In the manufacture of magnetic materials by the powder metallurgy technique, the alloy constituents must be thoroughly blended. During prolonged mechanical mixing and homogenizing annealing, the amount of impurities in metal powders increases, which adversely affects the magnetic properties of the resulting alloys. By employing electrolysis as a technique for the production of magnetic alloy powders, it is possible to increase the homogeneity and purity of the latter. The object of the present investigation was to select an electrolyte for producing nickel-iron alloy powder and to study the influence of electrolysis parameters on the properties of such alloy powders and the technical and economic characteristics of the process.

**EXPERIMENTAL**

The cathode in the powder-deposition tank was a St. 3 steel plate, while the anode consisted of St. 3 steel and N-0 nickel plates. The deposit was scraped off after 15 min, washed, first with dilute sulfuric acid and then with distilled water, and dried in a vacuum (10-15 mm Hg) at a temperature of 100°C. The electrolyte acidity was checked by means of a glass electrode mounted in the drainage container of the electrolysis tank. Electrolyte correction could be performed during electrolysis by adding sulfuric acid to the supply tank. The electrolyte temperature was maintained at 30°C. The current density in this series of experiments was regulated by varying the surface area of the cathode.

The electrolyte was analyzed trigonometrically for nickel and chromatometrically for iron. The iron content of the alloy was found by direct determination, while the nickel content was obtained as the difference. Beryagin's technique [1] was used to determine the specific surface area of the powder. The passivity of nickel in the test electrolytes was studied by plotting polarization curves (potentiodynamic method), using an ON-101 polarograph.

**Choice of Electrolyte Composition.** The principal disadvantage of the sulfuric acid electrolytes employed is their rapid pH variation in the course of electrolysis and the formation of nickel, and di- and trivalent iron hydroxides in the cathode space [2].

The buffering properties of the electrolytes were investigated by potentiometric titration with a potash solution (Fig. 1). Electrolytes containing a substantial amount of potassium and ammonium sulfates exhibit increased buffering activity, but the presence of a depassivating agent such as potassium chloride markedly decreases their buffering capacity (Fig. 1, curve 3). Since a rise in solution pH produces, in the first place, precipitation of iron hydroxide, it is reasonable to expect that converting the trivalent iron into a complex compound might prove effective in preventing hydroxide formation. Indeed, it is found that an electrolyte containing sodium fluoride has a high buffering capacity, which is preserved when chlorides are added to it (Fig. 1, curves 5 and 6). At the same time, adding a large amount of NaF may lead to precipitation of the

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Fig. 1. Curves of potentiometric titration of 100 ml of solution with 1 M KOH at 20°C. Electrolyte composition (moles/liter): 0.1 NiSO₄, 0.1 FeSO₄. 1) 3.3 NaCl, 0.85 NH₄Cl; 2) K₂SO₄, saturated; 3) K₂SO₄, saturated, 0.2 KCl; 4) 0.38 (NH₄)₂SO₄; 5) 0.38 (NH₄)₂SO₄, 0.07 NaF; 6) 0.38 (NH₄)₂SO₄, 0.07 NaF, 0.2 KCl.

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sparingly soluble compounds NiF$_2$ and FeF$_2$. To determine the optimum sodium-fluoride concentration and the permissible electrolyte pH value, an examination was made of thermodynamic-equilibrium conditions in the system under examination.

At pH 1.8, iron (III) may be present in the electrolyte in the form of hydroxide or, at a certain fluorine-ion concentration, as part of a fluoride complex. The most stable of such complex compounds are the anions FeF$_2^-$ and FeF$_4^-$ [3]. A calculation of concentration distribution for all forms of iron-fluoride compounds at various fluorine-ion concentrations in solution shows that, in a solution containing 0.1 g-ion/liter F$^-$, iron(III) combines to form the complex anion FeF$_4^-$, whose instability constant is $2.96 \times 10^{-5}$. The following equilibrium is established between the two iron(III) compounds:

$$\frac{[\text{FeF}_4^-] \cdot K}{[\text{F}^-]^4} = \frac{\Pi P_{\text{Fe(OH)}_2}}{[\text{OH}^-]^3},$$

where $K$ is the instability constant. Thus, we obtain the dependence of the concentration of the complex compound FeF$_4^-$ on electrolyte acidity and fluorine-ion concentration:

$$\rho \left[ \text{FeF}_4^- \right] = \rho \frac{\Pi P_{\text{Fe(OH)}_2} \cdot [\text{H}^+]^3}{K K_W^3} + 4 \rho [\text{F}^-].$$

Fluorine ions prevent hydroxide precipitation at relatively high values of electrolyte pH, but cannot be introduced in large quantities because of the low solubility of the compounds NiF$_2$ and FeF$_2$. In the case of an equilibrium between NiF$_2$ and NiSO$_4$, the following equality is valid:

$$\rho \left[ \text{NiSO}_4 \right] = \rho \frac{\Pi P_{\text{NiF}_2} \cdot [\text{SO}_4^{2-}]}{K'} - 2 \rho [\text{F}^-],$$

where $K'$ is the dissociation constant of NiSO$_4$, equal to $4 \times 10^{-5}$ [4].

By plotting Eqs. (2) and (3), it is possible to determine the region of solution stability at any given value of electrolyte pH. It will be seen from Fig. 2 that the electrolyte is stable within a relatively narrow zone of F$^-$ concentrations. When 0.07 mole/liter sodium fluoride is added to the electrolyte, the buffering properties of the solution are sufficiently high, and electrolysis may be conducted at pH 4.5-5.

As a result of a study into the passivation of a nickel anode in the presence of chlorides, it was decided that a 0.2 mole/liter concentration of potassium chloride in the electrolyte, ensuring dissolution of the nickel anode at current densities of up to 3500 A/m$^2$, was adequate. Subsequent investigations into the effects of electrolysis parameters on the composition and properties of nickel-iron alloy powder were conducted with an electrolyte containing (in moles/liter): 0.2 NiSO$_4$ + FeSO$_4$, 0.93 (NH$_4$)$_2$SO$_4$, 0.2 KCl, and 0.07 NaF.

**Influence of Electrolysis Parameters on Alloy Composition and Current Efficiency.** Since the electrodeposition of the alloy powder takes place under limiting conditions, the composition of the powder is determined by the ratio of the limiting discharge currents of the alloy constituents and, consequently, by the concentration of the component ions in the electrolyte. The validity of this statement has been confirmed by investigations into the dependence of alloy composition on the concentration of solution components. The iron content of the alloy is directly proportional to the concentration of iron ions in the electrolyte. Raising current density at constant electrolyte composition and temperature does not affect the chemical composition of the alloy. Similarly, changing the temperature has no effect on the amounts of the components in the alloy (Table 1).

The equality of the ionic charges of iron and nickel, and the similarity of the ionic radii and diffusion coefficients of these metals [5] suggest that the limiting discharge currents of iron and nickel must also be similar. Hence, a change in the ratio of iron and nickel ion concentrations in the solution will lead to an equivalent change in the discharge currents of these ions and also in the composition of the alloy powder. The results are presented below of an x-ray structural analysis of alloy deposits:

<table>
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<tr>
<th>Deposit composition, %</th>
<th>Fe</th>
<th>Ni</th>
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<td></td>
<td>49.8</td>
<td>50.2</td>
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<table>
<thead>
<tr>
<th>Deposit composition, %</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
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<td>23.5</td>
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<tr>
<td></td>
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Lattice types

- fcc
- bcc + fcc
- bcc