Nanosize Powders of Transition Metals Binary Systems

Yu.A. Zaharov¹², V.M. Pugachev¹, V.G. Dodonov¹, A.N. Popova¹², R.P. Kolmykov¹, G.A. Rostovtsev⁴, O.V. Vasiljeva¹, E.N. Zyuzykina¹, A.V. Ivanov¹, I.P. Prosvirin³

¹Kemerovo State University, 650000, Russia, Kemerovo, Krasnaya st., 6
²Institute of Coal-chemistry and Material science of the RAS SB, 650000, Russia, Kemerovo, Sovetskiy av., 18
³Institute of Catalysis of the RAS SB, 630090, Russia, Novosibirsk, ak. Lavrentieva av., 5

E-mail: zaharov@kemsu.ru

Abstract. The review of the results obtained by the authors in the field of synthesis of Fe-Co, Fe-Ni, Co-Ni and Cu-Ni nanosize binary systems (NBS) by the liquid-phase reducing of metal chlorides by hydrazine (pH>10) and sodium tetrahydroborate (NaBH₄) (pH = 7-8) by the process conditions variation (temperature of reaction medium, concentration and input order of reagents) as well as NBS properties investigation is presented.

1. Introduction
The review of the results obtained by the authors in the field of synthesis of Fe-Co, Fe-Ni, Co-Ni and Cu-Ni nanosize binary systems (NBS) by the liquid-phase reducing of metal chlorides by hydrazine (pH>10) and sodium tetrahydroborate (NaBH₄) (pH = 7-8) by the process conditions variation (temperature of reaction medium, concentration and input order of reagents) as well as NBS properties investigation is presented.

2. Experiment and results
The basic stages of NBS synthesis were established [1-4] by the methods of X-ray structural (RSA), phase (RPA), fluorescent (RFA) and small angle X-ray scattering (SAXS) analyses.

The reducing by hydrazine was carried out by adding alkali in reaction medium before or simultaneously with hydrazine. Thus at first the fast reaction of sedimentation proceeds (1, see below) with the formation of mixed hydroxides. The hydroxides of the iron group metals as known belongs to a highly symmetric hexagonal brucite structure type, therefore it is natural to expect their co-crystallization under the NBS synthesis conditions at any components ratios. It was confirmed experimentally that the dependence of lattice parameter on composition has monotonous almost linear character (Vegard’s law) (see, figure 1).
Figure 1. Unit cell volumes of mixed hydroxide [Co,Fe](OH)$_2$ (1) and oxide-hydroxide phases of Fe-Co (2), Fe-Ni (3).

After sedimentation the basic Red-Ox process of interaction of cations occurring by hydroxides dissociation (counterreaction to 1) with hydrazine proceeds. In the case of simultaneous adding of alkali with hydrazine the process goes somewhat simultaneously with more fast one of hydroxides formation. On scheme below the basic reactions at mole ratio of metals 1:1 (for example) are given:

1) $\text{M}_1^{2+} + \text{M}_2^{2+} + 4 \text{OH}^- = \text{M}_1(\text{OH})_2 \cdot \text{M}_2(\text{OH})_2$

2) $\text{M}_1^{2+} + \text{M}_2^{2+} + \text{N}_2\text{H}_4 + 4 \text{OH}^- = \text{M}_1 \cdot \text{M}_2 + \text{N}_2 + 4 \text{H}_2\text{O}$

Copper hydroxide has more complex structure, its orthorhombic unit cell looks like pair of deformed brucite cells. Therefore mutual solubility of copper and nickel hydroxides is limited. At the temperature 298 K and the content of copper less than 30 mass % (here and further in the text the composition corresponds to metal only) the high-dispersed X-ray-amorphous mixed hydroxide with the brucite type structure is formed. This mixed hydroxide gradually crystallize if obtained suspension heats during 15-30 min at 358 K. If the contents of copper is from 70 to 90 mass % the moderately crystallized orthorhombic phase with the structure of copper hydroxide is formed.

The formation of mixed hydroxides in the given composition regions is confirmed by the fact that the obtained products are stable with heating up to 358 K for a long time whereas the pure copper hydroxide is quickly decomposed by dehydration forming the phase of black CuO even at room temperature (about 298 K). It should be noted that the aging was carried out at the conditions of alkali medium (pH $\approx$ 9) that promotes dehydration.

If the contents of copper ranges from 40 to 60 mass % the X-ray-amorphous product is also formed. This product also becomes black with time and the reflexes of CuO on the X-ray diffraction picture arise. Obviously it indicates that in this range of concentrations an oversaturated by copper metastable solid solution with brucite structure is formed, which is gradually decompose giving off copper oxide and water.

The X-ray investigation ex situ of nickel and copper hydroxides coprecipitated at the temperature 348-358 K corresponding to synthesis conditions showed that in such conditions only mixed hydroxides containing not more than 20 mass % of copper are stable. It is possible that at high temperature and alkalinity of reaction medium the high-dispersed mixed hydroxide is less stable. It is also possible, that
the priority (for copper) reaction in such conditions is copper oxide formation. The high-speed synchrotron radiation diffraction measurements in situ, planned in future, might give more clear answer to that question. It may also allow to establish what actually is subjected to reducing – mixed hydroxide or its mixture with copper oxide.

In the systems containing iron the coprecipitated hydroxides may turn into oxide-hydroxide phases (OHP) due to oxidation of Fe$^{2+}$. So the hydroxide Fe(OH)$_2$ as a component of mixed hydroxide turn according to RSA data into FeOOH form. As a result the stoichiometry similar to a brucite structure type remains. Thus the oxidation process is not due to introducing of oxygen into the substance but due to withdrawal of proton taking away an electron of iron atom. X-ray diffraction methods showed that both atomic and superatomic structure of the substance by this process remain almost unchangeable. The composition of the OHP phase formed may be expressed as: [Fe,M](OH)$_2$·FeOOH.

The higher charge and smaller size of Fe$^{3+}$ cations promotes their partial transition into the tetrahedral voids which in normal brucite structure are occupied by protons. This makes the OHP structure similar to the spinel one. The long heating or aging of OHP in water leads to dehydration and transformation of OHP in spinel. It is known that the substances with spinel type structure are rather persistent and more inert chemically in comparison with mixed hydroxides. As a result the final product in case of iron-containing systems may contain impurities of spinel and OHP phases.

On the other hand the formation of spinel or OHP thin film covering on a surface of metal particles may provide a protection against their further oxidation [5, 6] that is especially important in case of systems rich by iron. For example, it was established that the suppression of oxidation process (synthesis in an atmosphere of nitrogen) allows to obtain pure (without OHP and spinel impurities) but rather pyrophoric product. On the contrary, if synthesis is in condition of high aeration, the content of OHP and spinel impurities in final product increases. For example, the corresponding reactions for mole ratio of metals 2:1 are given below:

3) $4\text{M(OH)}_2$·$2\text{Fe(OH)}_2 + \text{O}_2 = 4\text{M(OH)}_2$·$2\text{FeOOH} + 2\text{H}_2\text{O}$

4) $\text{M(OH)}_2$·$2\text{FeOOH} = \text{MO}$·$2\text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O}$

It was shown [7, 8] that the formation of mixed oxides as a intermediate products is a favorable factor for the formation by the reducing process of mixed metal phases – solid solutions. The scheme of reducing by sodium tetrahydroborate near pH=7 is much more compli-cated. The results of products studying obtained by us using RPA, RFA, derivato-mass-spectrometry and X-ray photoelectron spectroscopy (RPES) at the temperatures 550-650 K in view of results [9] allows to present it in the first approximation in a form:

$$5) \text{M}_j^{2+} + \text{M}_2^{2+} \xrightarrow{\text{THB}} \text{M}_j \cdot \text{M}_2 \xrightarrow{550-650\text{K}} \text{M}_j \cdot \text{M}_2 \xrightarrow{-}{\text{B}_2\text{O}_3, \text{B}_2\text{O}_3^{-}}$$

The products obtained are usually X-ray-amorphous. By the heating up to the temperatures 550-650 K the crystallization of metal phase remaining in nano-size conditions and the quantitative growth of the latter owing to the thermal decomposition of borides, borate compounds and complicated complexes with boron (III) oxide formation, segregation of boron on the particles surface and apparently B$_2$O$_3$ formation are observed.
The combination of the methods of small-angle X-ray scattering (SAXS), scanning electron microscopy, specific surface determination (BET) and porosity allows to establish that all examined NBS synthesized according to scheme (1-4) are characterized by qualitatively similar morphology of the particles: nanocrystallites by the size of 6-30 nm (for different NBS synthesized by various conditions) with narrow size distributions (3-6 nm on a half-height of maximum according to SAXS data) forms compact agglomerates undestroyable by mechanical charge and ultrasound action with zero open porosity but high closed porosity, lager units (60-250 nm for various systems with different shape depending on NBS composition and conditions of synthesis) in its turn give friable globules of micron sizes easy destroyable by ultrasound treatment up to smaller agglomerates. The spatial organization of the particles may also be controlled by realization of synthesis in a constant magnetic field (1-5 kOe). The morphology of Cu-Ni nanoparticles looks simpler: the material consists of friable agglomerates which are formed directly from nanocrystallites by the size of 10-40 nm. The typical shapes of the NBS particles and mass distribution functions computed from SAXS data are given on figures 2, 3.

![Figure 2](image1.png)

**Figure 2.** Typical SEM micrograph of nanosystems (Fe-Co, Fe-Ni and Co-Ni).

![Figure 3](image2.png)

**Figure 3.** Mass-functions of particle size distribution according to SAXS data (for solid solutions Cu-Ni, Fe-Co, Fe-Ni, Co-Ni).
The phase portraits of studied NBS as cross-sections of phase conditions are generally correspond to the known phase diagrams of massive (macro-size) alloys provided conception on specific for each nanosystem raised temperature connected with their energy saturation. The phase composition of each NBS depending on chemical composition does not correspond to a fixed temperature above the temperature of synthesis and RPA, but corresponds to a certain temperature range, the borders of which are difficulty defined rigorously (figure 4). This is probably due to the fact that these NBS consist of particles of different sizes with different energy saturation.

![Figure 4](image)

**Figure 4.** Part of phase diagrams (–) and phase portraits at $T_{\text{eff}}$ ( ), of nanosystems: a) Fe-Co; b) Fe-Ni; c) Co-Ni (1 – the lattice parameters). Upper figures (a, b) – evaluation of saturation magnetization versus the system composition.

It is established [10] that for pure cobalt in the particle size range of 20-40 nm the FCC-phase is more preferred at smaller particle sizes and HCP-phase at larger ones. It is also found by X-ray diffraction methods (including SAXS) that the sizes of the crystallites (nanoparticles) for pure cobalt and examined NBS correspond to a specified range (figure 3).

According to the idea of the phase portraits shifting up to higher temperatures, both normal (hexagonal - HCP) and high-temperature (cubic - FCC) phases are present in the synthe-sized systems.
containing large amounts of cobalt (as well as pure cobalt). The almost complete disappearance of the hexagonal phase in the Fe-Co system already at 2 wt.% of iron (figure 7) allows us to determine satisfactorily the lower limit of the range of effective temperatures (figure 4) in this range of composition. Besides the relative content of FCC phase considerably increases with particle size (SAXS data) decreasing, achieved by higher concentrations of the reducing agent (figure 7). The HCP and FCC phases are also formed in the Co-Ni system at low concentrations of nickel.

Another important consequence of the shift of phase portraits up to higher temperature is the changing of limits of components mutual solubility, which is especially evident in the Ni-Cu system. In spite of phase diagram the formation of limited solid solutions of the nickel is observed at temperatures of synthesis and storage 80 °C and 25 °C respectively.

This allows us to determine qualitatively the range of effective temperatures for the system in the region of these components ratio (figures 5, 6).

![Figure 5. The lattice parameter of FCC-phase Ni-Cu.](image1)

![Figure 6. Part of phase diagrams (–) and phase portraits (□□□) of Ni-Cu nanosystems (according to figure 5).](image2)

![Figure 7. The intensity ratio of cobalt reflections: 101 (HPC-phase) versus 200 (FCC-phase) at the stoichiometric concentration of hydrazine hydrate (▲), in 2 (●) and 3 (■) times greater than its.](image3)

It should be noted however that higher mutual solubility of the components can also be connected with the non-equilibrium character of the metal particles process formation.
In contrast, another feature of the phase portraits of this NBS is that the solid solutions are formed with reluctance in thermodynamically allowed region. In this case it is probably connected with a significant difference in redox potentials of nickel and copper. In the region of relatively high contents of copper at \( E_{\text{Cu}}^{\text{Ox/Red}} > E_{\text{Ni}}^{\text{Ox/Red}} \) the reducing of \( \text{Cu}^{2+} \) cations goes significantly faster and the complicated layer non-equilibrium structures instead of solid solutions (allowed by phase diagram) are formed (figure 5).

The process of NBS oxidation also has some features:
- the kinetics of the process for all investigated systems in the region 50-150 °C (automatic gas micro-burette, atmosphere of oxygen) is three-stage: the fast initial stage with low activation energy of oxide films formation (according to RPES data) by the thickness of several nanometers, the second stage with the usual “parabolic” kinetic dependence (for sphere-like aggregates) and \( E_a = 26\div40 \) kcal/mol for different NBS and then the third stage – not trivial process with the almost constant rate of oxidation – up to observed oxidation degree (≈7%);
- the phase composition of NBS essentially influences speed of oxidation (according to the obtained phase portraits);
- in the NBS containing the metal of variable valence the consecutive oxidation reaction takes place: \( \text{Me}^0 \rightarrow \text{Me}^+ \rightarrow \text{Me}^{2+} \), and the relative rates of the stages ambiguously depends on particles surface etching;

the passivation of the particles by specially formed oxide-spinel (in case of Fe-Co and Fe-Ni systems) or enriched by nickel (for Cu-Ni system) thin surface films is observed; the partial auto-oxidation of NBS in high vacuum (≈10^-9 mm hg) or in the inert atmosphere is observed at raised temperatures (400 °C and more) as a general phenomenon, as we guess it may be owing to \( \text{O}_2 \) and \( \text{H}_2\text{O} \) accumulated in closed nano- and micropores.

It is established (SQUID-magnetometer together with ITC SB RAS) that the synthesized pure (RPA) solid solutions of Fe-Co, Fe-Ni and Co-Ni systems with narrow crystallite size distributions and sphere-like aggregates at optimum compounds (40-50 weight % Co, ≈90 weight % Fe) in the region 5÷350 °K have the magnetization saturation values on 10÷15% greater than the ones achieved for massive alloys and produced by other ways NBS of similar compounds [11, 12].

3. Conclusions
For the first time the comprehensive research of both NBS synthesis by the reducing of metal aqua-chlorides and its properties is carried out. Besides, it is shown general scheme of synthesis. Additionally, it is presented phase portraits of investigated nanosystems.

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