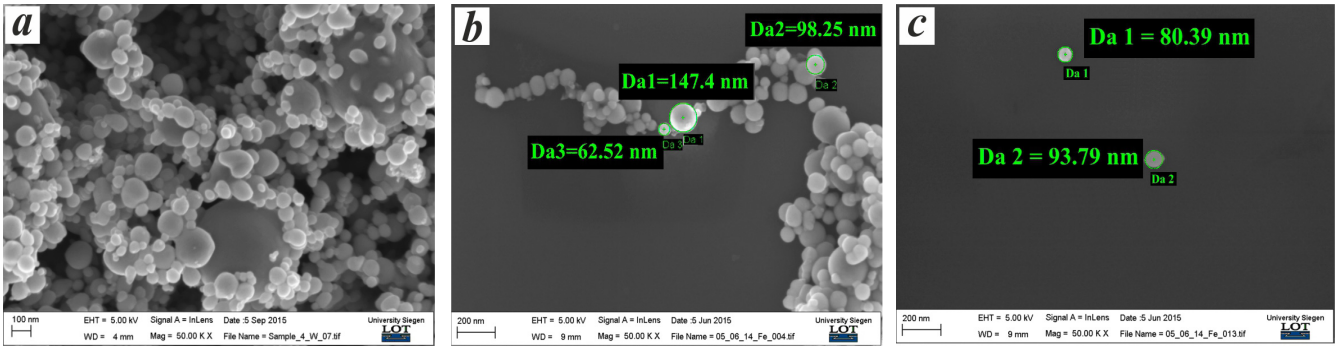

Fig. 1. SEM images of iron NPs (a), agglomerates of nanoclusters (b) and individual nanoclusters (c) after separation in hexane.

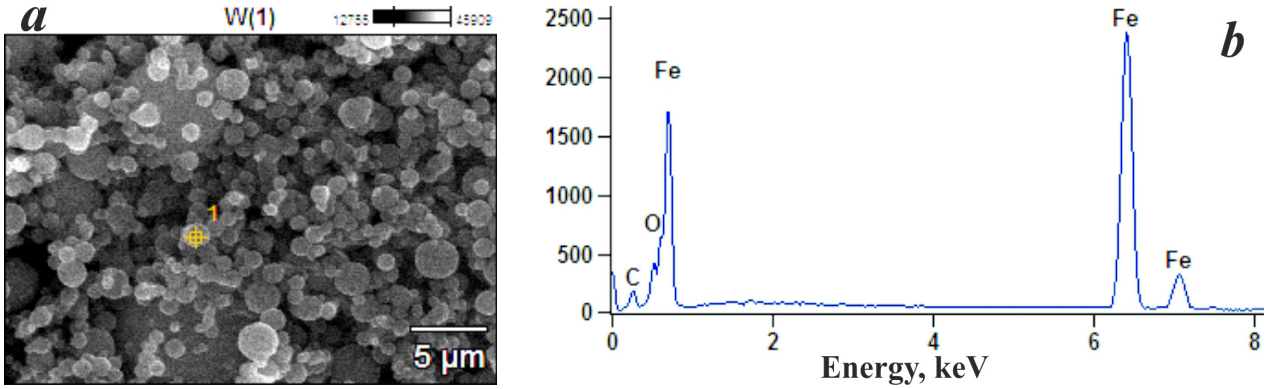

Fig. 2. Micrograph of Fe powder (a) and energy dispersive spectrum (b).

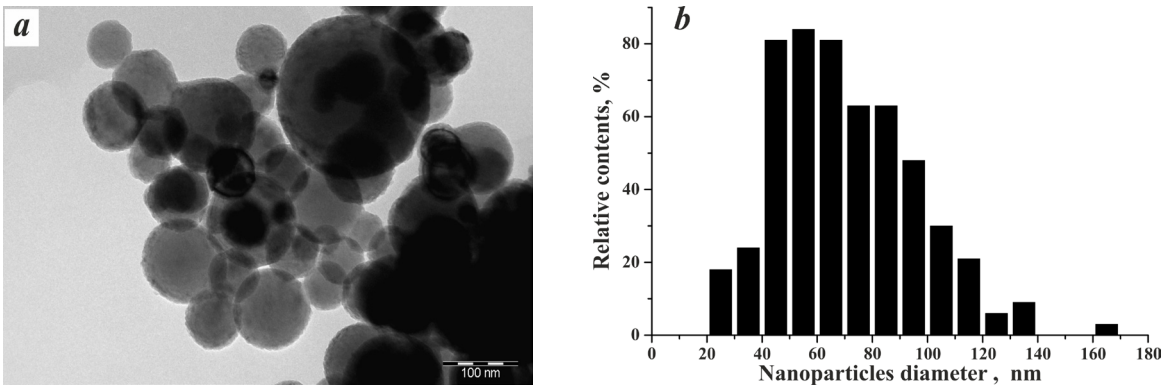

Fig. 3. TEM image of Fe NPs (a) and histogram of the size distribution (b).

As seen from the EDX spectrum, small amounts of carbon and oxygen impurities are present in the composition of Fe powder. The presence of carbon impurities is due to the conditions of passivation procedure of powders.

3.2. TEM results

Figure 3 presents the TEM image and histogram of the size distribution of EEW Fe NPs.

The results of TEM studies of iron NPs are consistent with SEM. Figure 3a shows that particles of iron NPs are spherical. The data of the histogram show that particles with the diameter of 40-70 nm predominate in the sample, the average diameter of which is equal to 65.5 nm. The analysis of histogram shows that distribution of iron nanoparticles according to the size is Gaussian with a standard deviation value σ = 30 nm.

3.3. The results of X-ray analysis

Figure 4 shows the X-ray spectrum of EEW Fe nanopowders.

X-ray diffraction results show that the main phase in the composition of the studied samples is the thermodynamically stable crystal modification (space group symmetry *Im3m*) characteristic of massive state (Fe – PDF # 060696). However, radiographs detected asymmetry and peak splitting. Splitting of the peaks was observed in the region of the maxima – (200), (211) and (220). The decrease in the interplanar distances was revealed for all three planes ($\Delta'_{(200)}$ = 0.008 Å, $\Delta''_{(200)}$ = 0.011 Å, $\Delta'_{(211)}$ = 0.004 Å, $\Delta''_{(211)}$ = 0.007 Å, $\Delta'_{(220)}$ = 0.002 Å, $\Delta''_{(220)}$ = 0.003 Å). The obtained results of splitting of the peaks could show itself on account of size effects. In particular, in [9] it is related to the influence of the oxide layer.

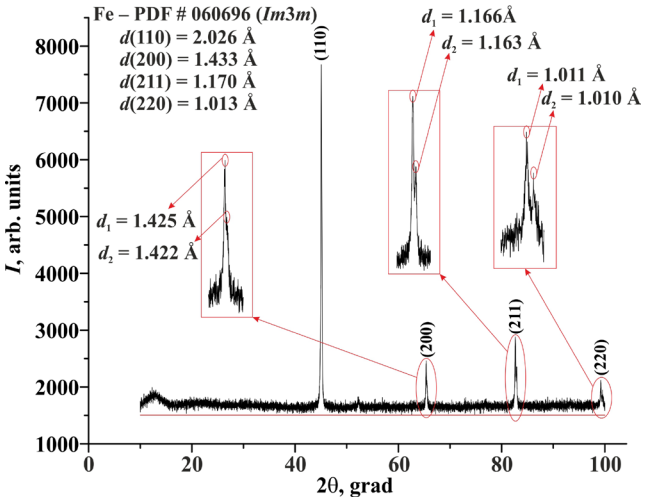

Fig. 4. Radiographs of EEW Fe nanopowders.

Distortion of the lattice is possible in the course of formation at the metal/oxide interface due to the orienting influence of metal oxide lattice (the energies of crystal lattices differ by several times). However, in [1], splitting of peaks is attributed to the change in the lattice parameter of metal nanoclusters.

3.4. Computer experiments

Recently, the method of molecular mechanics (MMM) has been widely used for the analysis of the structure and properties of nanomaterials. The main reason for the popularity of MMM is speed which makes it computationally feasible for general use. Alternative methods for generation of molecular configurations, such as ab initio or semi-empirical molecular orbital computations require much more computing time and power of PC. The main objective in the computing part of MMM is to minimize the strain energy in the

molecules making the atomic position closer to the optimum geometry. This means a reduction in total nonlinear energy of voltage represented by the equation of the force field with respect to the independent variables which are the Cartesian coordinates of the atoms [9]. Three-dimensional models were considered in the program ChemBio3D Ultra to estimate the change in the lattice parameter of nanoclusters (Fig. 5) and computer experiments on energy minimization at different temperatures were performed. Elastic deformation of the crystal lattice and the corresponding displacement of atomic coordinates take place during energy minimization [9–11]. Based on this, the average interatomic distances were calculated for both internal and external atoms (Table 1).

The tabulated data shows that lattice parameter of iron nanocluster decreases with the increase in temperature, which is consistent with the data of X-ray analysis.

At present, there is no model that enables a single point of view to describe the change in melting temperature, lattice parameter and experimentally observed surface roughening of metal nanoclusters. One of the effects arising from the reduction of cluster size is the change of the lattice parameter [12–21]. In a number of cases, the direction of parameter changes differs for the particles of the same substance and depends on the conditions of their preparation. For example, the experimental data on reduction [10, 16], increase [11, 15, 16], and absence of changes [18, 19] of the lattice parameter in the range of errors for gold clusters compared with the bulk samples are available. This ambiguity in the experimental results makes it difficult to answer the question to what extent the change in the parameter is due to the small size, and to what extent – other factors, such as impurities affect it, and what is the mechanism of the size change of the lattice parameter [18, 21].

Table 1

The unit cell parameter depending on temperature, Å

Temperature, ºC	300	500	700	900	1100	Standard conditions, 27 °C
IC	2.791	2.775	2.776	2.797	2.7338	2.492
NSL	2.819	2.783	2.819	2.792	2.8213	
SL	2.803	2.811	2.807	2.829	2.7823	

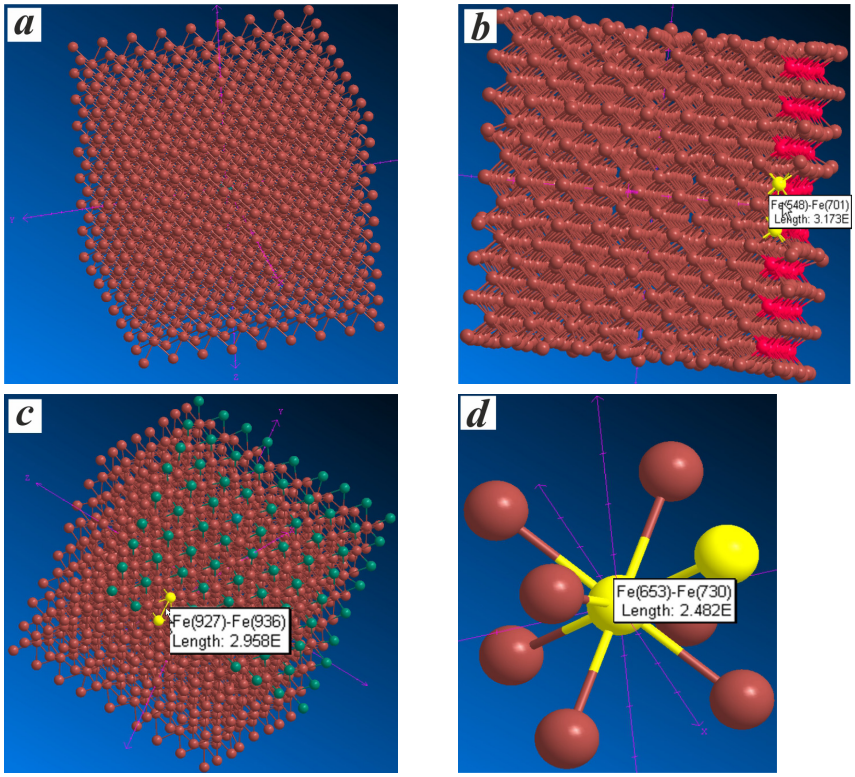

Fig. 5. Three-dimensional models of iron nanoclusters: a – 3D model of nanocluster with 1305 atoms; b – near-surface layer (NSL) – 41 atoms; c – surface layer (SL) – 41 atoms; d – inner core (IC) – 9 atoms.

4. Conclusions

SEM studies of Fe NPs showed that agglomeration of metal particles with a smaller size (from 10 to 50 nm) around the clusters with size from 100 to 200 nm is present. Thus, formation of chain-like structures of fine particles (10 to 30 nm) is observed. The shape of Fe particles is close to spherical. The agglomerates of particles with a large diameter usually coagulated with smaller clusters. The results of TEM studies of iron NPs are consistent with the results obtained by SEM. The data of the histogram show that particles with the diameter of 40–70 nm predominate in the sample, the average diameter of which is equal to 65.5 nm. Radiographs of Fe powder detected asymmetry and splitting of peaks. X-Ray analysis showed splitting of peaks which is observed in the region of the maxima – (200), (211) and (220). The decrease in the interplanar distances occurs for all three planes. Computer experiments have shown the results that coordinate with the data of X-ray analysis.

Thus, in the course of investigation it was shown that Fe nano-sized particles obtained in nonequilibrium conditions of electric explosion of wires have a crystalline structure with the lattice parameter different from the standard one.

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