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## Magnetic Characteristics of Fe–Co–Ni Nanopowders

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### Abstract

Reduction of freshly precipitated mixed hydroxides with hydrazine in strongly alkaline medium yielded nano-structured (5–20 nm crystallites) powders of the Fe–Co–Ni system in the entire region of compositions. They had different magnetic characteristics and were promising for the use as magnetic materials. The correlation between magnetic properties and phase composition, and also crystallite (species) sizes was explored. The reached values of saturation magnetization of samples in the region of an iron rich solid solution exceeded parameters of the known literature analogues. It was also found that dependencies, such as lattice parameter and composition for face-centered and cubic body-centered cubic phases of solid solutions were described by the flat surface equation.

**Keywords:** Fe–Co–Ni system, lattice parameters, magnetic properties, nanostructured systems

### INTRODUCTION

The Fe–Co–Ni system in the massive (macroscale) equilibrium state has been studied in considerable detail in view of broad use of three- and two-component alloys in various technique areas. However, properties of Fe–Co–Ni in nanoscale or nanostructured (NS) states have not been systematically explored despite the prospects of their use when developing magnetic information carriers [1, 2], magnetic films [3, 4] or nanometer diameter fibers [4, 6] with high characteristics, magnetic liquids, and other materials [2, 6]. In a few papers, obtaining Fe–Co–Ni as thin films [3, 4], structured nanocrystallites [7], powders [8], or particles deposited on carbon fibers [5], and some of their properties (mainly magnetic) have been considered only on examples

of individual compounds. In general (in the entire range of compositions), the system in the nano-state has not been studied, as there is no information about phase composition (except for our papers on NS of two-component systems [9–12] Fe–Co, Fe–Ni, Co–Ni that are fragments of the system considered); dependencies of properties on phase and chemical compositions of Fe–Co–Ni have not been set including practically relevant magnetic characteristics.

The present work studied the correlation between magnetic characteristics with phase composition and crystallite (species) sizes.

### EXPERIMENTAL

Synthesis of NS of Fe–Co–Ni powders in the entire range of compositions was carried

out in Anton Paar reactor by co-precipitation of mixed metal hydroxides with NaOH from pure for analysis solutions of  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{FeSO}_4$  followed by reduction of freshly precipitated hydroxides by hydrazine (as hydrazine hydrate). The conditions were optimized considering preparation of two-component NS powders of Fe-Co, Fe-Ni and Co-Ni [11–13]: the total amount of salts was 0.017 (in terms of obtaining 1 g of metal powder); the amount of hydrazine of 0.200 moles, pH 12–14, temperature of 363–368 K, the reaction volume of 100 mL, and intense stirring.

Determination of phase composition and structural parameters was carried out using Difrei-401 (Russia) and D8 Advance (Germany) X-ray diffractometers in iron irradiation. Small-angle X-ray scattering (SAXS) curves were obtained using KRM-1 diffractometer also in iron radiation. The composition was monitored by the method of atomic emission spectroscopy using iCAP-6500 spectrometer. Sample morphology was studied by the method of transmission electron microscopy (TEM) using JEM 2010 microscope. Magnetic characteristics of samples were measured using MPMSXL

magnetometer (SQUID) in magnetic fields up to  $2.0 \cdot 10^4$  E at a temperature from 5 to 300 K.

## RESULTS AND DISCUSSION

For the exception of compounds containing 85 % Fe and higher (hereinafter, mass percentage) samples are X-ray pure, as demonstrated by carried out their pre-certification [13]. The total content of impurity metals is less than 0.5 % (iCAP-6500 spectrometer). The set of the results of raster (JEOL JSM 6390), atomic force microscopy (Cypher) and small angle X-ray scattering (SAXS) coupled with determining specific surface and porosity (ASAP-2020 analyzer) allowed establishing a three-level spatial organization of NS particles (Fig. 1): crystallites (5–20 nm) – compact aggregates made up therefrom (40–80 nm) – mesoporous agglomerates formed from the latter (120–500 nm).

Phase composition of Fe-Co-Ni nanostructured system was obtained as an isothermal (at synthesis temperature of 80–90 °C) section of phase states resulting from analysis of diffraction patterns of powders

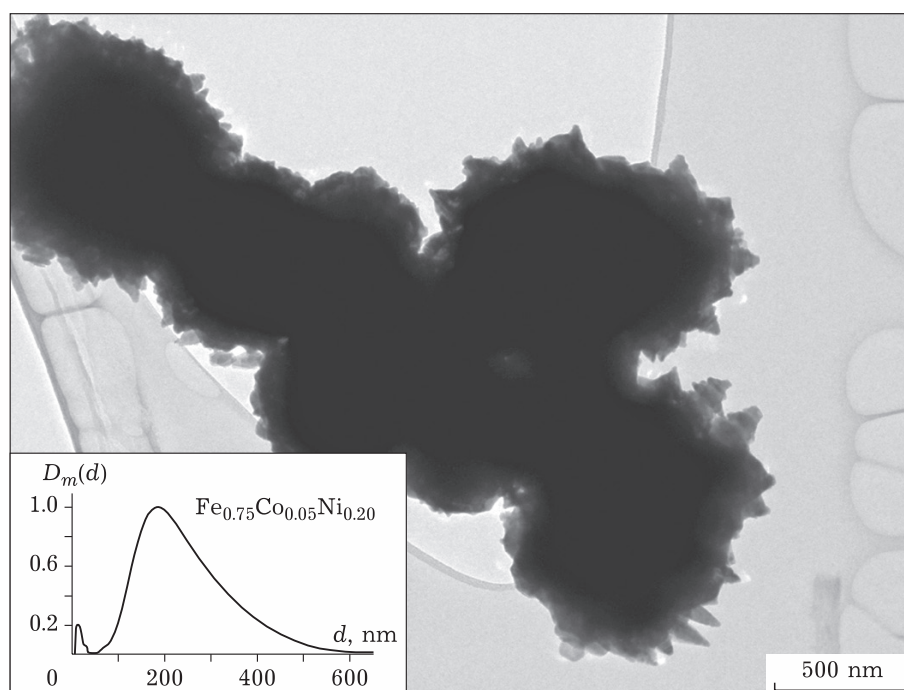


Fig. 1. Electron microphotography of mass function of the distribution of heterogeneities according to sample  $\text{Fe}_{0.75}\text{Co}_{0.05}\text{Ni}_{0.20}$  size.

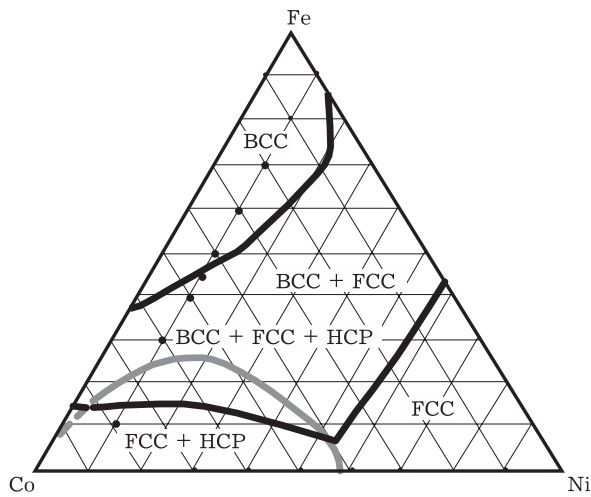


Fig. 2. Diagram of phase states of the NS system that meets preparation conditions. Dots indicate compositions with the measured magnetic properties.

(Fig. 2). Three phases typical for Fe, Co, and Ni are generated in the system. They are body-centered cubic (BCC), hexagonal close-packed (HCP), and face-centered cubic (FCC). The main differences from the phase diagram (PD) consist in broadening of two-phase regions of BCC + FCC and HCP + FCC right up to their overlap at relatively large cobalt content [14, 15]. There is also the disappearance of the monophase HCP region. These differences are driven by substantial nonequilibrium of the preparation process, the sequential nature of phase formation, and also high energy saturation of the NS. Phase composition of the resulting powders does not vary for 2–3 years despite nonequilibrium.

Crystal lattice parameters of samples were measured within the monophase FCC of the field and neighboring areas with a small number of other phases (see Fig. 2). Their dependence on the composition is described by flat surface equation

$$a = 3.524 + 0.1178x + 0.02301y \quad (1)$$

where  $x$  and  $y$  are molar fractions of iron and cobalt, respectively (Fig. 3). The average random deviation of the measured parameters from the plane (values calculated according to the equation) is 0.02 %. The values of the lattice parameters almost coincide with the tabular values for the known metastable FCC phases of iron and cobalt (3.64 and 3.5447 Å,

respectively) when extrapolating to the heights of the phase triangle (equation (1)). Thus, the resulting dependence of lattice parameters of three-component FCC solution on composition can be regarded as a three-dimensional analogue of Vegard's law. A similar area of the flat dependence of BCC lattice on sample composition has been established near the “iron” top of phase triangle (see Fig. 2):  $a = 2.8668 - 0.0290x + 0.0024y$ , where  $x$  and  $y$  are the molar fractions of cobalt and nickel, respectively. The mean deviation of the measured parameters from the plane is 0.01 %.

The preservation of the flat nature for the character of the dependence, such as lattice parameter versus composition at minor deepening into the two-phase region to the Fe-top and more significant to the side of Co is a peculiarity of properties for the resulting NS system. The flat character is disturbed beyond these limits and the surface bent down (experimental parameters become fewer than calculated) due to the appearance of the BCC phase that contains more iron than the FCC phase. The observed behaviour of lattice parameters is related to system nonequilibrium near the boundaries of phase regions. It is obvious that a decrease in parameters in an equilibrium system should have the fracture

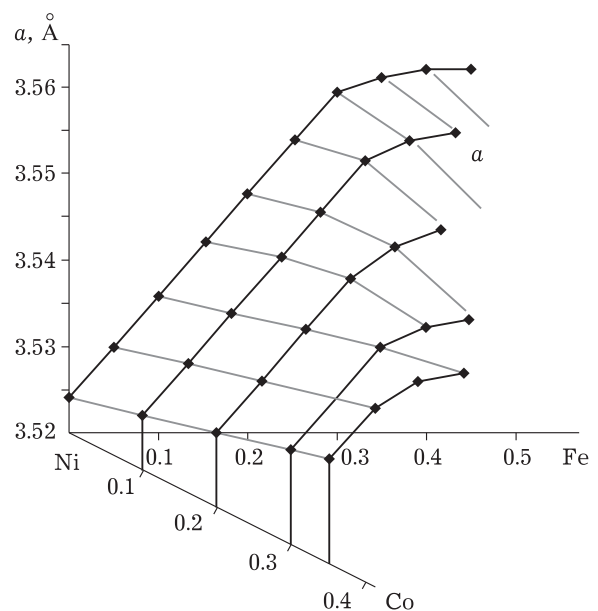


Fig. 3. Lattice parameter of the FCC phase ( $a$ ) versus the mass fraction of iron and cobalt.

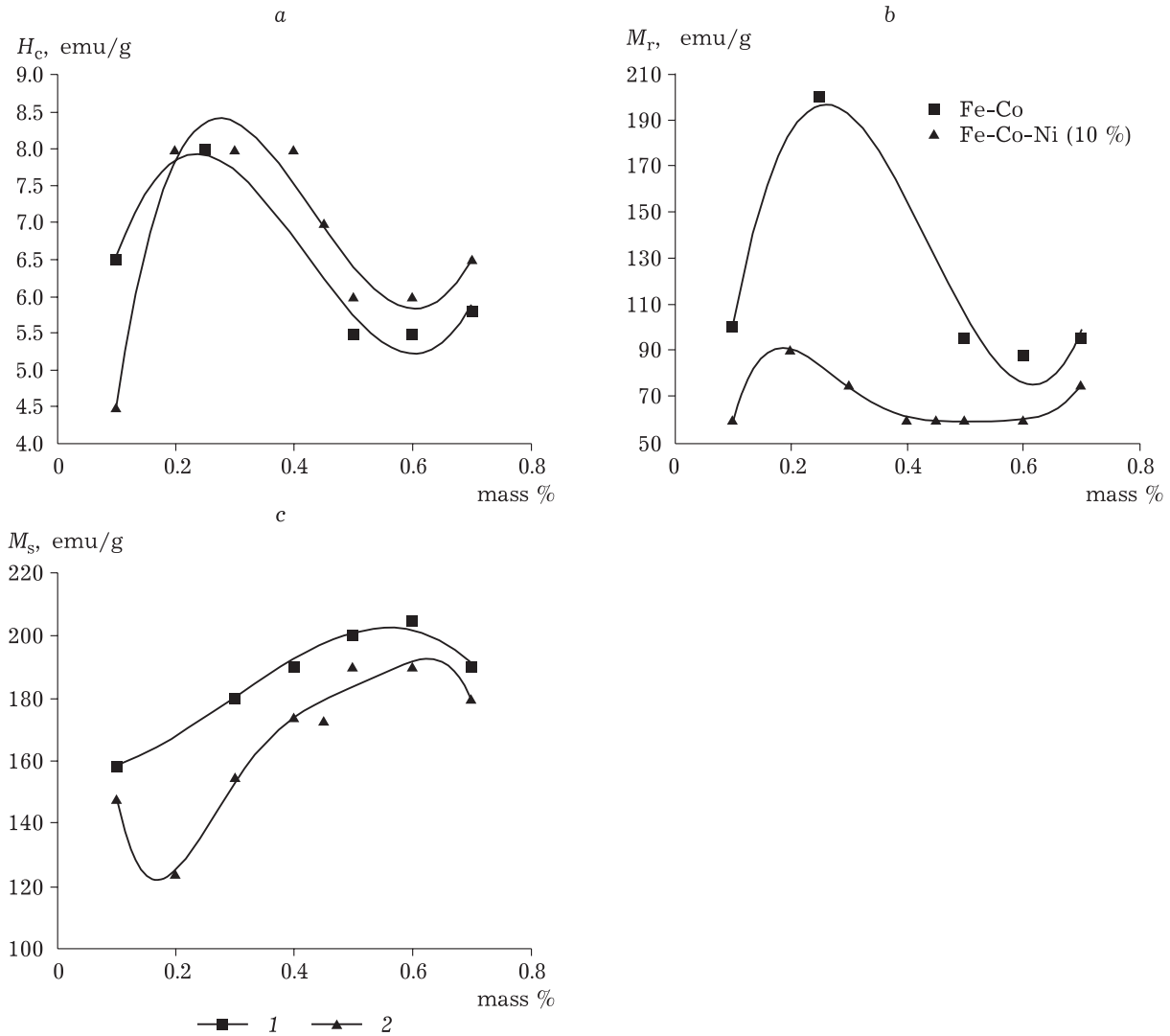


Fig. 4. Magnetic characteristics of NS of Fe-Co-Ni and Fe-Co systems versus the iron content: coercivity  $H_c$  (a); residual magnetization  $M_r$  (b), and magnetization saturation  $M_s$  (c).

pattern and be found since the appearance of the BCC phase.

Out of the carried out measurements of magnetic characteristics of the NS system under study, the results demonstrated in Fig. 4 are of the greatest interest. They are obtained for a series of sorbents with nickel content of 10 % and affect the major phase areas, including the BCC zone with the highest values of saturation magnetization ( $M_s$ ), and are interesting from the viewpoint of comparison with similar results for NS of the Fe-Co system, in particular, to assess the effect of small amounts of nickel. Moreover, in the given form, the graph reflects rather the effect of replacing cobalt (fixed part) for nickel,

therefore, in case of the decisive role of the composition, the effect of this replacement at small nickel content should be weaker than at large. However, in fact, the changes are more serious and complex.

According to the Slater-Pauling theory [16], there is maximum  $M_s$  (Fig. 4, c) that reaches 214–215 and 200 emu/g for Fe-Co system and Fe-Co-Ni, respectively, in monophasic BCC region (at large iron content). The maximum value is lower in the second case; it is also shifted to the side of a higher content of iron, which is qualitatively in agreement with the replacement of cobalt for nickel that is significant in relative terms. The effect of

a replacement for nickel should have been decreased with decreasing iron content and  $M_s$  graphs would have been got close, however, on the contrary, there is a sharp deviation downwards in the triple system, especially, in the three-phase region. At a replacement of 20 % of cobalt for nickel (deepening into the three-phase region), the deviation is even stronger.  $M_s$  values are brought closer again with a transition to the FCC region (7–10 % of iron), therefore, the dependence of  $M_s$  on iron content has a maximum in the three-phase region. The coercivity ( $H_c$ , see Fig. 4, *a*) and residual magnetization ( $M_r$ , see Fig. 4, *b*) characterizing the hysteresis of magnetization curves of BCC phases weakly depend on the composition and slightly increase with increasing iron content, apparently due to the formation of oxides in the surface of nanolayers.

$H_c$  and  $M_r$  increase and have the maximum values for Fe–Co in two-phase regions during transition to polyphase regions, and for Fe–Co–Ni – in two- and three-phase. Understanding of the causes of these nontrivial results obtained for NS multicomponent systems of a mixture of metals requires for the first time additional study. It may be noted that they are not related to a change in the composition of the system under study, in particular, on cobalt that has higher magnetization anisotropy than Fe. A probable cause of the observed consists in joint effect of the phase composition too on magnetic characteristics of nanocrystal sizes.

Determining quantitatively size distribution of nanometer crystallites folded in compact aggregates does not seem to be probable, however, this information on a qualitative level is provided by comparison of small angle X-ray scattering (SAXS) data and the character of  $M_s$  temperature dependencies (see Fig. 4, *c*) in different phase regions of considered Fe–Co–Ni and Fe–Co NS systems. In distribution functions of inhomogeneities in Fe–Co–Ni and Fe–Co NS, there are distinct mods (5–20 nm for Fe–Co–Ni and 5–30 nm for Fe–Co) referred by us to crystallites, as demonstrated by SAXS data in [17]. Inasmuch as broadening of diffraction reflexes corresponds to precisely these sizes, and the sizes of aggregates in the considered compositions regions (40–80 nm in Fe–Co–Ni and 120–220 nm in Fe–Co) assessed from the

same SAXS data directly correspond to those determined by the method of atomic force microscopy [13, 17]. The sizes of crystallites in Fe–Co and Fe–Ni systems do not significantly change with transition from single-phase BCC region to two-phase (BCC + FCC) to the extent of a decrease in iron content. On the contrary, in a triple system, the proportion of the smallest (nanoscale) fraction of crystallites increases and rises even more with transition to the three-phase region.

Based on the above stated, the observed decrease in  $\sigma$  for Fe–Co–Ni in transition to the two-phase region (see Fig. 4) is likely to be mainly related to changes in crystallite sizes that is the total decrease in the average sizes and an increase in the fraction of nanometer size particles in the superparamagnetic state. This regularity is total for low dimensional ferromagnetic individual metals of the iron group (*e.g.* in [18, 19] for particles with a size of 20–100 nm).

There are no data in literature on the dependence of magnetization curves parameters on particle size for Fe–Co–Ni, nevertheless, it appears to be unlikely to relate the observed increase in  $H_c$  and  $M_r$  values in polyphase regions of the systems under study with a change in the average sizes of crystallites. Firstly, judging by SAXS results, their bulk have the sizes less than 25 nm, that is in the region where  $H_c \sim D^6$ , which does not correspond to our results during both transition of Fe–Co–Ni from the monophasic region to two-phase one and during transition from two-phase area to three-phase one. Secondly, a significant increase in  $H_c$  and  $M_r$  for Fe–Co in the two-phase region is not accompanied at all by a visible change in crystal sizes. The observed effects are strictly related to changes in phase composition of systems, as suggested by us. Likewise effects were also observed in mono-nanoscale cobalt species [2, 18] and are likely to appear in our case when considering polycomponent systems with polydisperse nanocrystallite distribution.

The maximum  $M_s$  and minimum  $H_c$  and  $M_r$ , corresponding to the most magneto-soft state are obtained for the monophasic BCC region of a solid solution (see Fig. 4). Herewith, the reached values of  $\sigma$  are somewhat higher, and those of



$H_c$  and  $M_r$  are lower than for the same systems with close sizes of nanocrystallites obtained by other methods [7, 20].

## CONCLUSION

The relationship between magnetic characteristics with phase composition and crystallite (species) sizes has been explored for compounds with 10 % of nickel. Herewith, the effect of nickel is not limited to simple dilution of Fe–Co system. The key observed characteristics are the following: 1) a decrease in saturation magnetization ( $M_s$ ) in transition to the two-phase region and strengthening of this effect when transiting to the three-phase region; 2) an increase in coercive force ( $H_c$ ) and residual magnetization ( $M_r$ ) in transition to polyphase regions with reaching maxima in the three-phase region apparently driven by changes in phase composition.

Additionally, it has been demonstrated that dependencies, such as lattice parameter versus composition for body-centered cubic and face-centered cubic phases of solid solutions are described by the flat surface equation.

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