NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

Synthesis and Properties of Dispersed Systems Based on Elemental Iron and Tungsten Obtained through Precipitation on Aluminum in the Presence of Citric Acid

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Abstract—The process of coprecipitation of iron and tungsten from aqueous solution containing Fe(III) and tungstate ions in the presence of citric acid has been investigated. The element and phase composition of precipitates in the Fe–Al–W system has been evaluated. The synthesized precipitate particles were shown to repeat the shape and size of the initial aluminum matrix, have a developed surface, and comprised solid tungsten solutions in iron in the presence of the elemental aluminum phase.

INTRODUCTION

Tungsten alloys allow advanced physical and mechanical properties such as hardness [1] and corrosive [2] and abrasive resistance [3] to appear. These properties can be attained through high-temperature consolidation of powders synthesized in aqueous solutions [4]. However, the tungsten precipitation from aqueous solutions containing tungstate ions is hampered by oxide-film formation and low overpressure of hydrogen emission on tungsten [4]. Thus, electroprecipitation of tungsten has been carried out by "induced coprecipitation" [5] of alloys containing elements of the iron subgroup (Ni, Co, and Fe) [6–8]. According to the published data, it appears reasonable to produce alloys of the iron-group metals with tungsten by electroprecipitation of solutions containing a complexing agent, for example, the widely used citric acid [9].

Studies of coprecipitation of tungsten with elements of the iron subgroup by traditional electrochemical methods are normally carried out with Fe(II), Ni(II), and Co(II) ions. However, the solutions used to produce the Fe–W alloy could also contain Fe(III) compounds formed as a result of oxidation by oxygen or tungsten ions. The authors of [10] showed that the iron discharge into the Fe–W alloy was derived from complexes of Fe(III), so that it was advised to use Fe(III) solutions containing various iron coordination compounds.

The possibility of synthesizing polymetallic systems by reduction on the aluminum surface from aqueous solutions containing Fe(III) was shown earlier in [11–13].

The present work was devoted to studies of the process of coprecipitation of iron and tungsten in elemental forms on aluminum microparticles in aqueous solutions containing ions of Fe(III) and WO_4^{2-} in the presence of citric acid. This process can serve as a basis for production of complex polymetallic systems used in catalysis, powder metallurgy, etc.

EXPERIMENTAL

The studies were carried out with aqueous solutions of reagents of purities no lower than analytical grade: $FeCl_3 \cdot 6H_2O$, Na_2WO_4, $C_6H_8O_7 \cdot H_2O$, and NaOH prepared with distilled water. Aluminum powder of ASD-0 grade (fraction 71–100 µm) was used as delivered.

The process was performed in a glass reactor (volume 500 cm³) under constant stirring at 300 rpm. The conditions for producing dispersed metal systems are shown in Table 1.

Simultaneously, the platinum-electrode (EPV-1) potential in the reaction mixture was measured and compared to that of a silver chloride reference electrode. Electrochemical studies were carried out using a P-30IM pulse potentiostat (Elins). In addition, the temperature was measured directly in the reaction medium by a minithermocouple of the K-type, as well as an AM-1118 multimeter (Aktakom), from the moment of powder-aluminum introduction until cooling down of the reaction mixture after the process competition. Digital signals from the multimeter were

Table 1. Conditions for production of dispersed metallic systems

Sample no.	Concentration, mol/L			Precipitate treatment by NaOH solution
	Fe(III)	WO_4^{2-}	$C_6H_8O_7$	
1	1.00	—	—	—
2	1.50	0.15	0.30	—
3	1.50	0.15	0.30	3.00 mol/L

Table 2. Data of X-ray-fluorescence analysis (numbers of samples refer to Table 1)

Element	Contents of elements in samples, wt %		
	1	2	3
Fe	98.1	85.3	89.9
W	0.0	11.2	9.5
Al	1.8	3.0	0.0
Σ (Co, S, P)	0.1	0.5	0.6

processed on a PC using the Aktakom software. Additional temperature control of the initial solution and the reaction mixture was performed using a laboratory mercury thermometer.

Upon the process completion, the precipitate was separated from the stock solution by magnetic separation. The precipitate element and phase composition were studied by X-ray-fluorescence and X-ray-diffraction methods using S1 TITAN (Bruker) and D2 PHAZER (Bruker) devices. The microscopy studies of the produced systems were performed using a Mini-SEM SX-3000 scanning electron microscope (EVEX).

The granulometric composition of the dispersed samples was investigated using a Mastersizer 2000 laser particle analyzer (Malvern). Dispersing and feeding samples through the measuring zone of a flow-type cell were carried out using a special unit with a built-in stirrer (2500 rpm) and an ultrasonic titanium probe. The specific surface area (BET method) was measured by a Nova 1000 analyzer (Quantachrome).
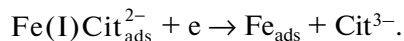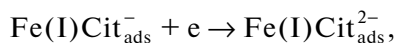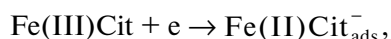
RESULTS AND DISCUSSION

The experimental data demonstrated that, during the iron precipitation from the solution containing only Fe(III), the elemental-iron nuclei shaping the shell of a new structure formed and grew (Table 2). In iron (III) chloride solutions containing tungstate ions, there occurred a joint formation of elemental iron and tungsten, which was corroborated by the X-ray fluorescence analysis data (Table 2).

The performed experiments showed that solutions containing Fe(III) and WO_4^{2-} produced recovered elemental irons at a high rate, which was indirectly corroborated by the data of the platinum-electrode chronopotentiogram (Fig. 1), as well as by the dependence of the reaction-medium temperature on time. A more pronounced exothermic character of the aluminum-ionization reaction, at a rather small average particle size and high transformation rate, resulted in reaction-mixture self-heating during the redox process (Fig. 2).
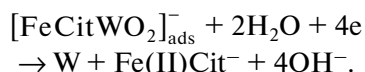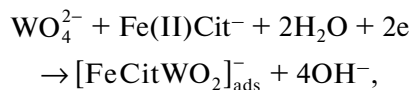
The dependences of the platinum-electrode potential and the reaction-mixture temperature on time are conditionally divided into three periods (Figs. 1, 2): (I) induction period, when Al particles are activated and their oxide-shell solidity becomes disrupted, (II) reduction of the iron ions contained in the solution simultaneously with Al ionization, and (III) process slowing down and establishment of a stationary potential.
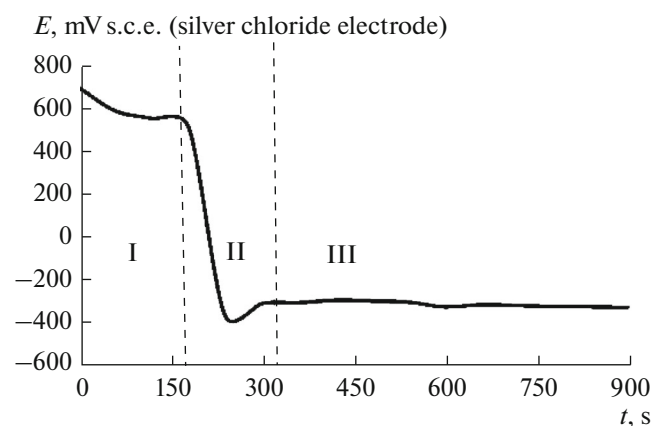
Fig. 1. Dependence of the platinum-electrode potential in the reaction mixture on time (sample 2).
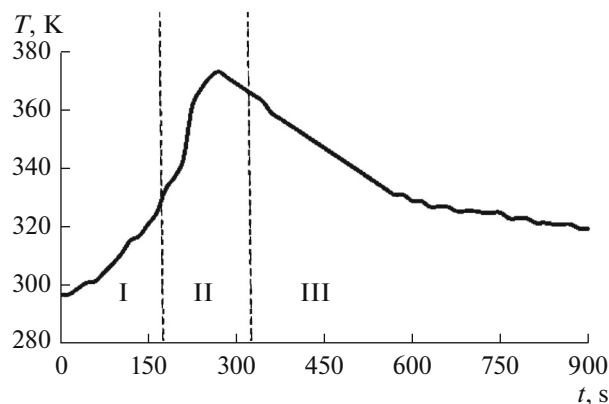
Fig. 2. Dependence of the reaction-mixture temperature on time (sample 2).

Analysis of published [10, 14, 15] and experimental data shows that Fe(III) reduction proceeds in several stages:

$$Fe(III)Cit + e \rightarrow Fe(II)Cit^-_{ads},$$

$$Fe(I)Cit^-_{ads} + e \rightarrow Fe(I)Cit^{2-}_{ads},$$

$$Fe(I)Cit^{2-}_{ads} + e \rightarrow Fe_{ads} + Cit^{3-}.$$

WO_4^{2-} reduction proceeds through the stage of intermediate product formation:

$$WO_4^{2-} + Fe(II)Cit^- + 2H_2O + 2e$$
$$\rightarrow [FeCitWO_2]^-_{ads} + 4OH^-,$$

$$[FeCitWO_2]^-_{ads} + 2H_2O + 4e$$
$$\rightarrow W + Fe(II)Cit^- + 4OH^-.$$

Simultaneously with iron coprecipitation, conjugated-hydrogen release takes place:

$$H_2O + e \rightarrow \tfrac{1}{2}H_2 + OH^-.$$
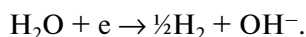
Hydrogen was partly absorbed and accumulated by the precipitate. This process was observed during heating of the dispersed samples up to 500°C in a vacuum-sealed quartz ampoule: the ampoule volume increased 1.7-fold. Hydrogen released during the iron precipitation is able to participate, at least in part, in the process of tungstate-ion reduction. The saturation of the solution and the precipitate by hydrogen allows preserving a majority of the formed elemental-metal atoms from oxidation.

The X-ray-diffraction analysis showed that the investigated dispersed samples contained respective irons in solid solutions (Fe + W), as well as elemental Al with a face-centered cubic lattice (Fig. 3). The process was accompanied by nuclei-size reduction (Table 3), which may be explained by introduction of the second element (tungsten) to iron, solid-solution formation, and intense hydrogen release and accumulation. This last process was followed by the breakage of shells of the formed particles and their disintegration into finer components. It was revealed that particles contained virtually none of the oxide phase, which was related to the conjugated reaction of hydrogen release in the process of metal-precipitate formation. The absence of oxidized forms of Fe and W in the precipitate proved that the "induced coprecipitation" method provided almost complete reduction of Fe(III) and WO_4^{2-} until a metallic state was reached. The qualitative composition of the synthetized samples was corroborated by identification of the diffractograms characteristics using NBS-US data.

The surface of the synthetized particles contained large numbers of pores and new phase nuclei (Fig. 4). The microphotograph of dispersed sample 3 of the Fe−W system contained, aside from spherical particles, a large amount of fission products (Fig. 4c) that
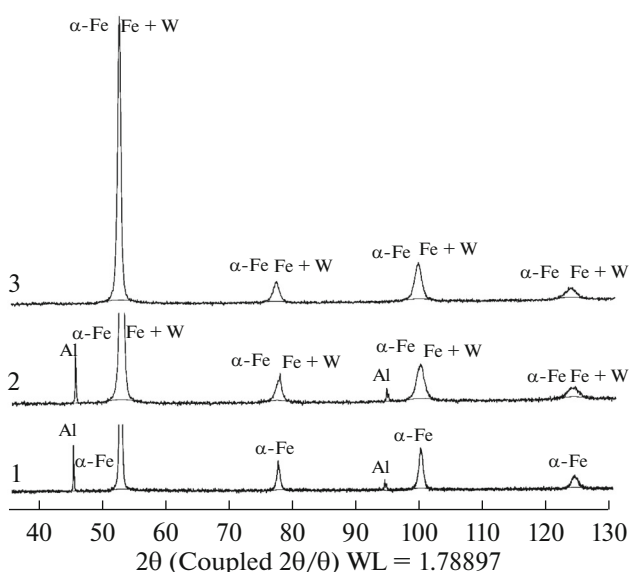

Fig. 3. Diffractograms of the investigated samples (numbers of samples refer to Table 1).

formed as a result of the synthesized precipitate treatment by concentrated NaOH, which was accompanied with intense hydrogen release and partial breakage of the formed particles' shells.

Investigation of the samples' granulometric composition showed that the synthesized particles were of the same size as the initial aluminum particles (Fig. 5). Dispersion of sample 3 particles (average size 75 μm) during the treatment by a concentrated alkali solution shown in Fig. 4c caused the distribution curve to shift to smaller sizes (average size about 50 μm) (Fig. 5c). The sample of the Fe−Al−W system had a quite developed surface characterized by values of 3.5−5.0 m^2/g.

To sum up, it has been shown that segregation of the metallic phase by citric acid progresses with high intensity (90% in 10 min), which was indirectly corroborated by the jump of potential of the platinum-electrode chronopotentiogram, as well as by changes in the temperature of the reaction mixture. This confirmed that citric acid served as a complexing agent promoting the metallic ions' discharge on aluminum.

It has been established that additional treatment of the produced precipitates of Fe−Al−W system with concentrated NaOH solution (3.0 mol/L) allows com-

Table 3. Data of X-ray analysis (numbers of samples refer to Table 1)

No.	Reflection (110)	a, nm	CSR, nm
1	α-Fe	0.2867	29.48
2	α-Fe + W	0.2873	16.35
3	α-Fe + W	0.2874	16.25

CSR—coherent-scattering region

Fig. 4. Microphotographs of samples (a) 1, (b) 2, and (c) 3. Numbers of samples refer to Table 1.

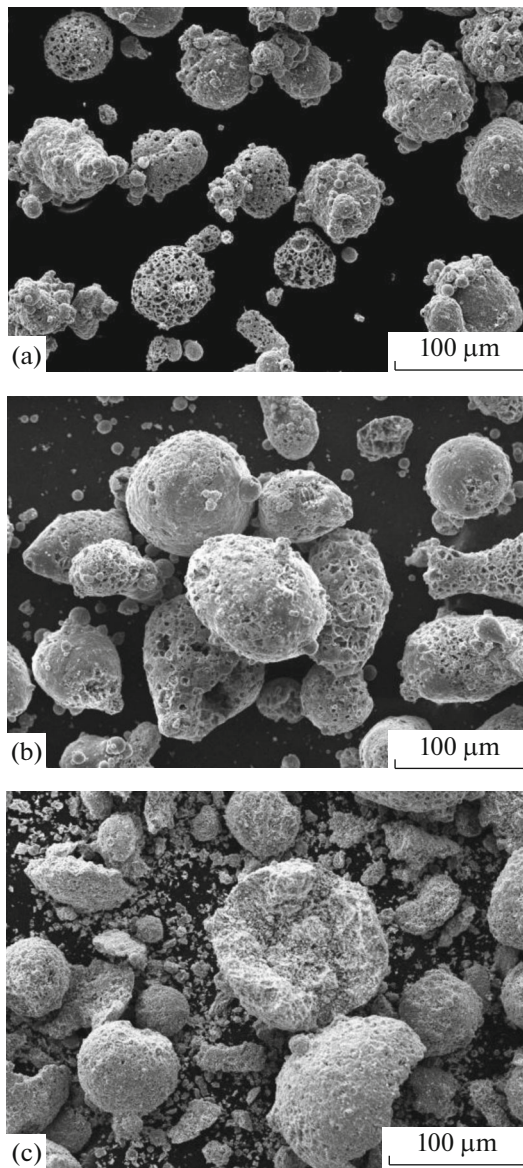**Fig. 5.** Particle-size distribution: (a) 1, (b) 2, and (c) 3. Numbers of samples refer to Table 1.

plete dissolution of the elemental aluminum and formation of the polymetallic system Fe–W.

The processes of formation of metallic iron, W and F solid solution, and hydrogen take place on aluminum particles. It has been shown that the formed particles repeat the shape and size of the initial aluminum matrix, have a developed surface, and contain hard solutions of tungsten in iron and segregated metallic phases of aluminum and iron in the absence of oxide and hydroxide phases. The surface of the synthesized Fe–Al–W system particles was characterized by the value of 3.5–5.0 m^2/g.
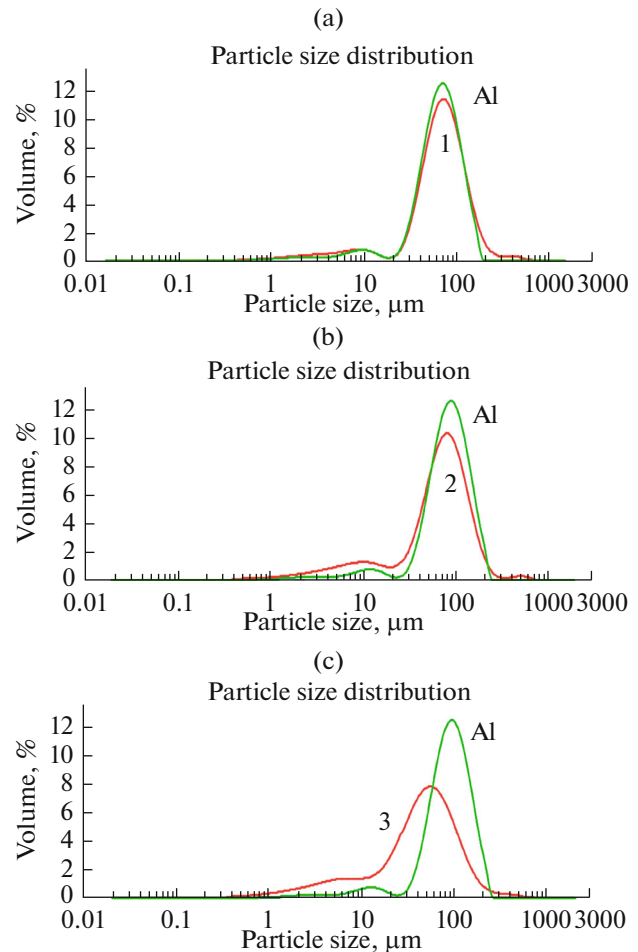
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