

Characteristic of the zinc- and nickel-containing iron-oxygen nanophases formed on the steel surface under the rotation-corrosion dispergation conditions

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The nanosized powders formed on the steel surface contacting with zinc and nickel inorganic water salt solutions under the rotation-corrosion dispergation (RCD) conditions have been studied using an X-ray diffraction method, thermal analytical measurements (TG / DTG, DTA) and scanning electron microscopy. It was shown that the formation of a single mineral phase of a non-stoichiometric spinel ferrite when zinc and nickel nitrate solutions were used as the dispersion medium, but in the presence of chloride-containing salts three mineral phases (spinel ferrite, lepidocrocite, and goethite) were determined in the phase composition of the surface powders. When sulfate solutions were chosen as the dispersion medium the mixed hydroxysulfate layered double hydroxides (LDHs) simultaneously appeared among other components of the powders. Due to exchange of cations Fe(II) and other 3d-metals between the disperse phase and dispersion medium the mixed LDH structures achieved stability against further oxidation and phase transformation. Hence, the presence of mixed LDHs in the phase composition of the powders significantly complicates the obtaining of monomineral phases of spinel ferrites or iron oxides when the RCD method is applied.

Key words: the rotation-corrosion dispergation method, non-stoichiometric Zn- and Ni-containing spinel ferrites, mixed layered double hydroxides (LDHs), nanopowders.

Introduction

Nowadays the interest in the obtaining of various functional materials is closely connected with the creation of new and improvement of the existent methods of nanosynthesis. Nanosized iron-bearing particles characterized by ferrimagnetic and superparamagnetic properties are widely used as a precursor material for technical and biomedical aims [1, 2]. For instance, polymorphic iron oxides and spinel ferrites as well as metallic iron nanoparticles may be related to the most typical structures belonging to such kind of materials. Due to the small particle size the physical-chemical and colloid-chemical properties of nanodisperse oxides and ferrites, such as mechanical, electrical, magnetic, thermal, optical, and chemical, differ from their macroscopic analogues [3]. Additional features of iron oxide particles are determined by the synthesis method [4] and the presence of doped elements, especially metals, in their structure [5].

Recently we have proposed a new method for the obtaining of nanosized iron oxyhydroxides, iron oxides, 3d-metal spinel ferrites and core&shell composites consisting of a ferrimagnetic core and precious metal shell. The method was called the rotation-corrosion dispergation (RCD) [6]. It is carried out on the iron or steel electrode surfaces contacting with water salt solutions under galvanostatic conditions in the open-air systems. The application of the

RCD-method permits to obtain various polymorphic iron-oxygen powders which phase composition and physical-chemical properties may be particularly regulated by the chemical composition of the water solutions contacting with the electrode surface [7, 8].

The purpose of our work is to study the phase composition, thermal behavior and morphology of the nanopowders formed on the steel surface contacting with nickel- and zink-bearing water chloride, nitrate, and sulfate salt solutions in the open-air systems under the rotation corrosion dispergation conditions.

Objects and method of the research

The formation of the nanosized iron-oxygen-containing powders on carbon steel surface via the rotation-corrosion dispergation route was provided by using a rotating disk electrode that periodically contacted with 3*d*-metal water salt solutions and the air [6]. The disk electrode was made of finished steel (St3), which composition had, %: C — 0,14—0,22; Si — 0,05—0,15; Mn — 0,4—0,65; Cr — 0,3; Ni — 0,3; P — 0,04; S — 0,05; N — 0,01. The steel surface was exposed to mechanical treatment and further activation using concentrated sulfuric acid. The activated disk electrode was repeatedly rinsed in distilled water and onwards it was placed into the cell filled with the 3*d*-metal water salt solution. We chose the following inorganic salt solutions: zinc and nickel chlorides, nitrates and sulfates as the dispersion medium. The concentration of the metal cations in water solutions got 100 mg/dm³ and pH value was set 6,5. The formation of disperse nanostructures on the steel surface lasted 24 h at the temperatures 20 and 50 °C. The temperature conditions were set using TS-1/80-SPU thermostat. Afterwards the disk electrode was dried in the air atmosphere and the surface nanostructures were exposed to a complex physical-chemical investigation including an X-ray diffraction (XRD) method, thermal analytical measurements (TG / DTG, DTA) and scanning electron microscopy (SEM). The phase composition of the surface nanopowders, their thermal behavior, as well as morphology and the primary particle size of the powder components were studied in our investigation.

The phase composition of the nanopowders was conducted using computer-aided X-ray diffractometer (DRON – UM1) equipped with two Soller's slits and filtered radiation of cobalt anode CoK_α. The rate of recording was set 1 °C/min, and the interfacial Woolf-Bragg's angle made up 80—90 degrees. The coherent scattering region (CSR) characterizing the size of the primary particles or crystallites was calculated according to the standard Debye-Scherrer's formula.

A simultaneous study of thermogravimetric and differential thermal properties (TG-DTA) of the powders was performed in the static air atmosphere by derivatigraph Q-1500D (Hungary). The record was made using computer data registration. The parameters of the pattern recording were the following: the samples of 150 mg were heated at the rate 10 °C/min from 20 to 1000 °C; the sensitivity was 20 mg; TG — 500, DTG — 500, and DTA — 250. The samples were placed into a corundum crucible and covered by quartz beaker to create the equal temperature field.

A scanning electron microscopy (SEM) using JOEL-6700 microscope equipped with an energy-dispersive and cathode-luminescence attachment to obtain EDS-spectra was chosen as the main visual method of the research. The mass ratio of iron to the second 3*d*-metal (nickel or zinc) in the samples was

determined using an X-ray fluorescence spectroscopy (XRFS) carried out in the automatic spectrometer "ElvaX" equipped with a titanium anode.

Results and discussion

The X-ray diffraction data of the nickel- and zinc-iron-oxygen-containing powders formed on the steel surface within 24 h at the temperatures 20 and 50 °C are present in fig. 1 and 2, respectively. Also, when the nickel chloride and nickel nitrate solutions were contacting with activated surface of the steel electrode at $T = 20$ °C the obtained powders included three iron-oxygen mineral phases such as spinel ferrite and polymorphic ferric oxyhydroxides — lepidocrocite γ -FeOOH and goethite α -FeOOH (fig. 1, *a—d*). But spinel ferrite phase got the predominant importance when the temperature was enhanced up to 50 °C, and under the following conditions both ferric oxyhydroxides were present in the patterns only as the admixtures. At that the temperature of the phase formation process strongly influenced not only the phase composition of the surface powders but their crystallinity degree. Whereas the powders, especially obtained in NiCl_2 and $\text{Ni}(\text{NO}_3)_2$ systems, at $T = 20$ °C

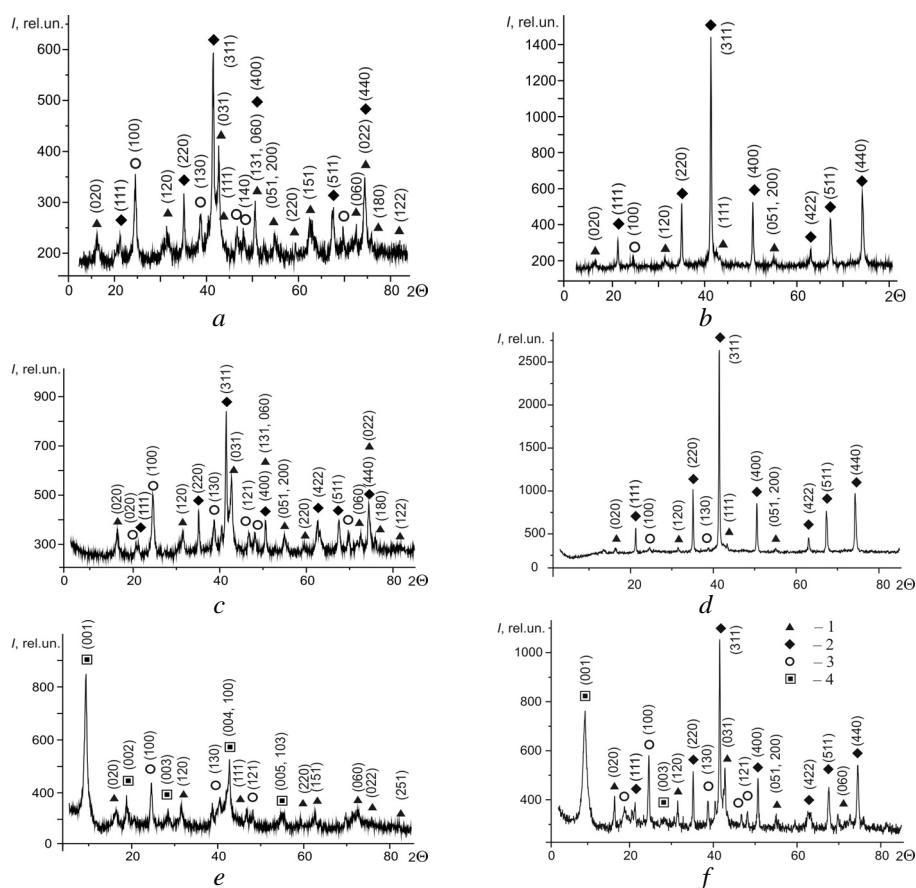


Fig. 1. XRD-patterns of the powders formed on the steel surface contacting with the following water salt solutions: *a* — NiCl_2 , $T = 20$ °C; *b* — NiCl_2 , $T = 50$ °C; *c* — $\text{Ni}(\text{NO}_3)_2$, $T = 20$ °C; *d* — $\text{Ni}(\text{NO}_3)_2$, $T = 50$ °C; *e* — NiSO_4 , $T = 20$ °C; *f* — NiSO_4 , $T = 50$ °C, where $c\text{Ni}^{2+} = 100 \text{ mg/dm}^3$, and $\text{pH} = 6,5$. Numbers correspond to the mineral phases: 1 — lepidocrocite; 2 — spinel ferrite; 3 — goethite; 4 — Ni(II)—Fe(III)— SO_4^{2-} —LDH.

may be characterized as weak crystalline structures, the spinel ferrite particles formed in the mentioned systems at $T = 50\text{ }^{\circ}\text{C}$ were well crystallized.

When nickel sulfate solution was chosen as the dispersion medium the phase composition of the powders formed at $T = 20\text{ }^{\circ}\text{C}$ included the mixed Ni(II)—Fe(II—III)— SO_4^{2-} layered double hydroxide (LDH) as a main mineral phase and relatively small amount of ferric oxihydroxides (fig. 1, *e*). But when the T of the process was increased to $50\text{ }^{\circ}\text{C}$ the mixed Ni(II)—Fe(II—III)— SO_4^{2-} LDH as well as spinel ferrite were determined as two main phases in the powders, but goethite and lepidocrocite played the role of mineral admixtures (fig. 1, *f*). According to the lattice parameters the mixed LDH corresponds to hydrohonessite-like Green Rust II (hydroxysulfate) (JCPDS file No 41-0014), that keeps stability against further oxidation and phase transformation within a relatively long term at sufficiently high temperatures.

The analysis of the XRD data obtained for the zinc-containing systems showed the differences in the comparison with the nickel-containing systems. So, spinel ferrite and lepidocrocite are present in the patterns of the powders formed at $T = 20$ and $50\text{ }^{\circ}\text{C}$ in the zinc chloride systems (fig. 2, *a, b*). In addition, the

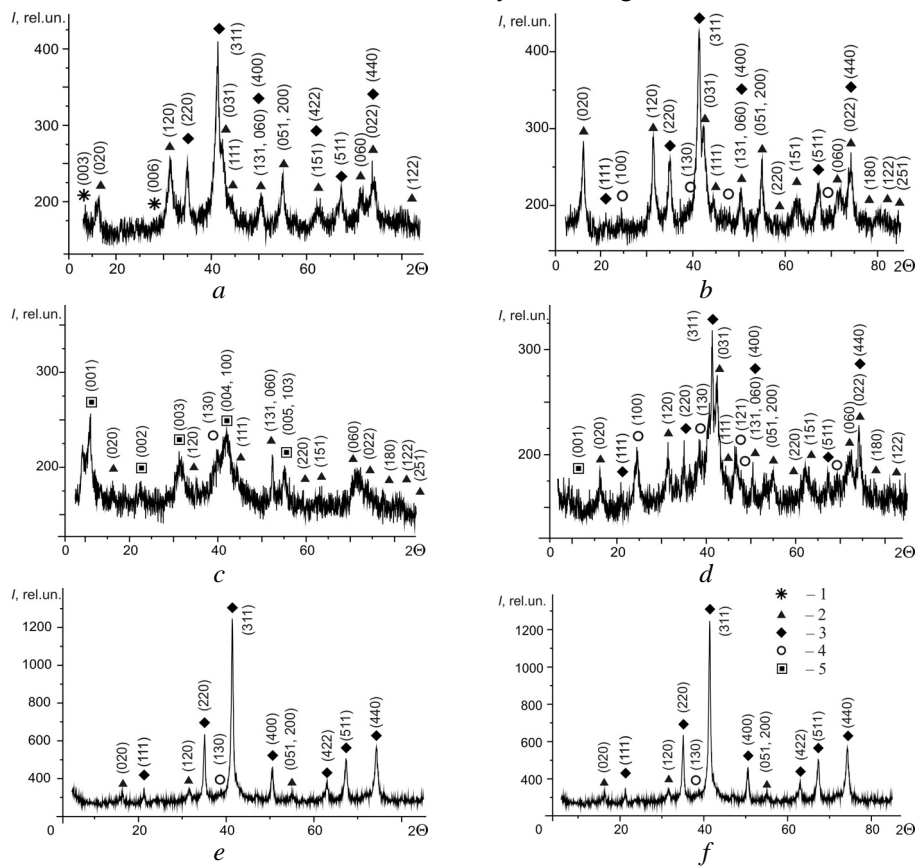


Fig. 2. XRD-patterns of the powders formed on the steel surface contacting with the following water salt solutions: *a* — ZnCl_2 , $T = 20\text{ }^{\circ}\text{C}$, 1 h in water; *b* — ZnCl_2 , $T = 20\text{ }^{\circ}\text{C}$, 3 h in water; *c* — ZnSO_4 , $T = 20\text{ }^{\circ}\text{C}$; *d* — ZnSO_4 , $T = 50\text{ }^{\circ}\text{C}$; *e* — $\text{Zn}(\text{NO}_3)_2$, $T = 20\text{ }^{\circ}\text{C}$; *f* — $\text{Zn}(\text{NO}_3)_2$, $T = 50\text{ }^{\circ}\text{C}$, where $c\text{Zn}^{2+} = 100\text{ mg/dm}^3$, and $\text{pH} = 6.5$. Numbers correspond to the mineral phases: 1 — Zn(II)—Fe(III)—Cl—LDH; 2 — lepidocrocite; 3 — spinel ferrite; 4 — goethite; 5 — Zn(II)—Fe(III)— SO_4^{2-} —LDH.

weak reflexes of mixed Zn(II)—Fe(II—III) LDH related to hydrotalcite-like Green Rust I (hydroxycarbonate or hydroxychloride) (JCPDS file No 40-0127) are seen in the first case, and weak goethite peaks appear in the pattern in the second case. All mineral components of the powders are weakly crystallized. When the steel surface was contacting with zinc sulfate solutions the mixed Zn(II)—Fe(II—III)—SO₄²⁻ LDH and lepidocrocite were formed at $T = 20$ °C (fig. 2, *c*), whereas spinel ferrite together with ferric oxihydroxides were formed at $T = 50$ °C (fig. 2, *d*). The powders obtained at both temperatures are characterized as weak crystallized structures. But when the zinc nitrate solutions were contacting with steel surface the phase composition of the powders did not depend on temperature: in both cases the main mineral phase was well crystallized spinel ferrite. Also, to the first approximation the usage of the metal (II) nitrate salts permit to obtain homogenous monomineral powders on the steel surface applying the rotation-corrosion dispergation method.

The crystal lattice parameters and the primary particle size (CSR) of the powder compounds are present in table 1. As it is clearly seen, the CSR of lepidocrocite varies from ~10 to ~23 nm and the smallest particles correspond to chloride systems whereas the biggest particles relate to sulfate systems. The range of the goethite particle size is narrow in comparison with the previous case and it equals 14—23 nm. But variation of the magnetite CSR is more significant and the smallest particles we can see in zinc chloride systems (~10 nm). Generally, the average particle size of magnetite formed in nickel-containing systems is bigger than in zinc-containing systems and it equals 22—28 nm in the first case and ~15—28 nm in the second case.

The mass. % distribution of the metals in the powders formed in the presence of nickel- and zinc-containing water salt solutions is seen in table 2. Also, the average ratio Fe to Ni in the chloride and nitrate solutions varies from 96 : 4 to 92 : 8 mass. %, but for sulfate-bearing system it gets 82 (86) : 18 (14) mass. %. The comparison of nickel- and zinc-containing systems shows the decrease of iron part in the powders and mass. % ratio Fe : Zn varies from ~85 : 15 to ~70 : 30.

We have chosen four samples to study the thermal behavior of the mineral powders formed on the steel surface under the RCD conditions in the presence of nickel and zinc-containing water salt solutions. The in-depth analysis of the nickel-bearing systems permits to determine the influence of anion composition on the phase transformation of the powder compounds. Moreover, due to the presence of the mixed Me(II)—Fe(II—III)—SO₄²⁻ LDH in the phase composition of the corresponding powders we have analyzed both NiSO₄ and ZnSO₄ systems. According to the obtained data we can follow the appearance of two endoeffects in all DTG curves. The first minimum is fixed in the temperature range of 110—137 °C and, probably, it corresponds to the loss of the adsorbed water. The second endothermic peak in the temperature range of 270—281 °C is related to the hydroxylation of oxyhydroxide lattice and formation of the iron oxide phases (table 3). But both sulfate-containing samples show an additional endothermic peak in the temperature range of 622—822 °C. Those thermal effects are accompanied by the mass loss of the powders on the TG curves (28—30%) probably because of the phase transformation (dehydroxylation) of mixed LDH and total destruction of SO₄²⁻-species. On the contrary, the mass loss of the nitrate- and chloride-containing samples amounts to only 4,5%. Two exothermic peaks point to the oxidation

Table 1. The lattice parameters and primary particle size of the mineral components of the powders obtained on the steel surface under the RCD conditions

Salt solution	T, °C	The characteristic of the mineral phases, nm				
		γ -FeOOH		α -FeOOH		Fe ₃ O ₄
NiCl ₂	20	a = 0,3875 b = 1,2695 c = 0,3022	V = 0,1486 d = 10,4	a = 0,4649 b = 0,9946 c = 0,3027	V = 0,14 d = 14,5	a = 0,8404 V = 0,5935 d = 21,9
	50	a = 0,3875 b = 1,2630 c = 0,2922	V = 0,1430 d = 13,3	a = 0,4668 b = 0,9874 c = 0,3007	V = 0,1386 d = 21,0	a = 0,8419 V = 0,5967 d = 28,2
NiSO ₄	20	a = 0,3876 b = 1,2546 c = 0,3059	V = 0,1482 d = 13,7	a = 0,4630 b = 0,9969 c = 0,3016	V = 0,1392 d = 14,6	a = 0,8370 V = 0,5864 d = 24,8
	50	a = 0,3889 b = 1,2608 c = 0,3022	V = 0,1482 d = 20,0	a = 0,4623 b = 0,9868 c = 0,3001	V = 0,1369 d = 18,9	a = 0,8389 V = 0,5904 d = 26,3
Ni(NO ₃) ₂	20	a = 0,3872 b = 1,2599 c = 0,3029	V = 0,1477 d = 14,3	a = 0,4637 b = 0,9650 c = 0,3022	V = 0,1352 d = 23,2	a = 0,8386 V = 0,5797 d = 21,9
	50	—	—	—	—	a = 0,8399 V = 0,5925 d = 26,3
ZnCl ₂	20	a = 0,3894 b = 1,2527 c = 0,3079	V = 0,1502 d = 8,9	—	—	a = 0,8399 V = 0,5925 d = 9,9
	50	a = 0,3876 b = 1,2638 c = 0,3067	V = 0,1502 d = 13,3	—	—	a = 0,8395 V = 0,5917 d = 10,4
ZnSO ₄	20	a = 0,3858 b = 1,2692 c = 0,3062	V = 0,1499 d = 21,7	a = 0,4626 b = 1,0106 c = 0,3013	V = 0,1408 d = 16,2	a = 0,8404 V = 0,5936 d = 19,1
	50	a = 0,3855 b = 1,2630 c = 0,3044	V = 0,1482 d = 23,4	a = 0,4636 b = 0,9950 c = 0,3007	V = 0,1387 d = 20,1	a = 0,8397 V = 0,5921 d = 27,4
Zn(NO ₃) ₂	20	—	—	—	—	a = 0,8403 V = 0,5933 d = 15,8
	50	—	—	—	—	a = 0,8398 V = 0,5923 d = 28,2

ferrous cations in the spinel ferrite lattice and phase transformation of Fe₃O₄ doped by Ni²⁺ or Zn²⁺ into maghemite γ -Fe₂O₃ at 200—245 °C and polymorphic transformation of γ -Fe₂O₃ into hematite α -Fe₂O₃ at 300—338 °C.

The SEM images of the mineral phases formed on the steel surface contacting with NiCl₂, Ni(NO₃)₂, and Zn(NO₃)₂ water solutions are present in fig. 4. Generally, the morphology of the iron-oxygen surface structures is similar and it does not depend on the anion composition of the dispersion medium contacting with the steel surface. Whereas ferric oxyhydroxides are characterized by plate-like or lamellar shape of the particles (fig. 4, a, e, g, h),

Table 2. Distribution of 3d-metals in the powders formed on the steel surface contacting with nickel and zinc water solutions under the RCD conditions

Salt solution	T, °C	Distribution of the metals, mass. %	
		Fe	Ni or Zn
NiCl ₂	20	93,9	6,1
	50	92,5	7,5
NiSO ₄	20	82,0	18,0
	50	85,9	14,1
Ni(NO ₃) ₂	20	95,9	4,1
	50	92,1	7,9
ZnCl ₂	20	79,4	20,6
	50	81,3	18,7
ZnSO ₄	20	69,3	30,7
	50	84,1	15,9
Zn(NO ₃) ₂	20	79,8	20,2
	50	84,9	15,1

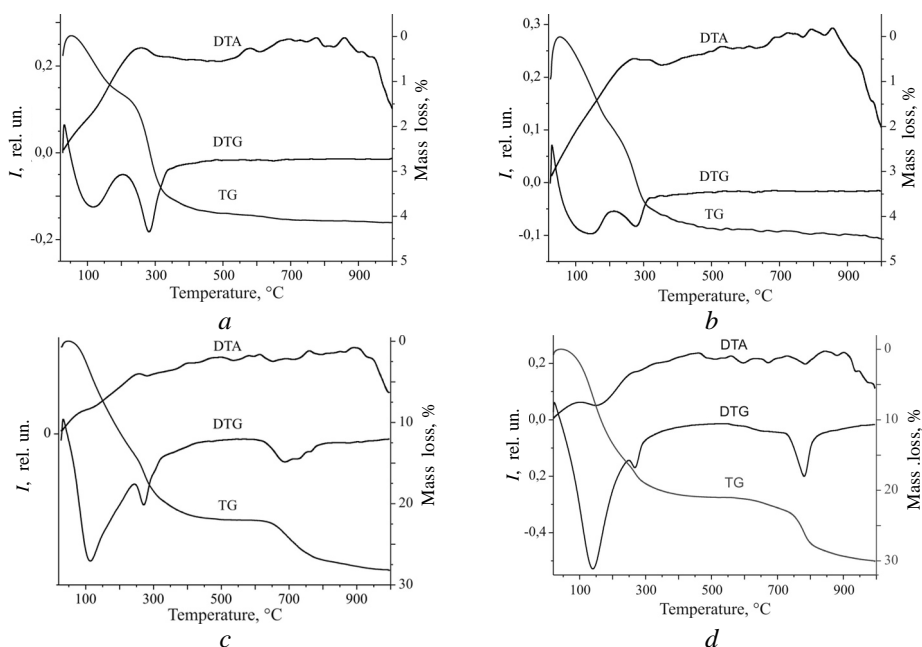


Fig. 3. TG-DTA curves of the powders formed on the steel surface contacting with water salt solutions: *a* — NiCl₂; *b* — Ni(NO₃)₂; *c* — NiSO₄; *d* — ZnSO₄.

the spinel ferrites form spherical particles and aggregates (fig. 4, *d–g*). The relicts of the mixed Ni(II)—Fe(II—III) LDHs belonging to Green Rust I structure are seen in fig. 4, *b, c*. Their morphology can be described as chaotic disordered plates and lamellas.

The EDS spectra of the mineral phases formed when the steel surface was contacting with NiCl₂ solution are summarized in table 4. Generally, the average quantity of nickel associated with lepidocrocite phase is ~4,9 mass. %, its quantity in goethite is ~0,75 mass. %, and in spinel ferrite ~ 8,7 mass. %. The

Table 3. The characteristic of thermal effects of the powders formed on the steel surface under the RCD conditions

The salt solution	Endoeffects, °C			Exoeffects, °C		Total mass loss, %
	H ₂ O _{ads}	Dehydroxilation	LGH destruction	Fe ₃ O ₄ → γ-Fe ₂ O ₃	γ-Fe ₂ O ₃ → α-Fe ₂ O ₃	
NiCl ₂	113	281	—	200	338	4,5
Ni(NO ₃) ₂	131	274	—	208	312	4,5
NiSO ₄	110	270	622—784	238	320	28,2
ZnSO ₄	137	272	725—822	245	299	30,2

manganese and sulfur admixtures got into mineral phases, probably, from the material of the steel. The average content of Fe in all probes reaches ~72,78 mass. %, and content of O, respectively, equals ~22,23 mass. %.

Also, the analysis of the experimental data points to the significant effect of anions of the water salt solutions on the phase compositions of the nanosized powders formed on the steel surface under the RCD conditions. Depending on the geometrical shape of anions two types of Fe(II)—Fe(III) layered double hydroxides (Green Rusts) may be formed on the steel or iron surfaces. Planar and spherical anions (Cl⁻, CO₃²⁻) coordinate iron hydroxide layers as GR I and three dimension anions (SO₄²⁻) take place in GR II structure [9]. Such metastable phases play the role of the precursor species for the various polymorphic ferric oxides and hydroxides. The presence of 3*d*-metal cations in the solutions leads to the exchange processes between Fe(II) of solid phase and Me²⁺ of dispersion medium. As a result the more stable mixed Me-Fe LDHs, inherited the Green Rust structure, appeared among other surface mineral phases. According to literature data nickel as well as zinc can incorporate into a Green Rust lattice and form various LDH structures corresponding to the first [10, 11] and the second [12—14] lattice's type of Green Rust, respectively. Whereas Fe(II)—Fe(III) layered double hydroxides under standard conditions do not keep stability against oxidation and solid state transformation into lepidocrocite [15] or its dissolution-re-precipitation into magnetite [16], the mixed LDH structures, due to Fe(II) exchange, lose the possibility for oxidation and, as a result, for phase transformation.

Hence, one of the mixed LDH applications is their thermal treatment to obtain chemically pure mixed oxides at $T \sim 450\text{—}600$ °C [17] or spinel ferrites in the range from $T \sim 750$ °C [18] to 1100 °C [19]. The formation of pure nickel spinel ferrites via calcination of tailored hydrotalcite-like hydroxysulfate layered double hydroxides as a single molecular precursor was mentioned in [20]. In such case the precursor species was heated at 900 °C for 2 h to obtain the powder including two phases: α-Fe₂O₃ and NiO, afterwards the oxide mixture was sintered at 1100 °C for 10 h and then slowly cooled to the room temperature. This kind of the procedure is sensitive to metal molar ratios and it needs to keep certain stoichiometry. But when the molar ratio of Me²⁺/Fe³⁺ is broken the non-stoichiometric iron oxides or magnetite doped by 3*d*-metal cations are formed in the system [21].

The comparison of the powders formed via rotation-corrosion dispergation route on the steel surface contacting with zinc and nickel inorganic salt solution

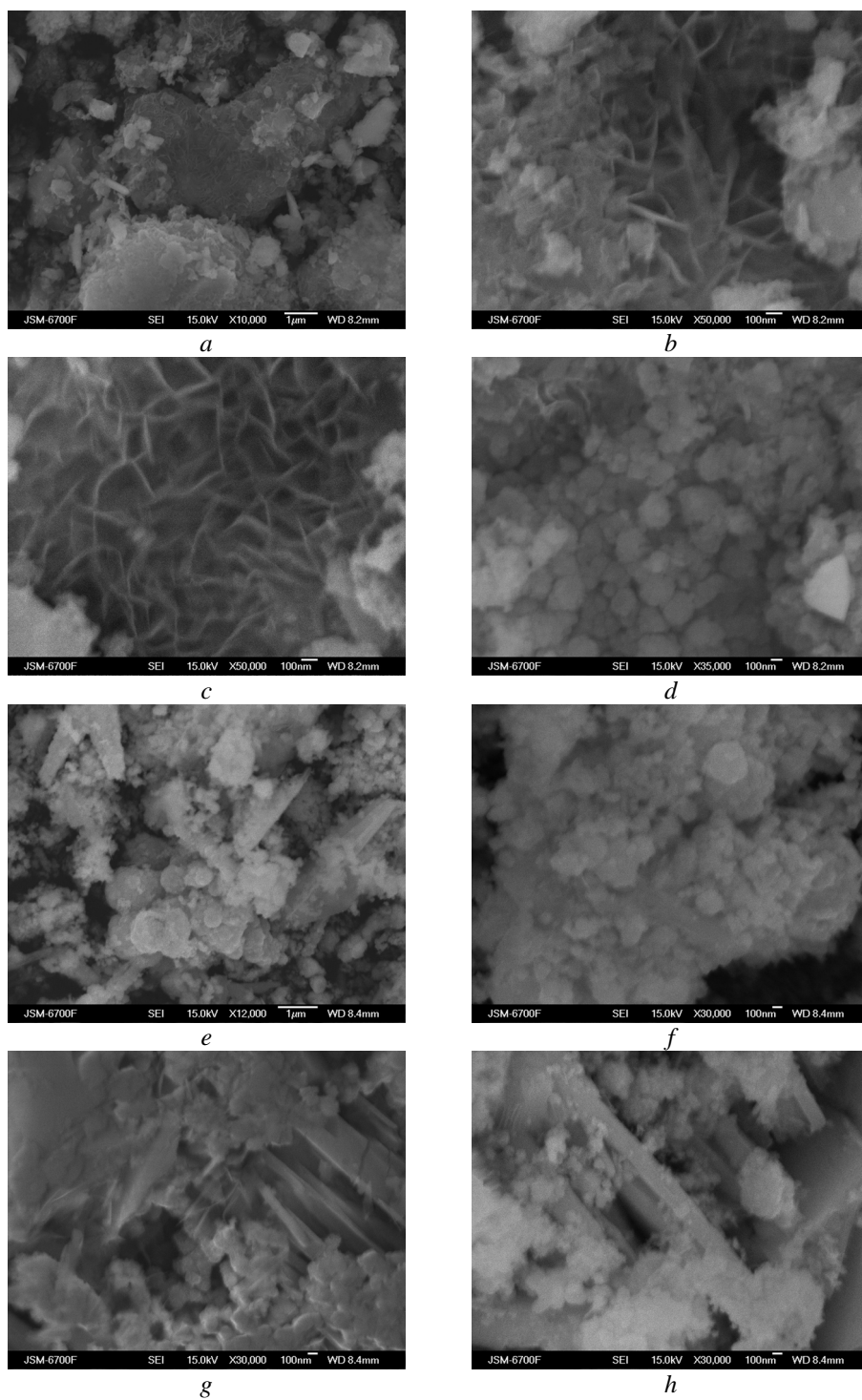


Fig. 4. SEM-images of the surface structures formed on the steel surface under the rotation-corrosion dispersion conditions in the presence of water salt solutions: *a* — the general view of the surface structures (NiCl_2); *b*–*c* — mixed Ni(II)—Fe(II—III) LDH; *d* — spinel ferrite ($\text{Ni}_x\text{Fe}_{(1-x)}\text{Fe}_2\text{O}_4$) (NiCl_2); *e* — the general view of the surface structures ($\text{Ni}(\text{NO}_3)_2$); *f* — spinel ferrite ($\text{Ni}_x\text{Fe}_{(1-x)}\text{Fe}_2\text{O}_4$) ($\text{Ni}(\text{NO}_3)_2$); *g*, *h* — lepidocrocite plates and spherical spinel ferrite particles ($\text{Zn}(\text{NO}_3)_2$).

Table 4. The chemical composition of the mineral phases formed on the steel surface contacting with nickel chloride solution

Mineral phase	Number of probe	The quantitative analysis of chemical elements, mass. %				
		O	Fe	Ni	Mn	S
Lepidocrocite	1	22,23	71,65	4,32	1,80	—
	2	22,23	69,86	4,88	3,03	—
	3	22,23	70,72	5,26	1,80	—
	4	22,95	67,83	6,46	1,98	0,79
	5	22,24	71,83	3,52	2,41	—
Goethite	1	22,27	77,73	—	—	—
	2	22,26	76,70	1,04	—	—
	3	22,25	75,90	1,85	—	—
	4	22,26	76,90	0,84	—	—
	5	22,27	77,70	0,03	—	—
Spinel ferrite	1	22,14	66,14	11,57	0,14	—
	2	22,21	70,45	5,82	1,51	—

with the products of the thermal transformation of mixed LDH precursors formed via co-precipitation of respective salts shows a few differences. Namely the appearance of the spinel ferrites as a single phase on the steel surface is fixed in the systems where the mixed LDH structures are not formed, for example $\text{Ni}(\text{NO}_3)_2$ (fig. 1, *d*) or $\text{Zn}(\text{NO}_3)_2$ (fig. 2, *e, f*). But when the relatively stable phase of mixed hydroxysulfate LDHs is formed the spinel ferrite is not obtained at $T = 20\text{ }^\circ\text{C}$ (fig. 1, *e, 2, c*) or co-exists with LDHs and ferric oxyhydroxides at $T = 50\text{ }^\circ\text{C}$ (fig. 1, *f, 2, d*). In our previous work we showed that the heating of the copper and cobalt-bearing powders formed under the RCD conditions at $T = 740\text{ }^\circ\text{C}$ led to the formation of a single hematite phase. No other oxide peaks were present in the XRD patterns. The XRFS study confirmed the association of iron and copper or cobalt in the chemical composition of the powders. Moreover, the relative quantity of the doped metal remained the same in the wide temperature range ($50\text{--}740\text{ }^\circ\text{C}$). So, such powders may be used to obtain monomineral polymorphic ferric oxides ($\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$) doped by 3*d*-metal cations.

In addition, the role of cations of the dispersion medium in the formation of polymorphic ferric oxyhydroxides was widely discussed in the scientific sources. In conformity with our objects nickel may be included into a goethite lattice without destruction of its crystal structure [22]. At that zinc cations protect the lepidocrocite particles against dissolution in ferrous sulfate medium, but nickel ions do not affect the morphology and crystallinity of $\gamma\text{-FeOOH}$ [23]. Ferrous cations are usually adsorbed on the lepidocrocite surface in water medium and may be exchanged for nickel cations to form surface-modified iron oxides [24]. The analysis of our systems confirmed that only $\gamma\text{-FeOOH}$ appeared on the steel surface contacting with all zinc-containing water solutions, but both γ - and $\alpha\text{-FeOOH}$ co-existed in the phase composition of the powders when the steel surface was contacting with nickel-containing solutions. At that, the relative quantity of goethite part was less in comparison with the lepidocrocite part.

Conclusions

The anion composition of the water salt solution contacting with steel surface under the rotation-corrosion dispergation conditions play an important role in the formation of not only the phase composition of the disperse surface powders but their crystallinity as well. Whereas, the usage of zinc and nickel chlorides leads to obtaining of two or three phases powders including non-stoichiometric spinel ferrites and ferric oxyhydroxides, nitrate salts permit to form the single spinel ferrite phase. But in the presence of sulfate solution the mixed layered double hydroxides appear among powder components.

A thermogravimetric and differential thermal analysis of the powders shows four thermal effects corresponding to the loss of the adsorbed water in the range of 110—137 °C, hydroxylation at 270—281 °C, transformation of Fe₃O₄ doped by Ni²⁺ or Zn²⁺ into maghemite γ -Fe₂O₃ at 200—245 °C, and polymorphic transformation of γ -Fe₂O₃ into hematite α -Fe₂O₃ at 300—338 °C. But both sulfate-containing samples show an additional endothermic peak accompanied by the mass loss (28—30%) in the temperature range of 622—822 °C.

All mineral phases that are present in the powders belong to nano objects and their primary particle size is 10—23 nm for lepidocrocite, 14—23 nm for goethite and ~15—28 nm for spinel ferrite. Depending on the chemical compositions of the water salt solutions the mass. % distribution of the metals in the powders (Fe : Me) varies from 96 : 4 to ~70 : 30.

The morphology of the iron-oxygen structures included in the powders does not depend on the anion composition of the dispersion medium contacting with the steel surface. Particularly ferric oxyhydroxides and mixed Ni(II)—Fe(II-III) LDHs have a plate-like or lamellar shape, and spinel ferrites form spherical particles.

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Характеристика цинк- и никельсодержащих железо-кислородных нанофаз, полученных на поверхности стали в условиях ротационно-коррозионного диспергирования

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Наноразмерные смеси железо-кислородных фаз получены на поверхности стали, контактирующей с водными растворами неорганических солей цинка и никеля, в условиях ротационно-коррозионного диспергирования. Смеси исследованы

методами рентгенофазового аналізу, дифференціального термічного аналізу (ТГ / ДТГ, ДТА) і скануючої електронної мікроскопії. Показано, що при використанні в якості дисперсійної середовища розчинів нітратів цинку і нікелю утворюється єдина мінеральна фаза нестехіометричної ферришпінелі. В той же час в присутності СГ-содержащих розчинів в складі порошків визначено три мінеральні фази (ферришпінель, лепідокрокит і гетит). При використанні в якості дисперсійної середовища SO_4^{2-} -содержащих розчинів в складі порошків одночасно з іншими фазами утворюються змішані шаруваті подвійні гідроксиди (ШПГ) заліза і цинку або нікелю. Обмін катіонами Fe(II) і 3d-металів між дисперсною фазою та дисперсійною середовищем веде до стабілізації структури ШПГ, що значно ускладнює отримання при їх термічному перетворенні мономінеральних фаз ферришпінелі або оксидів заліза.

Ключові слова: метод ротаційно-корозійного диспергування, нестехіометричні Zn- і Ni-содержащие ферришпінелі, змішані шаруваті подвійні гідроксиди, нанопорошки.

Характеристика цинк- і нікелевмісних залізоокисневих наночастинок, отриманих на поверхні сталі в умовах ротаційно-корозійного диспергування

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Нанорозмірні суміші залізоокисневих фаз отримані за умов ротаційно-корозійного диспергування на поверхні сталі, яка контактує з водними розчинами неорганічних солей цинку і нікелю. Їх було досліджено методами рентгенофазового аналізу, диференційного термічного аналізу (ТГ / ДТГ, ДТА) і сканованої електронної мікроскопії. Показано, що при використанні у якості дисперсійного середовища розчинів нітратів цинку та нікелю у складі порошків утворюється єдина мінеральна фаза нестехіометричної ферришпінелі. Водночас у присутності СГ-вмісних розчинів у складі порошків визначено три мінеральні фази (ферришпінель, лепідокрокит і гетит). При використанні у якості дисперсійного середовища SO_4^{2-} -вмісних розчинів у складі порошків, одночасно з іншими фазами з'являються змішані шаруваті подвійні гідроксиди (ШПГ) заліза та цинку або нікелю. Обмін катіонами Fe(II) і 3d-металів між дисперсною фазою та дисперсійним середовищем веде до стабілізації структури ШПГ, що значною мірою ускладнює отримання при їх термічному перетворенні мономінеральних фаз ферришпінелі або оксидів заліза.

Ключові слова: метод ротаційно-корозійного диспергування, нестехіометричні Zn- і Ni-вмісні ферришпінелі, змішані шаруваті подвійні гідроксиди, нанопорошки.