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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Joint Reduction of Fe(III), Ni(II), and Co(II) Ions in Solution in Contact with Aluminum

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Abstract—Joint reduction of iron group metals in aqueous solutions on a dispersed aluminum matrix was studied. The powders obtained were examined by X-ray phase analysis and electron scanning microscopy.

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The development of new generations of structural and functional materials is a topical problem. A possible way to solve this problem is variation of the composition of a system used a precursor.

It is well known that evolution of any physicochemical systems occurring under nonequilibrium conditions can lead to formation of fractal structures and nanocomposites [1]. For example, dendritic structures of frequently formed, e.g., in the course of nonequilibrium electrolytic deposition of metals and solidification of alloys under the conditions of strong supercooling, or in the course of phase decomposition. These methods can be considered as formation of nanostructures in the bulk of a matrix under the conditions of its chemical modification. This process allows the parameters of the particles in the matrix to be controlled in the step of their formation and varied in the course of material operation.

Much researchers' attention is attracted today by synthesis of metallic composites with elemental aluminum or its compounds as a matrix [2–6]. Owing to unique combination of the protective properties of surface oxide–hydroxide layers and intrinsic chemical activity, aluminum under definite conditions chemically reacts with the environment to form products exhibiting a set of specific properties [7, 8]. According to the results of numerous studies, the chemical activity of finely dispersed aluminum powders toward water and aqueous solutions of chemical compounds considerably exceeds the chemical activity of the compact metal [9, 10]. Many authors believe [7, 9, 10] that this is due to the developed surface of the powders and to the strongly defective state of the surface oxide–hydroxide coatings of the particles, and also to intense heating of the solid phase in the course of the oxidation [10]. These factors can strongly affect the extent and character of the interaction of compact and dispersed aluminum matrices with an aqueous solution containing metal ions. Of particular interest is contact deposition of iron group metals on a dispersed aluminum matrix. This process may lead to the development of powdered systems with variable composition and properties, showing promise as precursors of compact materials and coatings.

Alloys and composites based on iron and aluminum occupy a particular place among intermetallic systems promising from both theoretical and applied standpoint. They exhibit a unique set of physicochemical, mechanical, magnetic, and corrosion properties. However, iron aluminides are not still demanded by the industry because of the lack of a relatively simple and cheap procedure for their preparation. Today Fe–Al systems are prepared by mechanochemical methods which are not always efficient and are power-consuming.

It was proposed previously to prepare alloys and composites based on the Fe–Al binary system from aqueous solutions by contact exchange of metals on aluminum microparticles [11]. This process occurs in solution under normal conditions and is accompanied by the release of a large amount of heat, mainly due to ionization of aluminum. The deposition of Fe(0) from such solutions occurs in two steps: Fe(III) → Fe(II) → Fe(0), with simultaneous ionization of the aluminum base and formation of an α-Fe layer on its surface. As a result, dendritic spherical particles with large internal cavities and pores are formed, which determines the low bulk density of the powder [11]. In the process, threadlike nuclei of submicrometer cross section can be formed in particle pores.

EXPERIMENTAL

Experiments were performed with close-cut fractions of dispersed aluminum (85 ± 15 μm, purity no less than 99.0%), with a specific surface area of 260 $cm^2\ g^{-1}$. The chemicals we used were $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $CoCl_2$ (analytically pure grade). The molar ratio of the starting aluminum powder and precursor was 1.5 : 1 in all the experiments.

To study the process kinetics, we took samples at regular intervals of time and examined them by X-ray fluorescence analysis on a VRA-20L installation (Carl Zeiss) under the following conditions: LiF 200 analyzer crystal, voltage 55 kV, current 35 mA, X-ray tube with a tungsten anode, collimator 2, SZ counter, discriminator 1.0 V, and sensitivity 3×10^4–1×10^5 counts $s^{-1}\ cm^{-2}$. The degree of precursor reduction to metal was estimated from variation of the concentration of ions of the corresponding elements in solution. The experimental error was governed by the methods used and amounted to 5%.

The chronopotentiograms in a suspension of dispersed aluminum were recorded with an EPV-1 platinum electrode and an EVL-1MZ-1 silver chloride reference electrode.

The samples we obtained were analyzed with a DRON-2 X-ray diffractometer to determine their chemical and phase composition. To reduce the background from scattering of the primary X-ray beam in air, we used long-wave FeK_α radiation with a β-filter. The diffraction patterns were recorded in the following mode: voltage 30 kV, current 15 mA, recording range 2θ 10°–160°. The diffraction patterns were processed with MAUD 1.999 multifunctional software [12, 13]. As a reference for comparing the line profiles (to determine the size of coherent scattering regions and microstresses), we used annealed copper foil.

Analysis and recording of microscopic images of the initial aluminum and powders obtained were performed with a Philips SM XL-30 TMP scanning electron microscope at the following parameters: ΔE scale 10 keV (0–500), acquisition time T = 100 s, E_{probe} = 30 keV. The size of the microanalysis area was varied from 20 × 30 to 50 × 75 μm.

Electrolytic codeposition of two or several metals is of particular interest because of the mutual influence of the jointly reduced ions on the rate of electrochemical processes [14]. It is known [14–17] that, in joint reduction of Fe(II) and Ni(II) ions, the electrochemical reaction is conjugate, i.e., the rate of discharge of their ions differs from the rate at which these ions are reduced separately. It was shown in a number of papers [14, 17] that the rate of reduction of Fe(II) ions increases by a factor of almost 3 in joint electrodeposition with Ni(II). On the contrary, the rate of reduction of Ni(II) in joint deposition with Fe(II) decreases by a factor of approximately 8. In the course of nickel electrodeposition, hydrogen is released at a considerably higher rate than in joint deposition of iron and nickel, because of the lower overvoltage of hydrogen on nickel.

The experiments performed [18] suggest that the reactions of Fe(III) and Ni(II) reduction when these ions are present in solution simultaneously are conjugate, i.e., the successively occurring steps Fe(III) → Fe(II) → Fe(0) initiate the reaction Ni(II) → Ni(0).

Both conjugated reduction reactions can be adequately described by first-order rate equations

$$c(\mathrm{Fe}^{3+}) = c_0(\mathrm{Fe}^{3+}) \exp(-kt)\ ,$$

$$c(\mathrm{Ni}^{2+}) = c_0(\mathrm{Ni}^{2+}) \exp(-kt)\ .$$

Previously, in studying joint deposition of Fe and Ni on an Al surface, we showed [18] that Ni metal is mainly deposited on the surface of the iron formed, with a certain part of iron undergoing oxidation and passing into the solution. In joint deposition of Fe(III) and Ni(II), a dark gray ferromagnetic powder is formed. The reaction is accompanied by considerable (to 373 K) heat-up of the reaction mixture. In joint deposition of Fe and Ni on Al, the powder is enriched in the less noble component [18]. The similar effect observed in electrodeposition is attributed in [19] to a shift of the metal deposition potentials when the metals are present simultaneously and to possible formation of passive films on the iron surface, preventing the deposition of Ni. Hydrogen evolution occurs simultaneously with the metal codeposition.

Similar process is observed in the Fe(III)–Co(II) system. When the cobalt and iron ions are present simultaneously, they are reduced somewhat more slowly compared to the separate reduction. At equal content of the Fe(III) and Co(II) ions in the initial solution, the deposition of both metals is virtually simultaneous (electrolytic alloy formation), and high degrees of iron and cobalt deposition are attained (Fig. 1). Apparently, electrolytic alloy formation may take place in the course of contact exchange when the metals are deposited simultaneously. Karbasov et al. [20, 21] reported on the alloy formation in the course of contact exchange and proved the existence of various kinds of alloys by X-ray diffraction analysis and electron microscopy.

Both conjugate reactions in joint reduction of iron and cobalt can be adequately described by first-order rate equations

$$c(\mathrm{Fe}^{3+}) = c_0(\mathrm{Fe}^{3+}) \exp(-kt)\,,$$

$$c(\mathrm{Co}^{2+}) = c_0(\mathrm{Co}^{2+}) \exp(-kt)\,.$$

According to reference data [22], joint reduction of Fe(III), Co(II), and Ni(II) with Al to the metals is thermodynamically possible, because the redox potential of the Al(III)/Al(0) couple is more negative than those of the corresponding couples involving Fe, Co, and Ni. However, the process is stongly complicated by the presence of the natural oxide film on Al and high overvoltage of the reduction of iron ions.

Joint Fe–Ni–Co deposition is a still more complex process and is determined both by the state of the surface of dispersed Al and by the concentration of the ions of these metals in solution. Iron and cobalt are deposited at approximately equal rate, and nickel, at a somewhat lower rate (Fig. 2). In ternary solutions, iron and cobalt are deposited virtually synchronously (Fig. 2, curves *1* and *3*), but cobalt is deposited more completely (98%, against 90% for Fe). In the case of Ni, the deposition rate increases after the lapse of 90 s, at the time by which iron and cobalt have been 50% reduced. This result is consistent with the previous data on the joint deposition of iron and nickel [18].

The results of studying joint deposition of metallic iron, nickel, and cobalt showed that the reactions of the Fe(III), Ni(II), and Co(II) reduction are conjugate, i.e., the consecutive reactions with iron ions initiate the reactions with the cobalt [Co(II) → Co(0)] and nickel [Ni(II) → Ni(0)] ions. The conjugate reduction reactions can be described by first-order rate equations (Fig. 2).

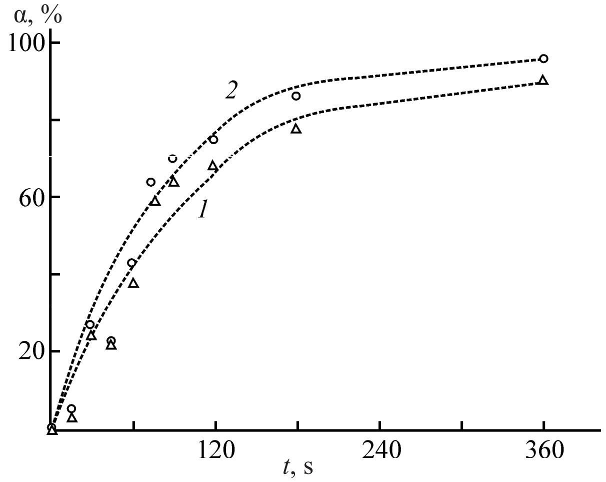

Fig. 1. Kinetic curves of joint deposition of (*1*) Fe and (*2*) Co from a 0.5 M $FeCl_3$ + 0.5 M $CoCl_2$ solution. Points refer to experimental data, and lines, to calculation; the same for Fig. 2. (α) Degree of deposition and (*t*) deposition time; the same for Fig. 2.

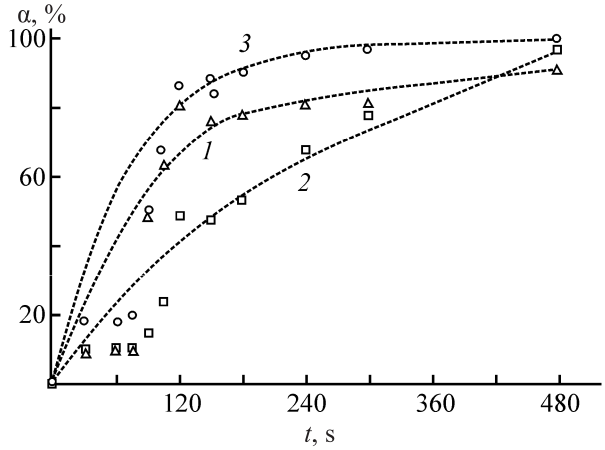

Fig. 2. Kinetic curves of joint deposition of (*1*) Fe, (*2*) Ni, and (*3*) Co from a 0.7 M $FeCl_3$ + 0.6 M $CoCl_2$ + 0.7 M $NiCl_2$ solution.

Deceleration of the reduction of Ni ions in joint deposition with Fe and Co may be due to increased adsorption of hydroxy compounds on the alloy surface, compared to deposition of the individual metals. The observed deceleration of the reduction of Ni ions indicates that the discharge of the ions is not facilitated by the alloy formation. Deceleration of the ion discharge in the course of the joint reduction can be largely attributed to a change in the concentration of the ions being discharged in the electrical double layer.

The reduction process can be illustrated by the chronopotentiograms obtained for dispersed aluminum suspended in the working solution (Fig. 3). Comparison of the chronopotentiogram (Fig. 3) obtained with a platinum electrode in the reaction mixture containing Al with the kinetic curves (Fig. 2) shows that, in the

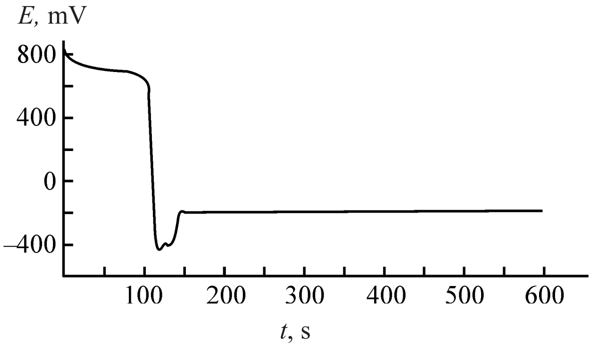

Fig. 3. Redox potential E as a function of time t in deposition of iron group metals (0.7 M $FeCl_3$ + 0.6 M $CoCl_2$ + 0.7 M $NiCl_2$).

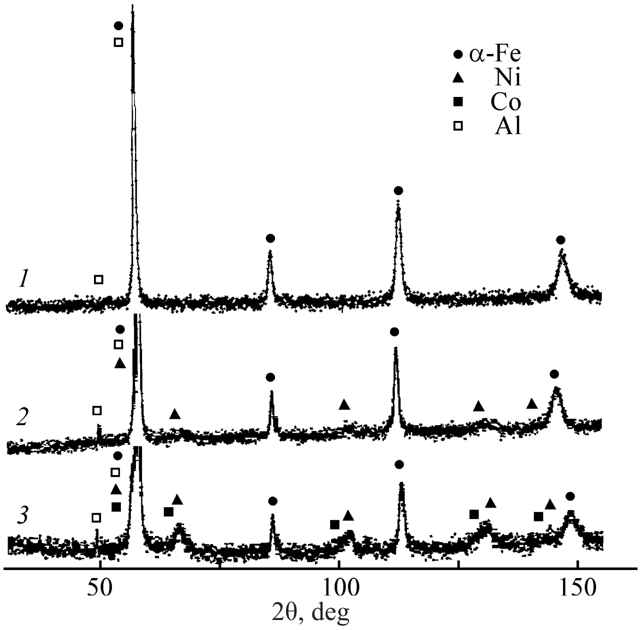

Fig. 4. Diffraction patterns of dispersed (*1*) Fe–Al, (*2*) Fe–Ni–Al, and (*3*) Fe–Ni–Co–Al samples. (2θ) Bragg angle.

course of the first 90 s, the potential smoothly decreases and the degree of metal deposition grows, also smoothly. The length of this portion of the curves strongly depends on the concentration of the starting reactants and is primarily caused by the presence of an oxide film on the aluminum particle surface. Furthermore, the potential does not decrease significantly until the nickel deposition starts. After the drop toward the negative region, the potential fairly actively shifts toward more positive values and then gets stabilized. It is known [23] that a metal being reduced can fully plug the pores of the powder, which leads to termination of the contact exchange. In the process, the electrode potential becomes close to the equilibrium potential of the more electropositive components (Fe, Ni, Co) in the solution. The chronopotentiogram (Fig. 3) indicates that the deposit fully blocks the aluminum surface. According to [20, 21], plateaus in the chronopotentiograms correspond to the formation of solid solutions or intermetallic compounds in the surface layer.

According to the results of X-ray phase analysis (Fig. 4) and local microanalysis, the powders obtained are mechanical mixtures of crystallites of iron group metals and aluminum, like the Fe–Al samples obtained previously [11, 24]. The amount of residual Al can be readily controlled by treating the powder with an alkali solution and can be reduced to tenth fractions of percent. When the powder is not kept in an alkali, an amorphous phase (probably pseudoboehmite) is detected, and with time bayerite crystals formed from metastable products of aluminum dissolution also appear [25]. In accordance with the results of X-ray structural and phase analysis and of local microanalysis, it can be concluded that the systems under consideration can be classed with substitution solid solutions with atoms of the major components (iron group elements) partially substituted in the crystal lattices by aluminum atoms. Furthermore, intermetallic phases of iron group elements are also detected. The process kinetics is strongly affected by the size and state of the surface of the aluminum particles.

Electron microscopic examination of particles taken from the solution after the metal deposition shows that they are virtually always spherical with the size similar to that of the starting Al particles (Fig. 5). This fact allows control of the properties of the synthesized particles by varying the parameters of the initial Al matrix. The presence of a large number of nuclei on the surface of coarse particles, in combination with the systems of cracks and pores, promotes the development of the metal surface, which may be very important in the possible use of such powders as heterogeneous catalysts. Furthermore, an important feature of the powders obtained is the presence of internal cavities.

It should be noted that, virtually in all the experiments, we clearly observed the formation of nanostructures in the form of whiskers (Fig. 5). However, on the surface of particles obtained in the Fe–Co system, there are also conical flaky individuals with a mean size of 100–200 nm (Fig. 5). Such a structure of the surface, in combination with the phase composition of the objects, is responsible for the specific properties of the Al–M systems (M = Fe, Ni, Co) obtained from aqueous solutions.

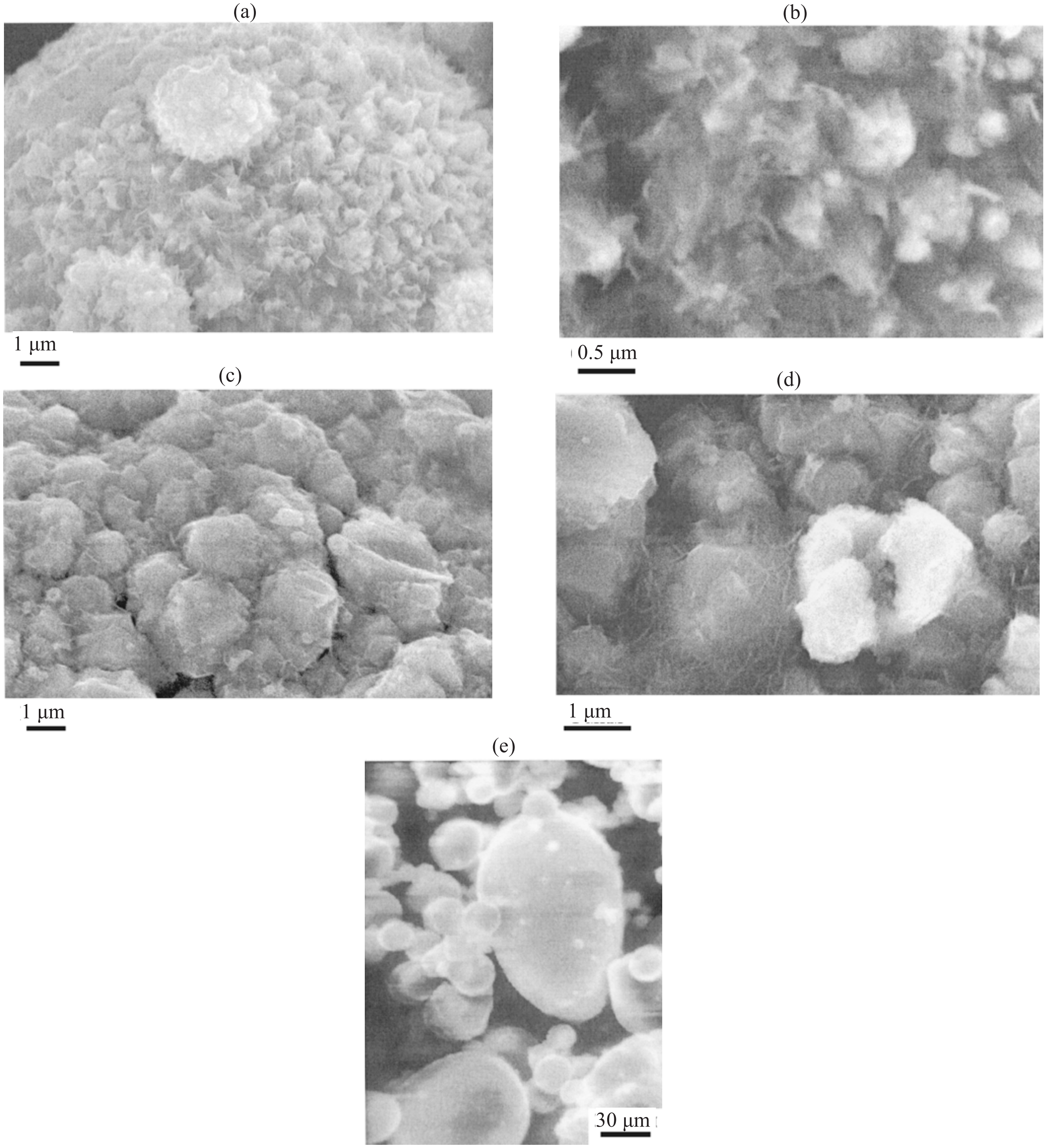

Fig. 5. Electron micrographs of disperse systems (a) Fe–Co, (b) Fe–Co–Al, (c) Fe–Co–Ni, (d) Fe–Co–Ni–Al, and (e) Al.

CONCLUSIONS

(1) Kinetic features of the formation of Fe–Co and Fe–Co–Ni deposits on dispersed aluminum matrix were elucidated.

(2) The reactions of Fe(III), Ni(II), and Co(II) reduction are conjugate and are adequately described by first-order rate equations with close rates of iron and cobalt deposition and lower rate of nickel deposition.

(3) It was found by X-ray phase analysis that the

precipitates obtained contain phases of aluminum and of individual iron group metals.

(4) Electron microscopic examination revealed nanosized whiskers and conical formations on the deposit surface.

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