Eurasian Chemico-Technological Journal 17 (2015) 193–200

The Temperature Effect on Properties of Fe-Co-Ni Nanostructured System

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Article info

Received:
18 March 2015

Received and revised:
17 April 2015

Accepted:
23 May 2015

Abstract

The influence of heating process (up to 200, 400 and 600 °C) on the phase transformation of non-equilibrium biphase Fe-Co-Ni systems was studied. The system was not changed at 200 °C, it remained nanostructured, and there were no phase transformations. At higher temperatures phase transformation BCC- into FCC-phase (high-temperature phase modification) was observed. The degree of phase transformation depended on the system composition. At 400–600 °C there was coarsening of the crystallites. In addition, there was the phenomenon of system oxidizing attended by iron outflow from phase; as a result, the lattice parameters were decreased. According to the measurements of the lattice parameters at cooling-down, parameters dependences on temperature and coefficients of thermal expansion were obtained. Changing of the system composition (due to metal oxidation) had low impact on the coefficients. The phases with different compositions and close lattice parameters had different coefficients of expansion. It was supposed that the expansion coefficients dependence from the composition was not additive. Magnetic characteristics of the samples were measured. It was found that heating changed it essentially. The main reasons of it was coarsening of grains (crystallites) and changes of the phase composition. The dependence of the magnetic properties of systems on phase composition and size of the crystallites (particles), as well as changes occurring under the temperature effect were required a more detailed study.

1. Introduction

It is obvious that there is progressive interest to Fe-Co-Ni nanostructured system (NSS) with various spatial organization (powders, films and layers, fibers) due to their observed features (firstly structural and magnetic properties) and expansion of the perspectives of its practical use [1–4]. This circumstance stimulates further research in this field.

In the work [1], it is shown that the generated in the electric field Fe-Co-Ni fibers have unusually high value of the saturation magnetization (Ms) (201 emu/g for the sample 46.9 at.% Fe – 23.8 at.% Co – 29.3 at.% Ni). Light doping (in a fraction of a percent) by diamagnetic Al and Si increases the value of the saturation magnetization (up to 257 emu/g), moreover it exceeds the theoretical limit obtained for the most highly magnetic materials ($Fe_{0.68}Co_{0.32}$) in the bulk state (245 emu/g). In addition, there is an unusual effect of the crystallite size on the coercive force. The author of [2] obtained values of Ms for thin films of Fe-Co-Ni which were closed to the limiting value for Fe-Co, the system was magnetically soft, but there was no information about morphology, phase composition of the films, long-term and temperature stability of its properties.

Earlier [4–6], the authors of the work for the first time defined phase composition in all component ratios that gave an opportunity to make the slice of phase diagrams (PDS) for Fe-Co-Ni nanopowders: it was founded and discussed its distinctions from the phase diagram (PD) for bulk system, moreover it was shown a significant effect of phase composition and particle size on the magnetic properties.

The study of high-temperature processes and the following changes of the properties of the Fe-Co-Ni NSS is a pressing issue due to the strong influence of temperature on the multicomponent NSS (PDS,

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coarsening of particles up to the loss in nanosized state that changes magnetic properties). However, the published information on these issues is scanty, and there are no results of the in-situ study of structural-phase properties of system at heating. In the paper these issues have been considered for the series of samples with biphase compositions (BCC + FCC phases) where the effects will be most pronounced.

2. Experimental

Powders of the studied Fe-Co-Ni system are obtained according to the procedure described earlier [3, 4].

Phase composition, structure and lattice parameters are determined by X-ray diffraction (Powder X-ray Diffractometer, Bruker D8 ADVANCE A25 (Germany) and DIFREY-401 (Russia), at iron filtered emission, Mn-filter). The phase compositions of NSS are studied in-situ at the various temperatures 30–600 °C in a high vacuum ($10^{-7} – 10^{-9}$ mbar) by mean of the high-temperature chamber «Anton Paar» HTK 1200 N (temperature stability ± 0.1 °C) and ex-situ at 30 °C after rapid cooling of the samples.

Magnetic properties are measured by mean of «MPMSXL» SQUID-magnetometer in magnetic fields up to 2.0 * 10^4 Oe at temperature 5–300 °K.

3. Results and Discussion

In the works [4-6], in view of a body of X-ray diffraction data, it was made the slice of phase diagrams for Fe-Co-Ni NSS: it was founded and discussed its features versus the known phase diagram for bulk system [7, 8]. It is shown (Fig. 1) that: 1) extension of biphase area (BCC + FCC phases) (more noted for poor cobalt compositions), 2) for the rich cobalt systems there is the existence of three-phase systems which prohibited Gibbs phase rule for equilibrium state, 3) diffusion of interphase boundaries due to the formation of non-equilibrium solid solutions. It is a result of nanodimension of the system and consequently energy-saturation of NSS and nonequilibrium synthesis processes.

The main purpose of this work is to study the nature of the interfaces shifts at heating, FCC – (BCC + FCC) and BCC – (BCC + FCC), i.e., the transformation of the first feature of PDS and its «approximation» to PD of a bulk equilibrium Fe-Co-Ni system, as well as the clarification of other effects accompanying the heating process (heat treatment).

So synthesized Fe-Co-Ni samples correspond to biphase area (showing in Fig. 1) and they are presented in Table 1.

Table 1

Composition of the sample

Sample	Composition, wt.%		
	Fe	Co	Ni
1	40	20	40
2	50	20	30
3	45	45	10

The samples were selected on the phase composition in such a way that the Sample #1 contains substantially FCC-phase, Sample 2 – mainly BCC-phase, Sample 3 – trace quantity of FCC-phase. Heating of the samples was carried out in three stages. At the first stage heating was carried out from 30 to 200 °C with step 50 °C, and then cooling with the same step. X-ray patterns were recorded at each temperature with prior keeping for 10 min. The second step is heating to 400 °C with registration of X-ray patterns after keeping for 10 and 60 min, and cooling to 30 °C, with registration of X-ray patterns, similar procedure was repeated with heating to 600 °C. The third stage is exactly the same operations of the first one, but to the heated sample. Thus, the effect of temperature was studied as in-situ, and ex-situ (Fig. 3).

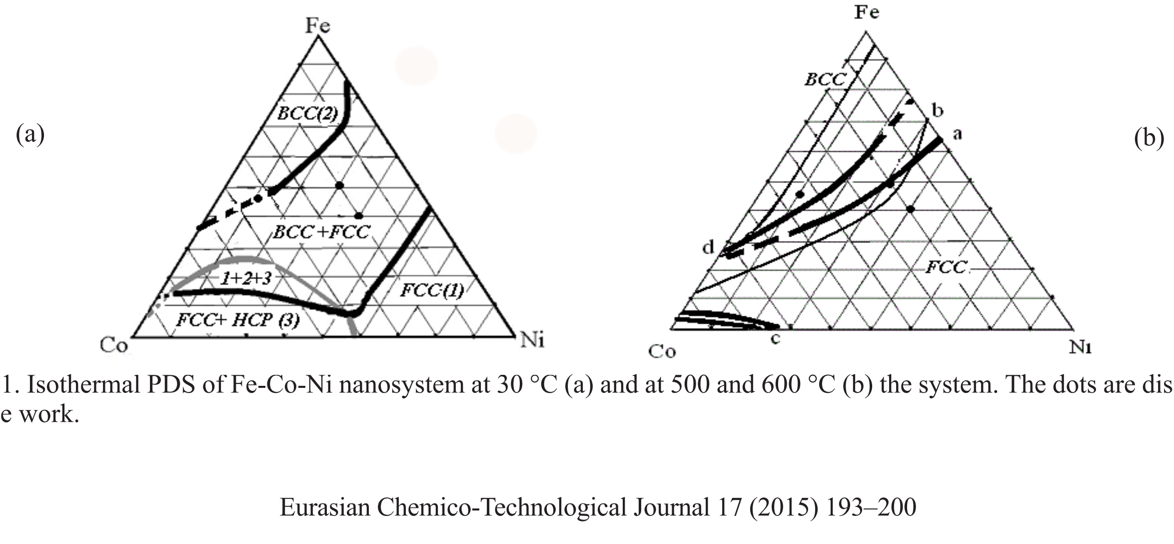


Fig. 1. Isothermal PDS of Fe-Co-Ni nanosystem at 30 °C (a) and at 500 and 600 °C (b) the system. The dots are discussed in the work.

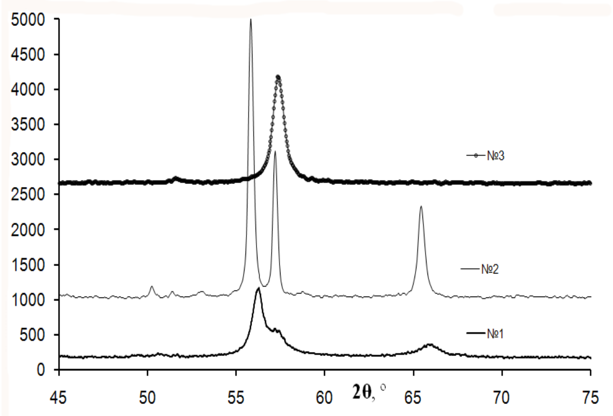


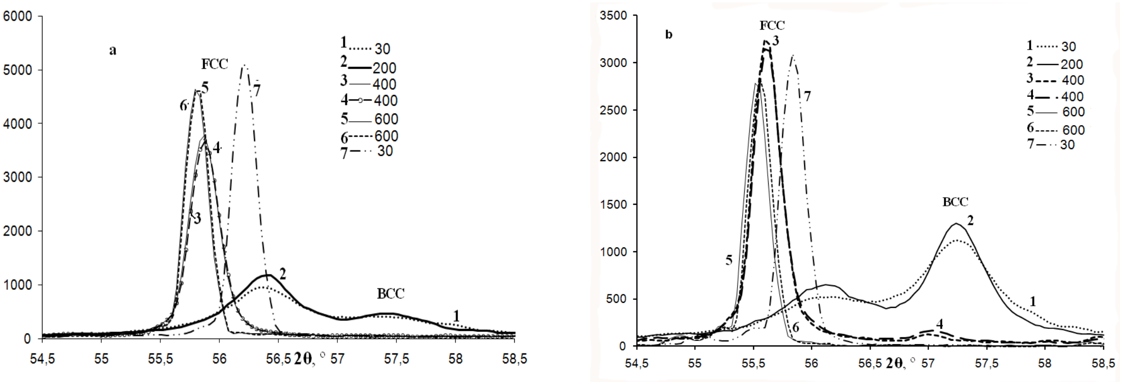
Fig. 2. XRD-patterns of the samples.

The selected program of heat treatment and registration of X-ray patterns allows us to consider in one measurement cycle three processes: that is thermal expansion of the metal, changing the phase composition of the system (registration at 30 °C was carried out to minimize the effect of the temperature shift of peaks) and the sample oxidation.

Figure 2 shows a part of obtained plain X-ray patterns, in details it is shown in Fig. 3 – transformation of the most intense peaks of FCC – and BCC-phases as a result of heating to the selected temperature in according with the above-described heat treatment program.

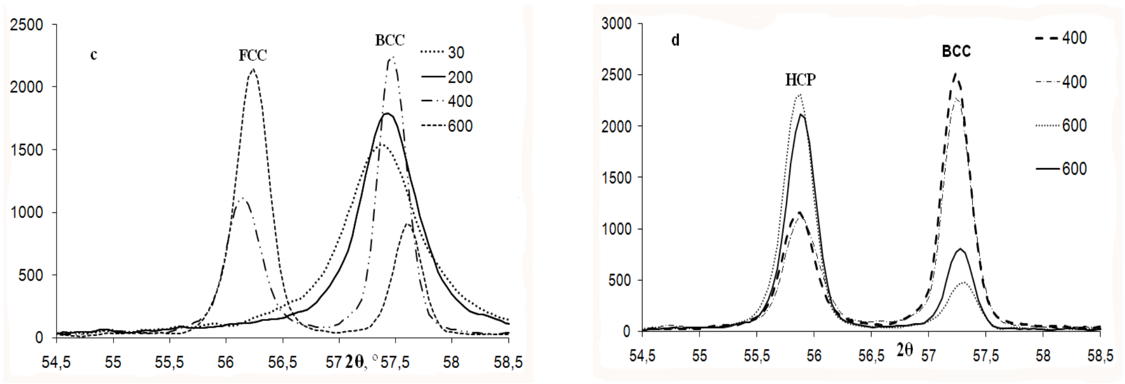
The results indicate coarsening of crystallites of both phases at heating, which is relatively weak at low temperature (below 200 °C), 1 h heating at 400 and 600 °C.

There is the expected PDF transformation of nanostructured systems during heating process and at increasing heating temperature and its approximation to the PD of a bulk system. In this case, there is a shift of interphase boundaries of the (BCC + FCC)-phase area in the BCC-phase direction. For Sample 1, almost complete transition to the single FCC-phase is observed at 400 °C; the Sample 2, as it supposed (according to Fig. 1) – transition is observed at higher temperature (600 °C); it is in agreement with the position of the monophase FCC-area boundary on the phase diagram shown in [7] than in [8] for a bulk system.



Sample 1

Sample 2



Sample #3 (ex-situ) after heating up to
indicated temperature

Sample 3(in-sity)

Fig. 3. XRD-patterns of the samples. Heating was performed in the following program 30-200-400-400 (keeping 1 h) -600-600 (keeping 1 h) – 30 °C.

Composition of the Sample 3 is on the interphase boundary between the (BCC + FCC) and BCC-area, which is «fuzzy» [3, 4] due to non-equilibrium nanosystem, so the sample is mainly represented by the BCC-phase with a very small fraction of FCC-phase (Fig. 1). At following NSS heating, the interphase boundary between the (BCC + FCC) and BCC-area does not change or it is slightly shifted «up» (in the iron-rich area), so that at 600 °C (corresponding to the PD slices in Fig. 1b) the system remains biphase (with FCC-phase growth at temperature increasing).

This result is consistent with position of the interphase boundary of (BCC + FCC) and BCC-area on PD for a bulk Fe-Co-Ni alloy that given in [2].

Thus, the results are consistent with the lower boundary of the two-phase area, shown in [7], and the upper boundary, given in [8]. The same corresponding to the literature data is given in [4], i.e., the comparison of interphase boundaries of Fe-Co-Ni nanosystem near Fe-Ni area (i.e. compositions with poor cobalt) with interphase boundaries of Fe-Ni nanosystem.

In general, the partial loss of nanodimension, at heating to 600 °C, and general approximation of system to an equilibrium state is transformed PDS to the phase diagram form.

In [1], sample of NSS with an atomic ratio of Fe: Co: Ni = 46.9: 23.8: 29.3, respectively, closing to the composition of the Sample 2 (but obtained by other means and other conditions), was described as a biphase (coexisting phases, $Fe_{1-x}Ni_x$ with FCC-structure and CoFe with BCC-structure), the composition of $Fe_{1-x}Ni_x$ is between FeNi and $Fe_{0.64}Ni_{0.36}$. This statement (about coexisting phases) may be taken only as a rough approximation. We have constructed dependence of the lattice parameters (of FCC- and BCC-phases) on two parameters of concentration, but also it is not allowed unambiguously to determine the composition [3–6].

The analysis of X-ray patterns of Samples 1 and 2 shows that peaks of BCC- and FCC-phases are shifted toward lower angles for the composition containing large amounts of relatively large iron-atoms. Parameter of the FCC – lattice increases sharply at the transformation to single phase state due to iron enrichment by iron-atoms from the more iron-rich BCC-phase.

The change of the lattice parameters, when heated, indicates the partial oxidation of NSS; consequence of this is the shifts of the peaks to large angles area observed in after heating at ex-situ registration at 30 °C (Fig. 3a-3c). Tendency to oxidation increases in the row Ni-Co-Fe and, therefore, during process the lattice parameters of the phases should be reduced, thus it is supposed that the oxidation will proceed more intensively in the BCC-phase containing more iron.

The results show that for Samples 1 and 2 at temperatures below 200 °C, oxidation is substantially not fixed by X-ray diffraction. Another situation for monophase Sample 3 (BCC-phase) oxidation is observed at this temperature range.

Heating the samples up to 400 °C and 600 °C is followed by oxidation of the two phases, wherein the BCC-phase is oxidized more rapidly. At these temperatures, formation of oxide phases is also registered by X-ray diffraction (Fig. 4). From experiments in-situ, it follows that the process of oxidation has finally completed at 400 and 600 °C in 10 min; additional keeping the sample for 60 min has virtually no effect on the position of the FCC- and BCC-peaks. At the same time, heating to 600 °C of samples, after prior keeping at 400 °C, leads to the further oxidation, especially it is registrated for Sample 3 with BCC-phase (Fig. 1c, 1d).

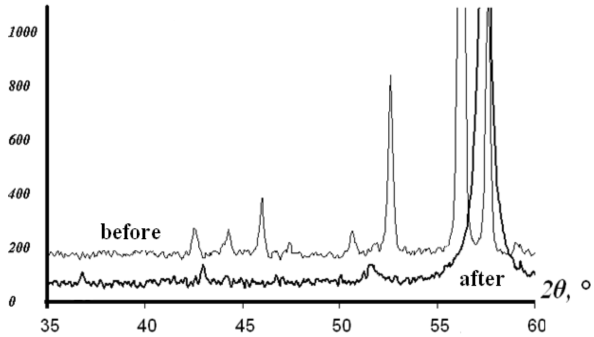


Fig. 4. XRD-pattern of the Sample 3 (before and after the heat treatment at 600 °C).

The observed oxidation is non-trivial, since the temperature keeping of samples, and the registration of the X-ray patterns was carried out in high vacuum (10^{-7} – 10^{-9} mbar). There are two schemes (mechanism) of the process:

1) as a result of solid-phase thermodynamically allowed reactions $xFe + yNiO \rightarrow Fe_xNi_yO$, $xFe + yCoO \rightarrow Fe_xCo_yO$ and consolidation of oxide phases at tempering to the size that may be detected by X-ray diffraction method;

2) as a result of metal oxidation by the isolated oxygen from meso- (micro-) pores in the aggregates formed from nanocrystallites during the synthesis of Fe-Co-Ni.

It was founded in [3, 4] that there are closed pores in the aggregates of Fe-Co-Ni nanosystem synthesized by chosen method, X-ray fluorescence analysis (energy-dispersive device to scanning microscope JEOL JSM 6390) and X-ray photoelectron

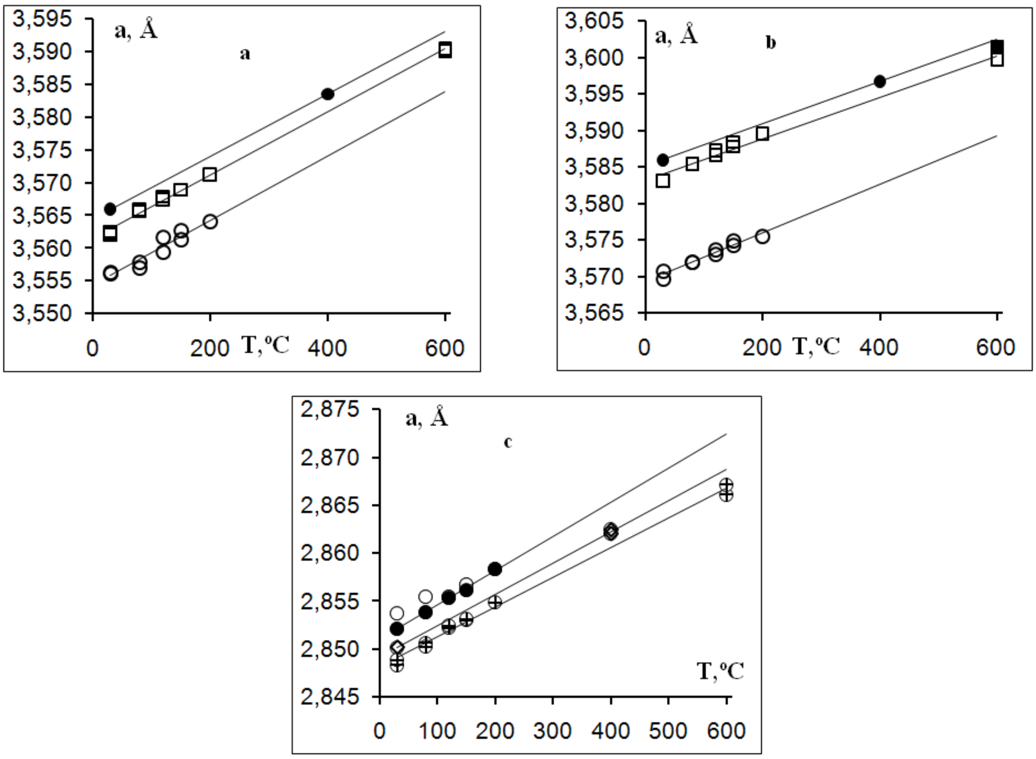


Fig. 5. The effect of temperature on the lattice parameter of cubic phases in the Samples #1 (a), # 2 (b), # 3 (c). Values of linear thermal expansion coefficients measured at heating up to 200, 400 and 600 °C, respectively: a) $133*10^{-5}$, $136*10^{-5}$, $1.39*10^{-5}$; b) $8.06*10^{-6}$, $7.93*10^{-6}$, $9.33*10^{-6}$; c) $1.25*10^{-5}$; $1.15*10^{-5}$ and $1.09*10^{-5}$.

spectroscopy (with sample etching by accelerated argon ion beam) (SPECS spectrometer with hemispherical analyzer PHOIBOS-150-MCD-9, Germany) shows that pores are filled by oxygen and (or) water.

To precisely determine of the causes and mechanism of the observed formation oxide phases under high vacuum in NSS Fe-Co-Ni it should be done additional series of experiments (for example, by XPS – to study during heating treatment changes f the proportions of NiO, CoO, mixed oxides, free and bound oxygen); at the same time, due to the obtained results, the second model is more probable.

Indeed, the iron content in the Sample 3 is slightly less and the ratio of Co/Ni is significantly higher, most likely, in both phases. Peak shifts to larger angles are expressed much stronger; it is the result of iron depletion of phases due to its more active oxidation in the Sample 3. It is to be expected for the process of the metals oxidation by oxygen (water vapor) in view of the difference of metals redox potentials. At the same time, if the reaction takes place on the first mechanism it would be expected the opposite situation since more favorable thermodynamically process is $xFe + yNiO \rightarrow Fe_xNi_yO$.

The results of in-situ measurements allow us to make the lattice parameters depending on the temperature and estimate the coefficients of thermal expansion. It should be considered the samples oxidation at high temperatures and because of it additional change in the lattice parameters. So a complete picture of the temperature dependence of the parameters can be represented by three line graphs corresponding to the three heat treatment temperature of 200, 400 and 600 °C (Fig. 5).

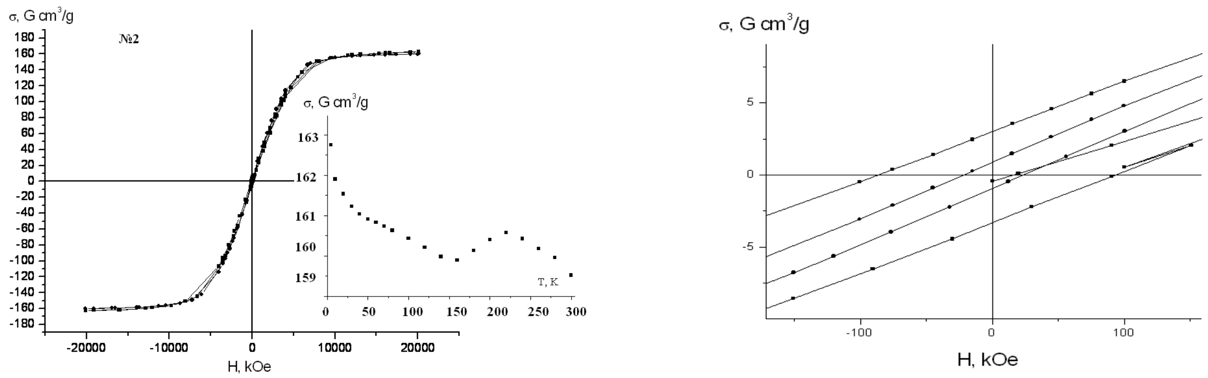
It was found that heating to 200 °C leads to oxidation and changes the composition only in the Sample 3, most iron-rich. Therefore, there is a different variation of the BCC lattice parameters at heating (light dots in Fig. 5c) and cooling (black dots).

Heating to 400 °C is followed by oxidation and, accordingly, the iron depletion of phases in all cases. The obtained lattice parameters dependences on the temperature are presented below, but its slope are not essentially changed, that is expected, because the composition of NSS is slightly changed. The appearance of oxide phases in general should also not significantly affect the lattice parameters of both the metallic phase and the coefficients of expansion.

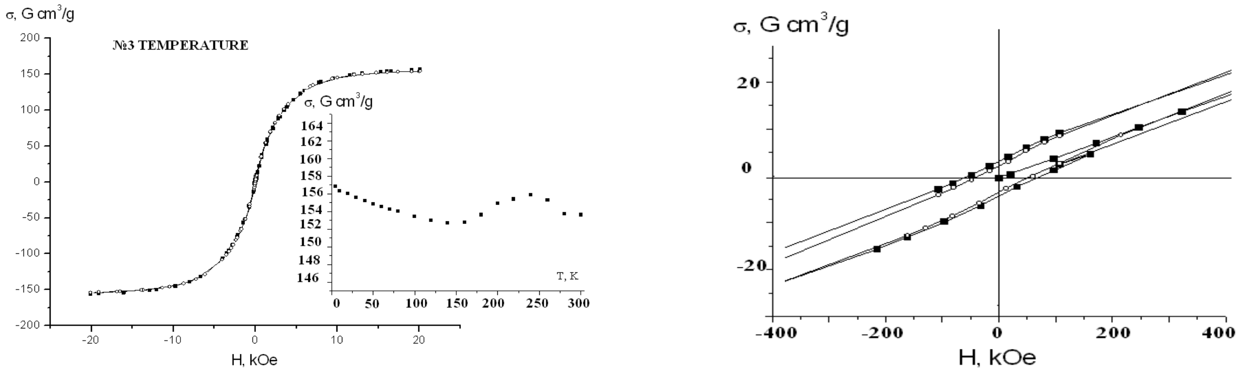
Oxidation by heating to 600 °C is most essential, so the lattice parameters dependence on the temperature is lower, but the slope of graphs and the coefficient of thermal expansion are changed insignificantly due to small changes of the composition.

However, it should be noted that the composition affects the coefficients of expansion, as can be seen by comparing the graphs of the FCC-phase for Samples 1 and 2. In spite of it the lattice parameters of the FCC-phases are nearest values, the FCC-phases have different capacity for expansion, and its coefficients are $1.4 \cdot 10^{-5}$ and $0.8 \cdot 10^{-5}$ deg.$^{-1}$, respectively. This difference should be considered as valid, due to the fact that differences in the measurements of the coefficients for the sample does not exceed $0.1 \cdot 10^{-5}$. The average value of the coefficients of the BCC-phase of the Sample 3 is $1.2 \cdot 10^{-5}$ deg.$^{-1}$, but here the nature of the expansion is affected by different structure in addition to the composition. In general, the measured coefficients of solid solutions is slightly lower than coefficients for individual metals of iron group ($1.3 \cdot 10^{-5}$–$1.6 \cdot 10^{-5}$ deg.$^{-1}$).

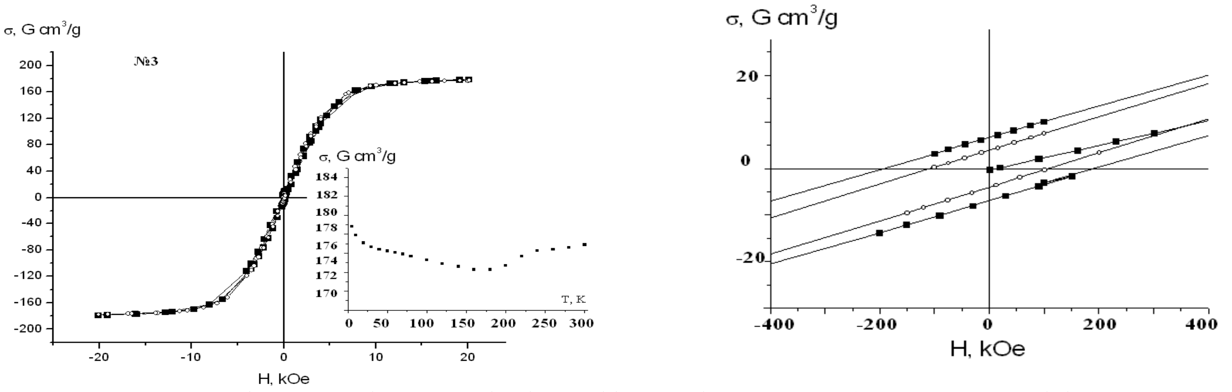
Summarized results of measurements of the magnetic properties of the Samples 2 and 3 are shown in Fig. 6.



Sample 2, saturation magnetization and hysteresis parameters (remanence, coercivity)



Sample 3, saturation magnetization and hysteresis parameters (residual magnetization, coercive force) after heat treatment



Sample 3, saturation magnetization and hysteresis parameters (remanence, coercivity)

Fig. 6. Main magnetic characteristics.

Comparison of the main characteristics of the Sample 2 (saturation magnetization – σ and coercive force – Hc) with the characteristics of NSS with closed composition (but synthesized in other conditions) and presented in [1] shows the relative proximity of its. According to [1] when grain size decreases from 267 to 47 nm the values of coercive force vary from 79 to 387 Oe and the σ values are from 201 to 188 emu/g.

The morphology of the synthesized Fe-Co-Ni particles is three-tier model (according to [3–6]): BCC-phase crystallites with size 6–9 nm and FCC-phase with sizes 12–17 nm form compact aggregates with size 40–80 nm without open pores but with closed pores, the aggregates make up porous (friable) agglomerates with sizes up to 200 nm. The σ and Hc values of our samples – 163–160 emu/g and 25–90 Oe at 5–300 °K, respectively, it is comparable with the data presented in [1] for the same conditions of measurement of the magnetic characteristics (at 300 K). The comparison shows that conditions of the samples synthesis do not affect the magnetic characteristics of samples in a biphase (BCC + FCC) area; defining parameters are the particle size and chemical composition.

The results of measurements of the Sample 3 show a marked effect of phase composition and particle size on the magnetic properties because of heating. The sharp decrease of the σ value after heating the sample up to 600 °C is due probably to increasing content of FCC-phase with smaller amounts of iron and which is relatively weak magnetic-phase, since there is a general coarsening of particles (Fig. 3) causing some increase in σ of ferromagnetic systems [10].

It is interesting that at low temperatures, where these processes do not take place, for a sample of all composition, it is observed a very weak dependence of temperature on the σ, with the appearance of extrema. Such a dependence is atypical, and the dependence of $\sigma = \varphi$ (T) differs from for conventional bulk ferromagnets including the systems Fe-Ni and Fe-Co [12].

Significant reduction of the coercive force at heating is probably due to the coarsening of the particles; this phenomenon is theoretically expected and observed for many nanocrystalline ferromagnetic materials [11]. The dependence $\sigma\sim D^{-1}$ is typical (D is a particle size of crystallites), the dependence is satisfied when the size of D is more than the size of a single magnetic domain in the system. Sizes of individual magnetic domains in Fe, Co and Ni are 24, 28 and 36 nm [13–15], and evaluated for the system Fe-Co – about 33 nm [16], it shows that samples are in the domain of dependence of $\sigma\sim D^{-1}$.

The possibility of changes in the magnetic characteristics of highly magnetic NSS Fe-Co-Ni by varying the size and phase composition of the particles is found, this phenomenon must be study in depth. To study the effect of heat on the phase composition and structure of the NSS Fe-Co-Ni it is must be consider in more detail the effect of temperature on the other features associated with nanoscale (stability of the three-phase area, the “fuzzy” of the interphase boundaries, etc.).

4. Conclusions

Thus, fine powders of Fe-Co-Ni synthesized by reduction of aqueous solutions of salts, as a rule, are nonequilibrium systems consisting of several phases. The main part is metal solid solutions with three main structural types of metal (FCC, BCC, and HCP). During the synthesis, metals are reduced in a definite order (sequence), so the obtained phase are nonequilibrium. By varying the synthesis conditions, it is possible to influence on the phase structure and composition of the phases, thus adjusting properties of the obtained system. In addition, it is probable to use external energy factors (heat, physical field, radiation) to affect the system composition and size of particles.

In practical terms, this system is very interesting for its magnetic properties, so a deeper study of the effect of the phase composition and particle size (especially for nanoscale system) on these properties is relevant. No less interesting and important transformations occurring when the system is heated, as it is also associated with changes in the composition and dispersion. The phenomenon of change in the properties during various treatment is not only interested, but it may serve as an indicator for external influence. Furthermore, the possibility of light compaction of nanostructured metal powders may be used in additive technology. Non-trivial nature of the influence of the phase composition on the thermal expansion coefficients is also a define-divided interest.

Acknowledgments

These investigations were carried out using equipment of Kemerovo Scientific Centre SB RAS, and financial supported by RFBR (grant № 14-03-31648 mol_a) and the Ministry of Education and Science of the Russian Federation (№ 2014/64).

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