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Intermediates in Synthesis of a Nanostructured Fe–Co–Ni System

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Abstract

With a view to optimizing conditions for preparation of promising high magnetic nanomaterials, the dimensional peculiarities of which find the increasing use, we explored mixed iron, cobalt, and nickel hydroxides, *i.e.* intermediate products of synthesis by the method of reduction of precursors that refer to this class of nanostructured Fe–Co–Ni powders using methods of X-ray diffraction and derivato-mass-spectrometry. Precipitation of hydroxides was carried out under conditions of preparation of a polymetal but without a reducing agent, both in coprecipitation mode and separately. As established by crystal lattice parameters, iron in coprecipitated mixed hydroxides is largely oxidized to Fe³⁺, which is probably due to their nanoscale dimensionality determined using XPA. The composition of the resulting oxide-hydroxide phases (OHP) can be expressed by a formula of $w\text{Fe}(\text{OH})_2 \cdot x\text{Co}(\text{OH})_2 \cdot y\text{Ni}(\text{OH})_2 \cdot z\text{FeOOH}$, that crystallochemically corresponds to a structural type of brucite. When mixing suspensions of separately precipitated oxides, there occurs recrystallization in two phases, such as macrocrystalline, rich with iron, and superfine one, with its lower content and oxidized to a lesser degree. In addition to OHP, a spinel phase in fine dispersion is generated. Liberation of significant amounts of CO₂ at elevated temperatures points to the presence of carbonates in samples. Since they are not detected by means of X-rays, one may assume that the carbonate anion is embedded into oxygen layers of the structure of brucite of OHP.

Keywords: iron, cobalt, and nickel hydroxides, oxide-hydroxide phases, nanostructured Fe–Co–Ni system

INTRODUCTION

Nanoscale and nanostructured powders of mutual systems of iron group metals are interesting primarily due to specifics of their magnetic properties [1–3]. One of the most feasible and cost-effective methods of their preparation is a joint reduction with hydrazine from aqueous solutions of metal salts in an alkaline medium. Herewith, the final metal product may be presented by different mixed phases in different amounts (from one to

three) [4–7]. Intermediates in synthesis (due to high alkalinity) are metal hydroxides, the phase composition and structure of which affect properties of the target product. In addition, hydroxide oxidation is probable and as a result, the final metal product may be contaminated with hardly reducible oxide and oxide-hydroxide phases (OHP). Thus, a special study of intermediates in the preparation of superfine polymetal powders is necessary to clarify formation processes of essentially metal products and develop methods to regulate their properties.

EXPERIMENTAL

Hydroxide coprecipitation was carried out under conditions similar to those for the generation during synthesis of metal systems: salts in the total amount corresponding to metals 1.5 g (about 26 mmol) were dissolved in 60 mL of water, and then treated with 15 g of dry NaOH (375 mmol) at 90 °C. After alkali dissolution (after 10–15 s), 100 mL of water was added to reduce the temperature and decrease alkali concentration, then, the precipitate was separated using a Buchner funnel under vacuum and dried in a vacuum oven. Precipitates with the same compositions were obtained in a similar fashion from mixtures of separately precipitated hydroxides stirring them for 15 s after pouring in the common reactor. Suspensions of hydroxides for mixing were prepared in 20 mL of distilled water using 5 g of alkali in each case (125 mmol). The qualification of all reagents ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and NaOH) was pure for analysis. Samples and phase obtained in the coprecipitation

mode were marked with the letter “C”, and separately precipitated – “P”. The compositions of the samples are indicated with three-digit numbers, in which the figures represent the relative mass fractions of each metal in the order iron – cobalt – nickel. For example, a symbol of C226 indicates that the sample is obtained by coprecipitation of hydroxides containing metals in a mass ratio of 2 : 2 : 6 (or 20, 20, and 60 %). In case of the generation of several phases, they are additionally marked by the symbols of Fe – with relatively large iron content, and Ni – with its lower concentration; S are spinel phases.

Diffraction patterns were obtained using Difray-401 apparatus (Russia) in iron radiation. Measurements of the intensity of small angle scattering (SAS) were performed at KRM-1 device (Russia) for transmission, and also in the iron radiation by counting the impulses at points in the range of angles from 0.05 up to $3^\circ(0.002\text{--}0.35\text{ \AA}^{-1})$. Mass functions of particle size distribution were calculated according to SAS curves, in accordance with [8].

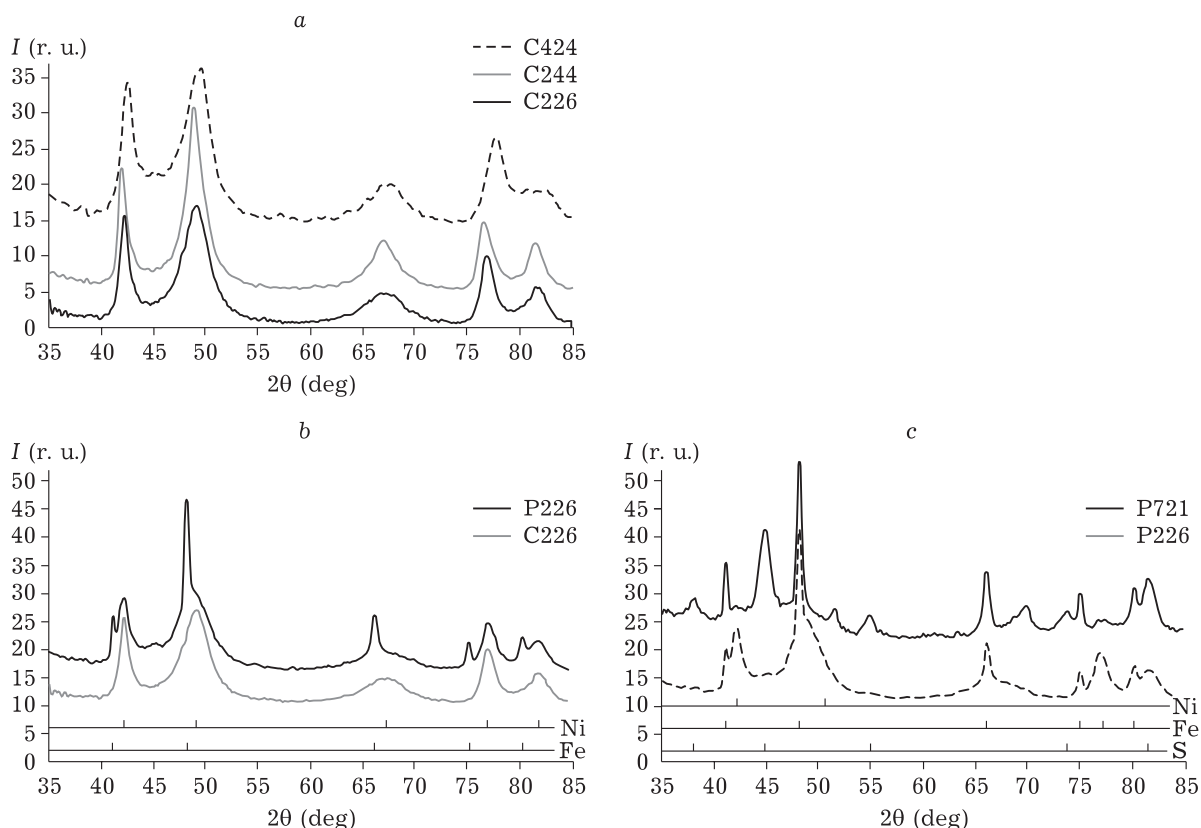


Fig. 1. Diffraction patterns of hydroxide products during separate and joint precipitation.

Differential thermal analysis (DTA) with simultaneous thermogravimetry was carried out using Netzsch STA 409 PC/PG derivatograph (Germany) combined with a quadrupole mass-spectrometer (10 °C/min heating rate, argon – carrier gas).

RESULTS AND DISCUSSION

Considered individual hydroxides have the brucite-type structure that is a two-layer dense packaging of hydroxide ions, in octahedral cavities of which cations are located. A close size of Fe^{2+} , Co^{2+} , and Ni^{2+} species suggests good miscibility of hydroxides, therefore, a monophasic system that is a three-component solid solution is generated indeed during coprecipitation (Fig. 1, a).

When mixing suspensions of three separately precipitated hydroxides, their partial cocrystallization occurs and, as a rule, two hydroxide phases with diffraction lines different by width are generated (see Fig. 1, b, c).

Nickel hydroxide and mixed hydroxides with its large content are usually generated as very small crystal flakes. This is due to the fact that neutral three-layer packages, where a layer of two-charged species is concluded, so that the packages themselves appear to be linked at the expense of relatively weak hydrogen bonds, and also the weak Coulomb attraction between the external layers of cations and those of hydroxyl anions from the neighboring packages. Apparently, in a series of nickel to iron, a bond between the packages increases and leads to an increase in sizes in this direction and the formation of larger crystals in as a whole. Figure 1 indicates phases with lower iron content and crystals smaller by size (2×14

nm) with symbol Ni; phases with higher iron content (conditionally iron) and larger crystals (20×100 nm) – symbol Fe.

In view of the above and according to the data of Table 1, there is an observed difference by line width and position when comparing C244 and C226 samples (phases). In general, based on data of Tables 1 and 2, crystal lattice parameters (CLP) are much lower than expected ones. The CLP of C424 phase that is richer with iron is even lower. This effect is already known [2] and driven by iron oxidation by air oxygen with the partial transformation of iron hydroxide $\text{Fe}(\text{OH})_2$ into OHP FeOOH . This phase may also crystallize according to brucite type because of the crystallochemical closeness of OH^- and O^{2-} ions. There are indications of the fact that both in iron hydroxide and mixed iron-containing hydroxides, this oxidation is carried out through “leaving” of hydrogen atoms from crystals and of course, is not accompanied by significant changes in the structure.

Thus, mixed iron-containing hydroxides, if protection measures from oxygen (air) are not taken, always consist of essentially hydroxides and OHP, for example, $x\text{FeOOH} \cdot y\text{Fe}(\text{OH})_2 \cdot z\text{Ni}(\text{OH})_2$, there will be no $\text{Fe}(\text{OH})_2$ component with complete oxidation of ferrous iron (hereinafter, simply iron). These transformations are of course more noticeable for nanoscale crystals. It is worth noting that the compositions of OHP phases indicated in ICDD databases as $2\text{FeOOH} \cdot \text{NiOOH}$ (see Table 2), apparently, in reality have a composition of $2\text{FeOOH} \cdot \text{Ni}(\text{OH})_2$, since the difference in one hydrogen atom is hard to detect when analysing the composition. Triply charged iron cations are smaller than doubly-charged ones of all three considered metals. Precisely this explains the fact that CLP of the resulting mixed

TABLE 1

Lattice parameters of some hydroxides of oxide-hydroxide phases (OHP) from ICDD databases

Parameter	PDE No.					
	13-0089	45-0031	14-0117	13-0087	14-0556	14-0558
	Composition					
	$\text{Fe}(\text{OH})_2$	$\text{Co}(\text{OH})_2$	$\text{Ni}(\text{OH})_2$	FeOOH	FeNi-OHP	FeCo-OHP
a , Å	3.258	3.191	3.126	2.941	2.965	2.970
c , Å	4.605	4.664	4.605	4.490	4.596	4.565
V , Å ³	42.33	41.13	38.97	33.63	34.99	34.87

TABLE 2

Lattice parameters of the resulting hydroxide phases

Parameter	Code No.					
	C226-Ni	C244-Ni	C424-Ni	P226-Fe	P226-Ni	P721-Fe
a , Å	3.120(4)	3.124(3)	3.090(2)	3.181(1)	3.116(4)	3,182(1)
c , Å	4.50(2)	4.617(12)	4.615(7)	4.649(2)	4.750(6)	4,657(2)
V , Å ³	38.8(2)	39.0(2)	38.16(9)	40.75(3)	39.93(14)	40,84(3)

iron-containing hydroxides including OHP are relatively small, while lines in diffraction patterns are shifted to larger angles.

Iron oxidability degree in the obtained compounds can be assessed within the accepted model, combining volumes of their elementary cells (VEC) from cell volumes of individual compounds additively (similarly to Vegard's law) and varying VEC of iron component ($x\text{FeOOH} \cdot y\text{Fe}(\text{OH})_2$) within 33.63–42.33 Å³ (see Table 1). These volumes (calculated in additivity approximation) for samples (phases) obtained by coprecipitation are 36.0; 34.8 and 36.0 Å³ for C226, C244, and C424, respectively. Hence (also according to the additive scheme), the molar fractions of Fe³⁺ in them are 0.73; 0.86 and 0.73, *i.e.* iron oxidation level in nanostructured mixed phases obtained by coprecipitation is quite high.

Two phases obtained from separately precipitated hydroxides are also four-component (considering two iron states), but iron oxidation level in them is clearly lower. Thus, VEC of both phases of P226 sample (40.8 and 39.9 Å³) are greater than the volume for the mixed C226 phase of the same composition (39.8 Å³). In principle, one may simply combine VEC of individual hydroxides in such a way to obtain values observed experimentally upon additive addition of volumes, for example, if P226 sample is resolved into phases with a composition of 1 : 1 : 1 and 1 : 1 : 5 (totally, the same 10 mass units). However, it is extremely unlikely that iron would not oxidize at all during synthesis from separately obtained hydroxides, especially since iron oxidation is visually noticeable (by the darkening of suspensions).

The generation of two phases during recrystallization of individual hydroxides is untrivial; one may presume that only P226-Ni phase is mixed, while the other one does not contain cobalt and nickel. There is a certain

logic in this: for example, the iron phase is dissolved slower, since its crystals are quite large, and this can be seen according to a small width of reflexes. However, to obtain an experimental value of VEC of 39.9 Å³ for P226-Ni phase, it is necessary to combine this phase volume considering 1.4 mass units (of two available) of non-oxidized Fe(OH)₂, and for the bulk of purely OHP, 0.6 units, *i.e.* 6 % of the total sample mass would remain, while it can be seen from the diffraction pattern that this fraction should be higher (see Fig. 1, b). Herewith, iron oxidation level in OHP would be 18 % (out of VEC of 40.8 Å³). If a value of 39.9 Å³ is combined with the involvement of OHP, and not just Fe(OH)₂, the proportion of purely iron phase would be even lower. Among other things, the calculation of phase composition is complicated by the presence of also the spinel phase of Fe₃O₄ (the brightest reflexes near 45 and 55°).

Thus, recrystallization into two mixed phases occurs during the interaction of three metal hydroxides after mixing. The degree of conversion of Fe²⁺ into Fe³⁺ in them does not exceed 18 %. The weak iron oxidability in a phase with its higher content can be explained by larger crystal sizes. There is much less iron in P226-Ni phase, if it is compared with C226 phase; apparently, iron is also less oxidized because of that. However, as a whole, the Fe³⁺ fraction also in samples of P type is not so small, it is simply concentrated in spinel phases, which is more apparent in samples with higher iron fractions, for example, P721 (see Fig. 1, c). While the Fe³⁺ fraction in these phases may reach 70 % and above.

A very weak dependence of CLP (line positions in X-ray patterns) on system composition should be noted for iron OHP (see Fig. 1, c, 2, a, and Table 2). Apparently, CLP auto-levelling occurs, when there is more iron in the system, the parameter of this

phase decreases (compared to iron hydroxide) due to the greater degree of iron oxidability, when there is less iron – due to the greater content of relatively small cobalt and especially nickel cations therein. The Fe^{3+} depletion of OHP that contain relatively much iron and are definitely capable of deeper oxidation proceeds due to the generation of separate superfine spinel phases of various compositions ($w\text{FeO} \cdot x\text{CoO} \cdot y\text{NiO} \cdot z\text{Fe}_2\text{O}_3$). CLP of these mixed spinels is very weakly dependent on the compound, therefore, it is hard to judge by line position even about the fact, if there are cobalt and nickel in spinel composition.

To assess the rate of recrystallization of hydroxides into mixed phases, experiments with different times of carrying out the process were conducted. Recrystallization proceeds fast and mainly ends in 15–20 s after mixing hydroxide suspensions, which is natural, as freshly-precipitated hydroxides are more dispersed than aged ones and (due to a larger surface) relatively fast, despite the low solubility, yield a material to generate new phases, apparently, even less soluble. Changes during further carrying out the process occur; however, they are not very significant (see Fig. 2). A decrease in the amount of macrocrystalline P217-Fe phase with a simultaneous increase in superfine spinel (a reflex near 45°) is most noticeable, in other words, iron oxidation into P217-Fe becomes the main process.

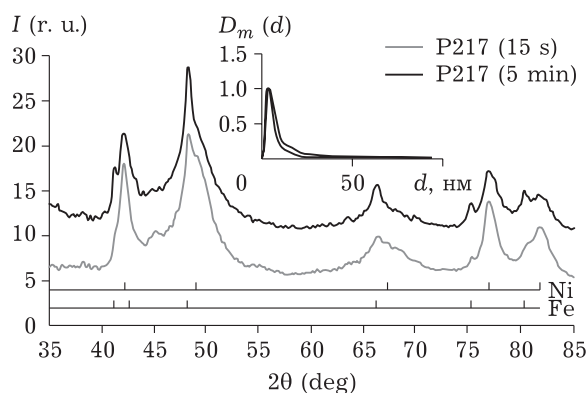


Fig. 2. Diffraction patterns of a mixture of separately precipitated Fe, Co, and Ni hydroxides (20, 10 and 70 %) isolated from a reaction medium after 15 s and 5 min of ageing; in the insert: a change in the mass functions for particles size distribution in P217 sample in time at a relatively long recrystallization process.

The SAS spectra and a change in particle size distributions calculated therefrom confirm the marked rearrangement of sizes (see the insert in Fig. 2).

Iron is oxidized stronger with its large content in the system and already after 15–20 s, iron-rich P217-Fe becomes the main phase in the system after mixing hydroxide suspensions. The lines of P217-Ni that contain significant amounts of Fe^{3+} are low-intense and are mainly lost in the background of the main phases (see Fig. 2).

Iron oxidation process proceeds most intensely during mixing hydroxides because of a high temperature of the medium; therefore, the difference in the number of P217-Fe and P217-S phases after cooling and a long procedure of separation, drying, and storing until obtaining diffraction patterns remains substantial.

The amount of spinel remaining after reduction with hydrazine of hydroxides and OHP decreases dramatically, in other words, only the strongest line near 45° can be seen in diffraction patterns (Fig. 3). Apparently, cobalt and nickel are present in this spinel in the minimum amounts, since iron oxidation mainly proceeds even before mixing hydroxides. Reduction processes become the dominant ones after mixing. The main metal phase is the body-centred cubic phase, typical for this composition region of Fe-Co-Ni nanostructured system [9]. A small amount of the face-centered cubic phase is the result of the reduction of nickel and cobalt at reference time in regions locally enriched by them. From this point on, these midget crystals are partially enlarged, aligned by composition, and also partially absorbed by crystals in the body-centred cubic phase.

Herewith, lack of the third possible phase with a hexagonal dense packing, typical for cobalt in the temperature range up to $420\text{--}430^\circ\text{C}$ is consistent with the concept being developed by the authors [5, 10], according to which the energetic state of nanoscale crystals can be characterised by so-called effective (elevated) temperatures (T_{eff}), which on the phase diagrams correspond to phase compositions close or equal to the observed ones in nanoscale systems at low temperatures. According to our estimates [4], T_{eff} of the nanostructured system of Fe-Co and Fe-Ni bimetal lies in the $380\text{--}450^\circ\text{C}$

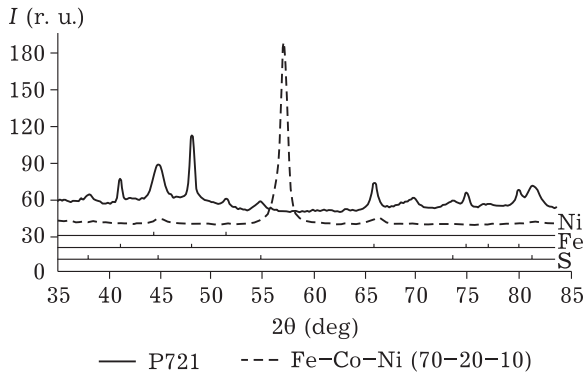


Fig. 3. Diffraction patterns of the mixture of separately precipitated of Fe, Co, and Ni hydroxides Fe, Co, Ni (70, 20 and 10 %) and their reduction products.

region; therefore, the generation of precisely the face-centered cubic phase in Fe-Co-Ni nanostructured system is more favourable.

The resulting mixed hydroxides contain significant amounts of sorbed gases, *i.e.* H₂O and CO₂ (mainly) and O₂, as demonstrated by combined TGA-DTA-MSA measurements (Fig. 4). This is due to high dispersion of powders, their plate-like structure (see above) and, accordingly, a large surface. Thermal desorption of gases is carried out in the 50–130 °C range and accompanied by the endothermic effect. Multi-stage processes

accompanied by isolation of water and CO₂, and also endothermic (according to DSC) thermal decomposition of impurities proceed at elevated temperatures. Extrema (DSC, DTG, and MSA-H₂O) in the range of 170 °C is the display of thermal decomposition of impurity hydroxides. Isolation simultaneity of H₂O and CO₂, and also endoeffect and mass loss (extrema in DTG, DTA, and MSA curves) at 260 and near 360 °C are a sign embedding of small (from the ratio of ion currents with me 18 and 44 in MSA) amounts of CO₃²⁻ into OHP lattice. For that reason, separate carbonate phase generation is not recorded by XPA and DMA methods and decomposition is observed as thermal decomposition of a single OHP. Herewith, the presence of stages of the process probably reflects different coordinations of hydroxide groups and differences in their energy bonds with Fe²⁺, Co²⁺, and Ni²⁺ species, which causes the presence of different reaction regions.

CONCLUSION

When coprecipitating crystallochemical related brucite-like iron, cobalt, and nickel hydroxides from salt solutions with alkali, brucite-like mixed hydroxides are also

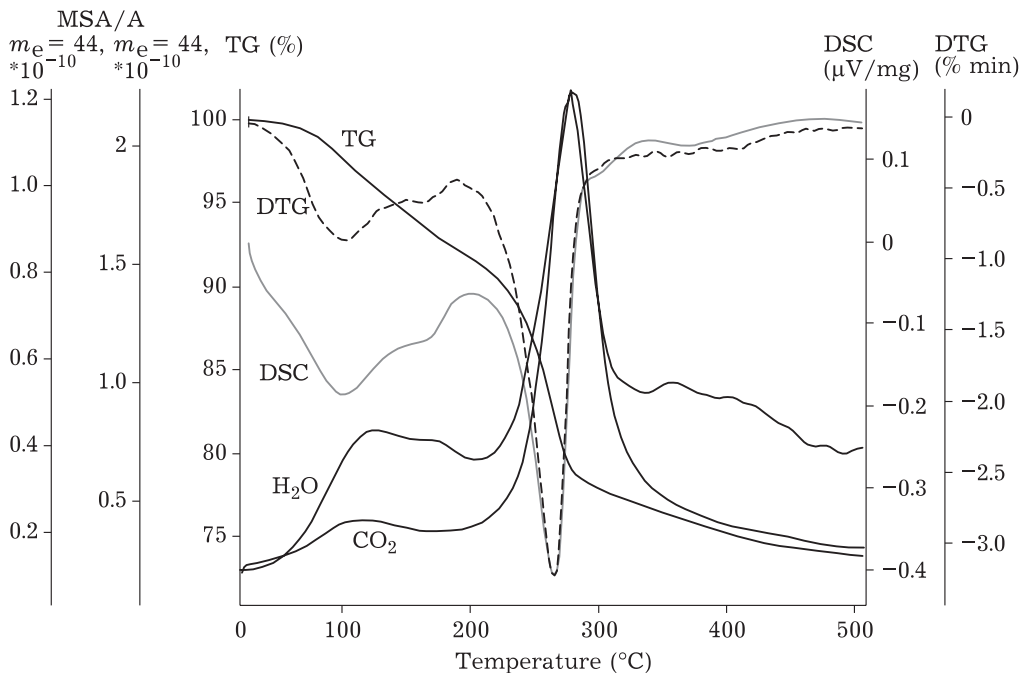


Fig. 4. Thermogravimetry (TG), differential thermogravimetry (DTG), differential scanning calorimetry (DSC), and mass spectra of C226 sample.

generated. The latter act as precursors for obtaining Fe–Co–Ni nanostructured system during their reduction with hydrazine. Iron in the resulting hydroxide phases is mainly present in +3 oxidation state, as established. High iron oxidability degree is due to small size of hydroxide crystals. When obtaining mixtures, similar by composition, from separately precipitated hydroxides, two brucite-like phases are generated. The latter substantially differ by diffraction line width: a phase with more narrow lines (macrocrystalline) contains relatively more iron, the one with wider ones (low dimensional) – relatively less. In addition, spinel phases are also generated. Herewith, iron in coprecipitated brucite-like hydroxides is substantially less oxidized than in obtained ones from separately precipitated. Ageing of lightly oxidized phases at elevated temperatures leads to their deeper oxidation, dehydration, and transformation to superfine spinels.

On the contrary, if a reducing agent (hydrazine) is added to the reaction mixture right after mixing three hydroxides, spinel generation is minimized. In addition to OH^- , mixed hydroxides also contain CO_3^{2-} и O^{2-} anions. Triangular carbonate anions are able to be readily embedded into the brucite structure, oxygen layers of which also consist of regular oxygen triangles. Therefore, separate phases of carbonates in mixed hydroxides are not formed and their stricter definition is carbonate-containing oxide–hydroxide phases.

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