

TEMPERATURE DEPENDENCE OF SPECIFIC MAGNETIZATION OF METAL-CARBON NANOCOMPOSITES SYNTHESIZED BY ARC DISCHARGE IN LIQUID

Zaginaichenko S.Yu⁽¹⁾ *, Perekos A.E., Schur D.V., ⁽¹⁾ Dubovoy A.G., ⁽¹⁾ Zolotareno A.D., ⁽¹⁾ Zolotareno An.D., ⁽¹⁾ Zolotareno Al.D., ⁽¹⁾ Kotko A.V., ⁽¹⁾ Efimova T.V., Zalutskiy V.P., Rugitskaya T.V.,

*Author for correspondence

*⁽¹⁾ Frantsevich Institute for Problems of Materials Science,
NAS of Ukraine,
3, Krzhizhanovsky st.,
Kyiv, 03142
Ukraine,
Institute for Metal Physics of NASU,
36 Vernadsky blvd.,
Kiev, 03142
Ukraine

E-mail: shurzag@ipms.kiev.ua

ABSTRACT

Many of unusual physical and chemical properties of nanoparticles are defined by high ratio of their surface area to volume. Possibilities of changing surface area and its chemical composition open far-reaching perspectives for synthesis of new magnetic materials.

Evaporation of metals in carbon-containing liquids or simultaneously with graphite allows the preparation of nanometallic particles in the carbon matrix which properties are scantily known.

In the present work, Me-C composites have been produced by the arc discharge method in toluene using a powder metal anode (ADLP); their structure, phase composition and magnetic properties have been studied.

The performed studies have shown that Me-C composites have a significantly changed phase composition. α -Fe powder transforms into Fe_3C carbide almost completely, and solid carbon solution in nickel, Ni-C forms in the Ni powder.

Heating the synthesized nanocomposites also leads to the change in their phase composition: after heating, a crystalline phase, Ni-C disappears in the Ni(B-2) powder, and oxides, FeO and Fe_3O_4 appear in the powder Fe(B-5-2) as well as the ratio of crystalline phases, α -Fe and Fe_3C changes.

INTRODUCTION

Materials which physical properties can be controlled by varying them within wide limits occupy a particular place

among modern metallic materials. These materials are used extensively in different fields of engineering and industry and define to a large extent the pace of scientific and technical progress. Magnetic metals and alloys can be realistically assigned to such materials [1-2].

Magnetic properties of metals and alloys depend on many technological and physical factors: conditions of their production, chemical composition, structural state, number and distribution of different stable and metastable phases in a material etc. which in turn are determined to a large measure by different types of external actions on a material during its production (mechanical, thermal, magnetic, thermomechanical, thermomagnetic, ultrasonic etc. treatments) [3].

Synthesis of superfine, ultradispersed and nanodispersed magnetic materials provides unique possibilities for physicists and technologists. Magnetic properties of materials with the superfine or ultradispersed structure can be changed over very wide limits by varying their dispersion, phase state, surface state and other factors [4-5]. This paper realizes one of such possibilities by the example of superfine iron and nickel powders produced by the method of electric arc dispersion in dielectric liquid media.

After the discovery of fullerenes and carbon nanotubes methods of their synthesis has been constantly investigated and improved. In parallel with the arc method in the gaseous phase and the pyrolytic method of synthesis of carbon nanostructures, since 2000 we have investigated and developed the method of

arc synthesis in the liquid phase. For the last decade, this method is used in increasing frequency to produce different nanostructures as the method alternative to the arc discharge in the gaseous phase (ADG).

In the eighties we began our work on producing ultradispersed metal powders by the electroerosion method [6-8] and continue it today. Besides carbon nanostructures produced by evaporation of carbon electrodes in the liquid phase, there appears a possibility to produce metal-carbon composites by sublimation of metal in the carbon-containing liquid. In this case the metal nanoparticles form along with carbon nanostructures on their surface.

The main positive features [5, 8] of the method used are as follows:

1. high temperature in the arc zone, > 4000 K;
2. high cooling rate of evaporated products, > 10⁹ K/s;
3. high degree of dispersion. The particles range in size from 1 to 100 nm;
4. high nucleation rate at a low growth rate of a particle.

This method does not require using of unhealthy gases, vacuum equipment or expensive lasers. The proposed method provides a possibility of producing a wide range of materials by varying the conditions for synthesis and it presents a way of modifying the chemical composition of electrodes and a medium, in which the synthesis is carried out [9]. At present time different research groups over the world are engaged in such studies [10-19]. The liquid phase may be of different chemical compositions that affect the structure and composition of the produced nanoobjects being studied (Fig. 1).

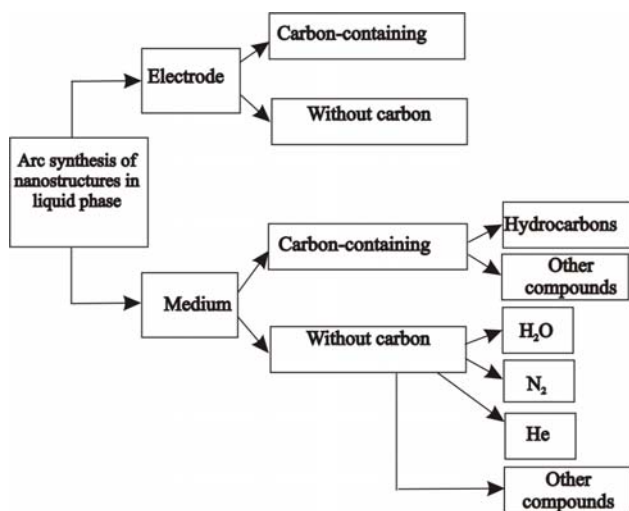


Figure 1 Diagram for possible combinations of medium and electrode materials in synthesis of nanostructures by the arc method in the liquid phase

For the last decade, arc discharge in the liquid phase is used in increasing frequency to produce different nanostructures as the method alternative to arc discharge in the gas phase. ADL is considered to be a profitable method of nanostructures synthesis. In the present work we consider the processes occurring on the electrodes and in the liquid phase during the ADL process and explain the mechanism of carbon nanostructures (CNS) formation proposing the model based on the analysis of existing regularities in behaviour of charged particles under extreme temperature and pressure gradients.

NOMENCLATURE

Subscripts

ADL	arc discharge in the liquid phase
CSR	coherent-scattering region
CNS	carbon nanostructures
ADLP	arc discharge in the liquid phase where a layer of powder reagent is used as an anode

EXPERIMENTAL

Synthesis of nanoparticles in the liquid phase has been carried out in the installation specially designed for these studies (Fig. 2). This installation allows the metal and graphite electrodes to be evaporated by an electric arc in the liquid medium in the temperature range from 4 to 340 K. In the neighbourhood of the cathode the arc temperature may be as much as 1,2·10⁴ K at currents of 200-300A (Fig. 3).



Figure 2. The installation for synthesis of nanocarbon structures and Me-carbon composites in the liquid phase

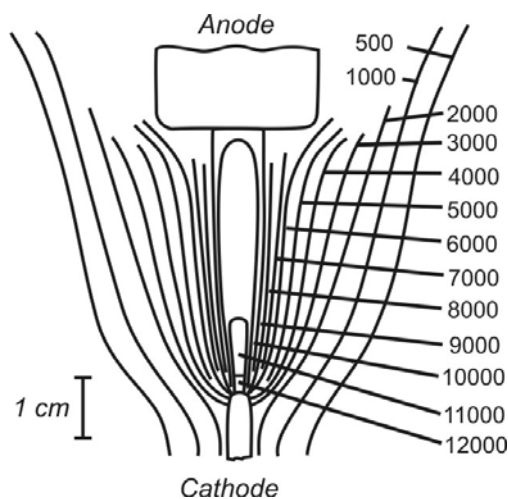


Figure 3 Temperature distribution (in K) in different regions of the electric arc between the carbon electrodes at strength of current equal to 200 A [19]

The electronic control block is simple to operate and provides a possibility of varying and measuring voltage and electric current. These changes make it possible to affect the conditions of the plasmachemical process in the reactor and the product morphology and yield.

All the chemical reagents used in the synthesis have been subjected to the prior purification and rectification. Type MPG-7 graphite has been used. The graphite rods have been pre-annealed in vacuum. The metallic rods have been remelted repeatedly in an arc furnace in the spectro-pure argon medium.

RESULTS AND DISCUSSION

Crystalline structures and phase compositions of powders were determined using X-ray diffractometer DRON-3.0 in Cokα irradiation; magnetic properties were measured on a ballistic magnetometer; extent of the coherent-scattering region (CSR) were calculated by broadening X-ray lines according to Selyakov-Sherrer formula.

Table 1 represents the results of studies on initial iron and nickel powders and the product prepared by arc discharge in the liquid phase using a powder anode (ADLP) in toluene. Also, the table gives the data on Fe(B-5-2) and Ni(B-2) powders before and after thermo-magnetic measurements.

Table 1
Phase composition and extent of CSR for iron and nickel powders.

Sample	Phase composition	Content, %	D, nm
Fe powder, initial state	α- Fe	100	270
Fe powder (B-5-2)	α- Fe Fe ₃ C	24 76	- 24
Ni powder, initial state	Ni	100	150
Ni powder (B-2)	Ni Ni- C	96 4	150
Fe powder (B-5-2), after heating	α- Fe Fe ₃ C Fe ₃ O ₄ FeO	73 11 16 16	110 40 100 100
Ni powder (B-2), after heating	Ni	100	130

Figures 4-9 and Table 2 illustrate the results of measurements of magnetic properties: specific saturation magnetization, σ_s , coercive force, H_c , and residual induction, B_r .

Table 2.
Magnetic properties of iron and nickel powders.

Material	σ_s , A·m ² /kg		Oe, ϑ	Br, Gs
	20 °C	-196 °C		
Ni, init.	56	58.5	50	1434
Fe, init.	219	222	6	102.2
Ni(B-2)	56	58	50	860
Fe(B-5-2)	84.3	95.8	20	108.7

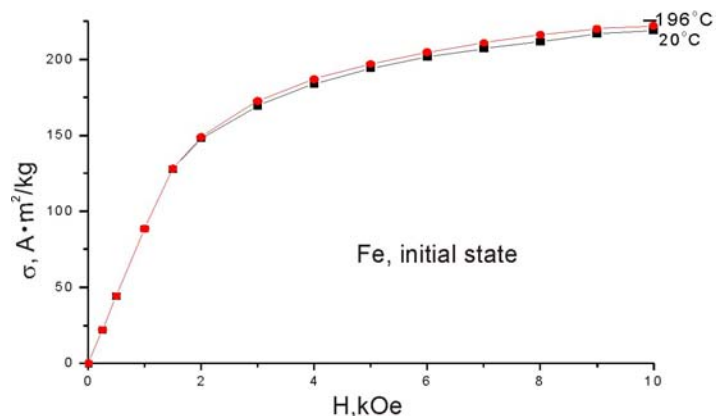


Figure 4 Field dependence of initial iron powder at temperatures -196 °C and 20 °C

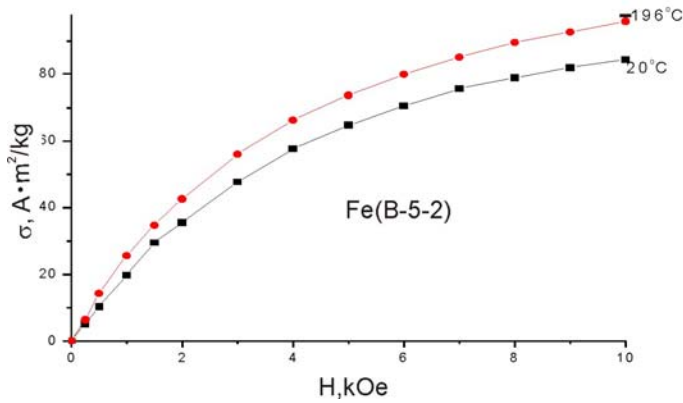


Figure 5 . Field dependence of specific magnetization of Fe-C nanocomposite at temperatures $T = -196^{\circ}\text{C}$ and 20°C .

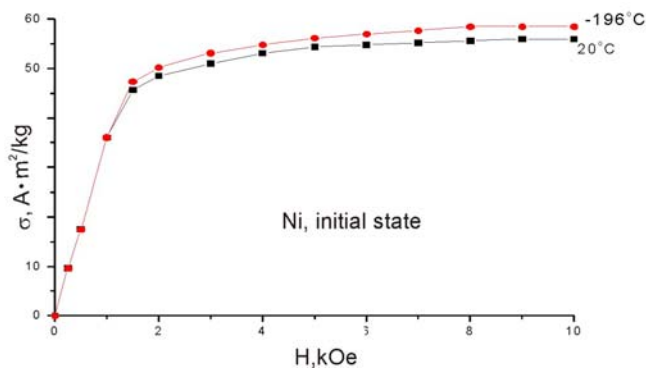


Figure 6 Field dependence of initial nickel powder at temperatures -196°C and 20°C

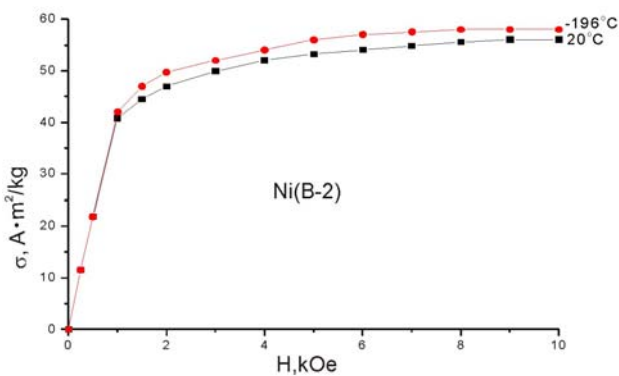


Figure 7 Field dependence of specific magnetization of Ni-C nanocomposite at temperatures -196°C and 20°C

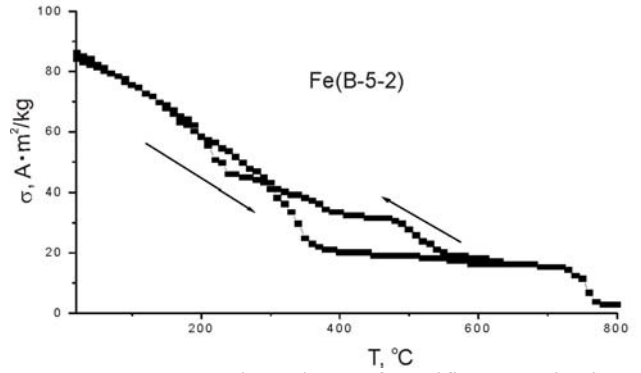


Figure 8 Temperature dependence of specific magnetization of Fe-C nanocomposite before and after heating to 800°C

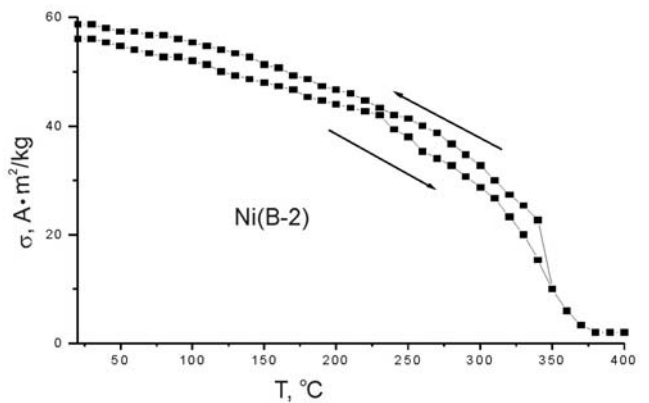


Figure 9 Temperature dependence of specific magnetization of Ni-C nanocomposite before and after heating to 400°C

Figures 4-7 demonstrate field dependences of specific magnetization, and Figures 8-9 show temperature dependences.

Diffraction patterns of initial iron and nickel powders show only lines from bcc iron and fcc nickel, respectively. After ADIP treatment in toluene, the phase composition of synthesized powders has changed. The diffraction pattern of Fe(B-5-2) powder demonstrates two crystalline phases, $\alpha\text{-Fe}$ (~24%) and Fe_3C (~76%). In addition to the lines from pure nickel, the diffraction pattern of Ni(B-2) powder has the most intensive line from carbon solid solution in nickel. In magnetic thermograms, Curie temperatures, 400 and 760°C for iron powders (Figure 8) and 225 and 360°C for nickel powder (Figure 9) correspond to these phases. For M-C composites, specific saturation magnetization of nickel powder is almost unchangeable (Figures 6 and 7, Table 2); this is related to a low amount of Ni-C crystalline phase that is formed in powder by ADIP treatment. Specific saturation magnetization of Fe-C composites changes more significantly (Figures 4 and 5, Table 2). This is conditioned by the considerable change in the phase composition of iron powders after ADIP treatment. In synthesis, initial $\alpha\text{-Fe}$ transforms into carbide, Fe_3C almost completely (Table 1). For the products, changes in coercive force, H_c , and residual induction, B_r , can be attributed to the corresponding changes in the phase composition and dispersion of the powders.

The results of changing the phase composition of the powders after heating in measuring the temperature dependence of specific saturation magnetization are also of interest. These results are shown in Figures 8, 9 and Table 1. As can be seen, the phase composition of iron and nickel in the synthesized powders has considerably changed on heating. After heating, the line from Ni-C solid solution has disappeared from the diffraction pattern of Ni(B-2) powder. After heating, intensities of the lines from Fe₃C carbide have reduced in the diffractogram of Fe(B-5-2) powder, intensities of lines from α -Fe increased, and the lines from crystalline phases, FeO and Fe₃O₄ appeared. According to the X-ray data, after heating and in subsequent cooling the knee at ~225°C (Ni-C solid solution) has disappeared from the magnetic thermogram of Ni(B-2) powder. In subsequent cooling, in addition to the knees at ~760°C (α -Fe) and ~400°C (Fe₃C), the knee at ~600°C corresponding to the Curie temperature for Fe₃O₄ oxide has also appeared in the thermogram of Fe(B-5-2) powder.

On the basis of TEM observations, one can note that the synthesized nanocomposites of both iron and nickel contain particles 1-400 nm in diameter. The major part of particles has a diameter ranging from 10 to 20 nm (Figures 10-11).

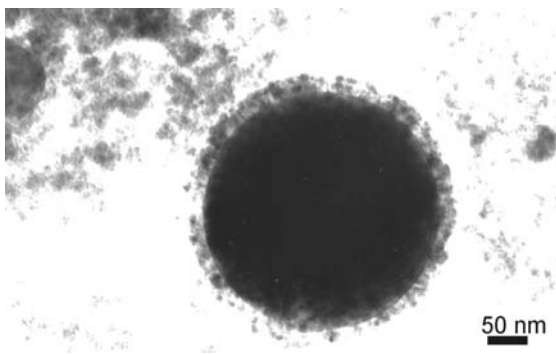


Figure 10 TEM photograph of Ni microgranule (250 nm) in nanocarbon shell

The shell on the large nickel particles (Figure 10) indicates that this particle is formed from the melt. Interaction of melted Ni and carbon vapor gives rise to Ni₃C carbide that decomposes during the alloy crystallization, liberating carbon. The carbon forms graphite-like nanostructures on the surface of a particle.

Large iron particles (~ 150 nm) do not have such prominent boundaries, although all particles of 10-30 nm fractions are wrapped into carbon shells.

In addition, iron nanoparticles formed by the arc magnetic field exhibit sufficient magnetization. This causes the nanoparticles to agglomerate in spherical clusters up to 1 μ m in diameter (Figure 12).

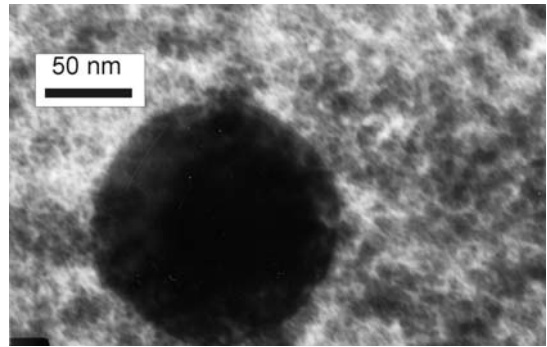
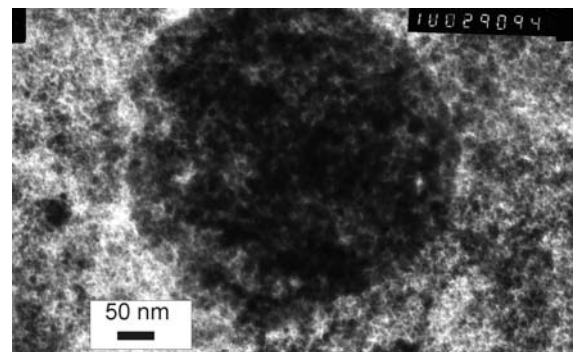
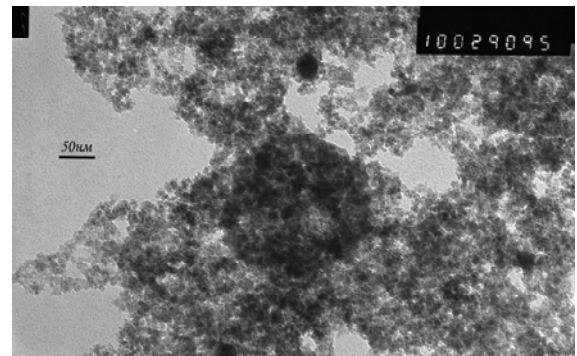


Figure 11 TEM photographs of Ni microgranule (100 nm) in nanocarbon shell



a)



b)

Figure 12 Spherical clusters consisting from ferromagnetic nanoparticles

CONCLUSION

In the present work Me-C nanocomposites have been produced by the ADIP method. Their structure, phase composition and magnetic properties have been studied.

The performed studies have shown that Me-C composites have a significantly changed phase composition. α -Fe powder transforms into Fe₃C carbide almost completely, and solid carbon solution in nickel, Ni-C forms in the Ni powder.

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