

3D COMPOSITES BASED ON OPAL MATRIX AND HETEROMETALLIC NANOPARTICLES

S. N. Ivicheva^{1*}, Yu. F. Kargin¹, E. A. Ovchenkov², Yu. A. Koksharov², G. Yu. Yurkov¹

¹*Baikov Institute of Metallurgy and Materials Science of the Russian Academy of Sciences, Moscow, Russia*

²*Lomonosov Moscow State University, Physics Department, Moscow, Russia*

[*ivicheva@mail.ru](mailto:ivicheva@mail.ru)

Keywords: supercritical, opal, heterometallic, nanoparticles.

Abstract

3D nanocomposites based on ordered opal matrices (OM) and metallic nanoparticles were prepared via reduction of salts or oxides of metals from the iron subgroup (Ni, Co, Fe), either as individual salts or their binary or triple mixtures, using supercritical iso-propanol. Effect of the precursor salt nature (nitrate or chloride) on composition of respective product has been studied. For the first time, nanoparticles comprised of metallic iron or its intermetallides with ordered structures (Ni₃Fe, NiFe, CoFe) were detected in composites prepared from Fe, Ni-Fe, or Co-Fe nitrates using the method described. Also, magnetic properties of the composites prepared have been studied.

1 Introduction

Composites based on macro- of mesoporous silica and nanoparticles comprised of the iron subgroup elements compounds (sometimes with addition of noble and other metals) are widely used in catalysis, magnetic or optically active materials, electronic components, medicines. Synthesis of magnetic nanoscale metallic particles or metal clusters and composites based on polymers, carbon, ordered 2D or 3D dielectric media and magnetic bi- or polymetallic nanoparticles is of special interest.

The iron subgroup metals are easily alloyed with many metals, whether heavy or light metals, noble or rare-earth, ferrous or nonferrous metals. The forming alloys have a number of important properties. Hence low-temperature synthesis of nanocomposites with polymetallic nanoparticles appears to be very prospective.

All methods for synthesis of nanocomposites comprised of on macro- or mesoporous media (silica, zeolites, anodized Al₂O₃, mesoporous molecular sieves, etc.) and metallic nanoparticles can be divided into two groups. The first group includes methods based on impregnation of a porous matrix with metal salts with subsequent thermal treatment and reduction of salts in different atmospheres, usually in hydrogen at 450–800°C. Methods of the second group are based on impregnation of a mesoporous medium with organic metal complexes with subsequent chemical modification of the latter.

In this work we study the effect of precursors and synthesis conditions on the final product (3D opal matrix (OM) with impregnated nanoparticles) prepared by reduction of metal (Fe, Co, Ni) salts or oxides, used either individually or in binary or triple mixtures, with supercritical (SC) alcohols.

2 Materials and testing methods

An opal matrix comprised of spherical silica nanoparticles 280 nm in size was soaked in a 50% water-alcohol solution of Co, Ni or Fe (III) nitrate or chloride, either in individual form or in the form of a binary (Co:Ni, Co:Fe, Ni:Fe) or triple (Co:Ni:Fe 1:1:1) mixture. The samples prepared were dried in air at room temperature, heated to 450°C and subsequently treated with supercritical *iso*-propanol at 250–300°C, 10 MPa in steel 200 cm³ autoclaves.

The metal-containing precursors used were Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, and FeCl₃·6H₂O (all they were analytical grade). The opal matrix used is a well-ordered 3D array of monodispersed amorphous silica globules 280–300 nm in size with the cubic or hexagonal close packing structure. Its specific area is ~ 10 m²/g, the effective porosity is 45%. The overall volume of tetrahedral and octahedral interstices is ~ 26%.

The phase and chemical compositions of the nanocomposites prepared were determined using the X-ray powder diffraction analysis (XRD 6000 “Shimadzu” X-ray powder diffractometer), scanning electron microscopy (SEM), and electron probe X-ray microanalysis (JSM-7001F JEOL electron microscope) of thin cleavages of the samples in different directions. The structural features and sizes of metal-containing particles, as well as the other products of the incomplete reduction of the salts, were determined using transmission electron microscopy (TEM) (JEOL JEM_1011 transmission electron microscope).

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis of the samples prepared were performed using the NETZSCH STA 409 machine equipped with a mass spectrometry (MS) gas analyzer.

The magnetic measurements were carried out at room temperature in magnetic fields up to 5 kOe on an EG&G PARC vibrating-sample magnetometer (model 155).

The electron magnetic resonance (EMR) spectra, which represented the first derivative of the microwave absorption signal with respect to the applied magnetic field, were recorded on a Varian E-4 X-band EMR spectrometer. The microwave field frequency was 9.14 GHz, the microwave power was 1 mW, the modulation frequency was 100 kHz, the modulation amplitude was 10 Oe, and the magnetic field scanning range was 4 kOe.

3 Results and discussion

Single- and multicomponent solutions of iron salts were subject to hydrolysis. They were stable for 2–4 weeks, depending on type of salt; highly dispersed sediments formed after that. However, the stability time sufficient for soaking the OM.

Binary and triple solutions (Ni²⁺-Fe³⁺, Co²⁺-Fe³⁺, Ni²⁺-Co²⁺-Fe³⁺) prepared from chlorides or nitrates also had different stability which affected the phase composition of the samples produced. The multicomponent solutions with FeCl₃ were more stable compared to multicomponent solutions of nitrates. Solutions with high hydrolysis rate (low stability) mainly produced ultradispersed (on the order of several nm) or amorphous phases, whereas the stable solutions produced crystalline solid solutions of salts.

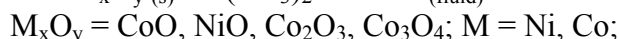
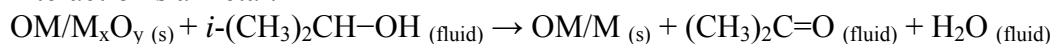
Therefore, Ni:Co nitrate solutions (1:1, 1:2), after drying in OM at room temperature, produced solid solutions of aqueous nitrates [1]. XRD patterns of the samples revealed the presence of a monoclinic lattice solid solution based on Co(NO₃)₂·H₂O. Interaction of NiCl₂ and CuCl₂ in the CuCl₂-NiCl₂-H₂O system lead to formation of a simple eutonic system.

XRD data indicate that all the samples, after being thermally treated at 450°C, are comprised of the amorphous silica matrix (the “halo” with the diffraction maximum shifted towards that of cristobalite) and crystalline or amorphous phases of the filler. The intensity and position of the “halo” do not change after any treatment performed, so the chemical transformations during these treatments must only occur in the pores of the matrix. The calculated sizes of the coherent scattering zones are 10–60 nm and do not exceed the pore size.

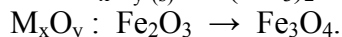
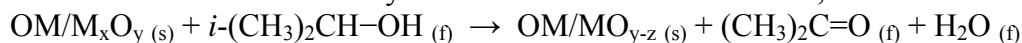
During the thermal treatment (up to 450°C), nitrates impregnated into the OM decomposed producing nitrogen oxides and metal oxides. Thermal decomposition of metal chlorides occurred at higher temperatures (with the exception of FeCl₃ which was subject to heating to 300°C). When Ni/Co nitrates are decomposed along with FeCl₃, exchange reactions can take place, and Ni/Co chlorides or complex salts can form. According to TG/MS data for the multicomponent system Ni(NO₃)₂-Co(NO₃)₂-FeCl₃-C₂H₅OH-H₂O, decomposition of nitrates finishes at 300°C, whereas decomposition of chlorides starts at 650°C and finishes at 800°C. As a result, this system produced solid solutions of Co/Ni chlorides and oxichlorides after thermal treatment at 450°C.

Metal compounds used in this work can be divided into two groups:

- 1) Salts and oxides which readily react with the SC alcohol; the prime product of this interaction is a metal:



- 2) Salts and oxides which mainly reduce to lower oxidation states, but not to a metal [2]:



Structure of the resulting metallic cobalt can be controlled by variation of synthesis conditions. Depending on the SC treatment time, we have produced [1] hexagonal α-Co, cubic β-Co or their mixture. Reduction of Ni compounds produces the fcc Ni.

The phase composition of iron compounds after thermal treatment and subsequent reduction in SC *iso*-propanol is affected by the nature of the precursor (iron chloride or nitrate). In spite of the complete decomposition of iron chloride in the OM/Fe(Cl) composite after treatment at 450°C with formation of the iron oxide with the hematite structure, further treatment with SC *iso*-propanol produced crystalline Fe₃O₄ with the magnetite structure. Interaction of the SC alcohol with iron oxides produced from the iron nitrate lead to formation of Fe₃O₄ and metallic iron.

A mixture of Ni and Co compounds (1:1) in OM produced a cubic modification NiCo solid solution after the SC *iso*-propanol treatment [1]. Fig. 1 depicts an XRD pattern of the composite produced and an insert with fragments of both this pattern and the same site (the (111) plane) in the patterns of Ni/OM and cubic Co/OM. The presence of nickel stabilizes the fcc structure. However, changing the Ni:Co ratio to 1:2 leads to formation of both the fcc solid solution and hcp cobalt (or solid solution based on it) which is thermodynamically stable at room temperature.

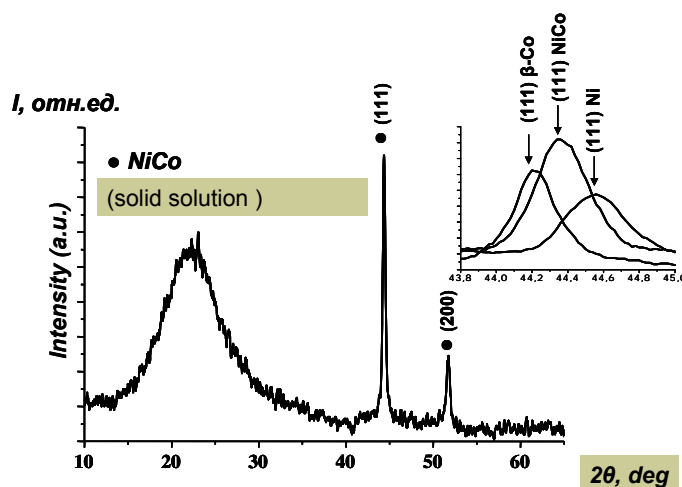


Figure 1. XRD pattern of the composite comprised of OM and a NiCo (1:1) solid solution produced after treatment of precursors with supercritical *iso*-propanol. The insert shows the shift of the (111) reflection of the NiCo phase compared to Ni and β -Co.

The binary systems Ni-Fe and Co-Fe produced from FeCl₃ are comprised of metallic Ni, α -, β -Co, and spinel-like solid solutions MFe₂O₄ (M = Ni, Co). Such systems prepared from nitrates, besides the spinel-like phases, are also comprised of Fe-containing metallic phases. The CoFe phase with the AuCu-like structure was found in the OM/Co:Fe (1:1) composite. FeNi₃ with the AuCu₃-like structure (Fe atoms are presumably at the vertices, whereas Ni atoms are at the face centers) was found in the OM/Ni:Fe (1:1) composite, whereas the AuCu-like NiFe was found in the OM/Ni:Fe (1:2) composite. These results comply with the state diagrams of the Co-Fe and Ni-Fe systems [3].

Reduction of the triple mixture Ni-Co-Fe(Cl) leads to formation of highly dispersed solid solution particles (the size of the coherent scattering zone is on the order of 10 nm) of a metallic phase which has the fcc structure and a spinel-like oxide phase with the cell parameter $a = 0,8392$ nm. According to XRD data, the metallic solid solution resembles FeNi₃. Prolongation of the SC *iso*-propanol treatment stage leads to decrease of the spinel-like phase content.

The OM/Ni-Co-Fe(N) composite completely reduces to ordered intermetallide phases (Ni₃Fe, NiFe, CoFe).

The fraction of individual metals in the composites was found to be up to 10% wt.

SEM micrographs of the nanocomposites reveal the presence of metal-containing particles both on the surface of silica granules and in the OM interstices.

Fig. 2 depicts dependencies of magnetization as a function of applied magnetic field $M(H)$ at room temperature for Ni/OM (a), a mixture of cubic and hexagonal Co/OM (b), and cubic Co/OM (c). Metal nanoparticles impregnated in the OM behave like relatively large 3D nanoparticles [4], which indicates that they are in the blocked state, and the $M(H)$ dependence forms a hysteresis loop with the coercive force on the order of hundreds of oersteds. The absolute values of magnetization are 3–4 A·m²/kg for Ni/OM and 6–10 A·m²/kg for Co/OM. As the concentrations of nanoparticles in the samples are ~10%, magnetization of Ni and Co nanoparticles can be as high as 30–40 A·m²/kg or 60–100 A·m²/kg, respectively. These values are 2–3 times smaller than those for the respective bulk metals and are specific for nanoparticles. The decrease of magnetization of the latter is caused by a change of magnetic properties of the surface atoms which can be a result of oxidation and high fraction of the surface atoms.

Magnetization curves for Ni/OM (fig. 2a) approach the saturation much sooner compared to the Co-containing samples, which is obviously due to the low magnetocrystalline anisotropy of Ni. The curve (b) is closer to saturation compared to the curve (c), despite just the opposite might be expected because the anisotropy of the cubic Co is lower than that of hexagonal Co. This contradiction can be easily explained by the fact that the $M(H)$ irreversibility zone is much wider for the hexagonal form of cobalt: the magnetization curves close at higher field strengths. The coercive force is also higher for the hexagonal Co.

The curve for the mixture of cubic and hexagonal Co approaches saturation slower. Perhaps it is caused by a higher fraction of an antiferromagnetic component (probably, cobalt oxide on the surface of the particles) whose curve is almost linear. This effect will be more prominent for smaller particles, which complies with the tendency of smaller cobalt particles to have the cubic structure. The lower magnetization values of the cubic Co/OM composition also indicate higher oxidation of the sample.

The magnetization curve for the NiCo solid solution resembles that of the mixed cubic/hexagonal Co/MO sample. As the fraction of cobalt in the NiCo solid solution rises, the

$M(H)$ curves become more flat (fig. 2d). It should be noted that the absolute values of magnetization for the sample with the higher Co concentration are lower, despite they might be expected to be higher due to the higher magnetization of Co compared to Ni. This contradiction can be explained by the difference in particle sizes and concentrations. Decrease of nanoparticles size leads to decrease of the fraction of ferromagnetic phase in a sample.

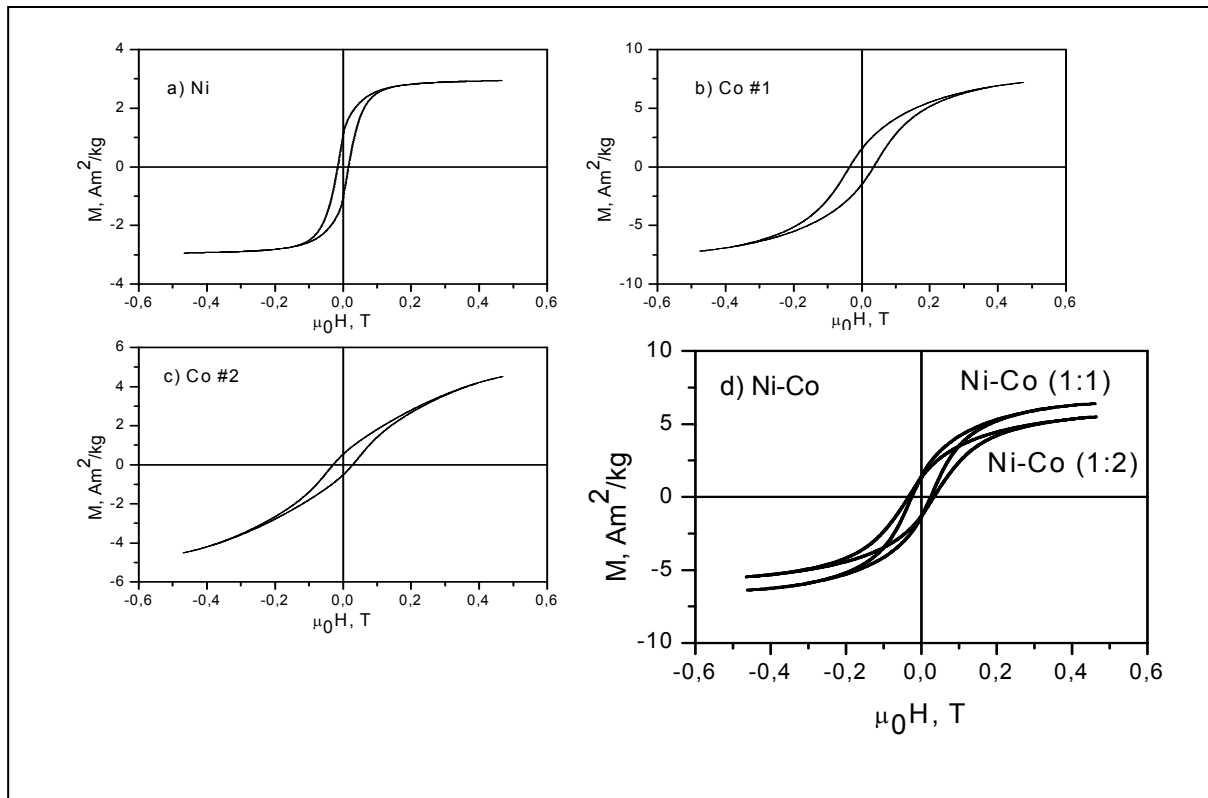


Figure 2. $M(H)$ dependencies measured at room temperature for a) Ni/OM, b) cubic + hexagonal Co/OM, c) cubic Co/OM, d) NiCo solid solution in OM.

The EMR spectra of the studied samples of the nanocomposites containing nanoparticles of cobalt and nickel (Fig. 3) are symmetrical. Since the asymmetry of the spectrum can be caused by the contributions from different types of resonant absorption sources (for example, nanoparticles of different sizes, isolated nanoparticles, or nanoparticles combined into complexes), it is expedient to perform the decomposition of the spectrum into individual components. For this purpose, we use a standard method of decomposing spectra into lines of simple shapes, i.e., the Gaussian or Lorentzian lines [5].

Usually, the Gaussian line shape indicates an inhomogeneous broadening of the spectrum, which can be caused, among other factors, by the heterogeneity of the system, or, more specifically, for example, by the difference in the magnetic properties of different types of resonant absorption sources contained in the sample.

Specific magnetization of the synthesized nanocomposites as a function of applied magnetic field strength was measured. High coercive force and low effective magnetic moment values of Co-containing nanoparticles in OM are due to the presence of both metallic cobalt and cobalt oxide in the samples; the latter is formed on the surface of nanoparticles and provides additional contribution of quantum exchange effects to magnetic anisotropy of the nanoparticles.

Two types of magnetic Ni nanoparticles were found from data EMR studies in the OM/Ni samples which are caused by the different sizes of Ni nanoparticles located in octahedral and tetrahedral cavities of the opal matrix.

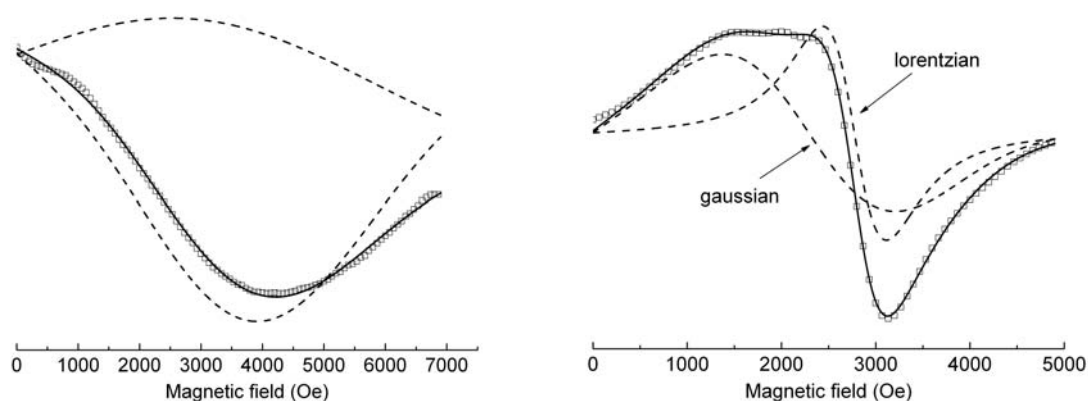


Figure 3. Decomposition of the experimental EMR spectra into components. Symbols are the experimental data, dashed lines represent the components of the decomposition, and solid lines correspond to the sum of the components. (a) EMR spectrum of the OM/Co nanocomposite with (смесь гексагональной и кубической модификации) metallic cobalt particles, Gaussian ($\Gamma = 2690$ Oe, $g = 3.27$), Gaussian ($\Gamma = 4830$ Oe, $g = 1.12$); and (b) EMR spectrum of the OM/Ni nanocomposite, Lorentzian ($\Gamma = 590$ Oe, $g = 2.34$), Gaussian ($\Gamma = 1080$ Oe, $g = 2.84$).

4 Summary

Single-, two-, or three-component nanoparticles 10 to 60 nm in size (comprised of metals, solid solutions of the iron subgroup elements (Fe, Co, Ni), or spinel-like ferrites) impregnated in silica opal matrix have been synthesized via reduction of metal salts or oxides with supercritical *iso*-propanol at temperatures below 270°C and pressure up to 10 MPa.

This work was financially supported by the RFBR (project 10-08-00608-a).

References

- [1] Ivicheva S.N., Kargin Yu.F., Shvorneva L.I., Kutsev S.V., Yurkov G.Yu. Ni, Co, Cu, Ni-Co, and Ni-Cu nanoparticles in opal matrices and mesoporous silica gels. *Inorganic Materials*, **48**, pp. 289–297 (2012).
- [2] Ivicheva S.N., Kargin Yu.F., Ovchenkov E.A., Koksharov Yu.A., Yurkov G.Yu. Properties of three-dimensional composites based on opal matrices and magnetic nanoparticles. *Physics of the Solid State*, **53**, pp. 1114–1120 (2011).
- [3] Lyakishev N.P. *Diagrammy sostoaniya dvoinykh metallicheskih system: Spravochnik (Phase Diagrams of Binary Metallic Systems: A Handbook)*. Mashinostroenie, Moscow (1997).
- [4] Skomski R. Nanomagnetism. *J. Phys.: Condens. Matter*, **15**, pp. R841–R896 (2003).
- [5] Koksharov Yu.A., Sherle A.I., Tikhonov A.N. Thermo-induced changes in EPR spectra of metal-free oligo- and polyphthalocyanines. *Synth. Met.*, **149**, pp. 19–29 (2005).