

Research article

Electrochemical deposition of NiFe films from a chloride electrolyte with low concentrations of essential salts and supplemented by ammonium hydroxide

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Abstract

A study of diluted chloride electrolytes with a C_{Ni}/C_{Fe} ratio of 4.26 for the deposition of a $Ni_{81}Fe_{19}$ film was conducted using spectrophotometry and electrochemical deposition analyses. In weak salt solutions, the electrolytic dissociation of the salts and the content of doubly charged iron ions both increase compared to the content of singly charged ions. The principle governing the influence of the iron ion charge in the compositions of the permalloy films is confirmed. The magnetic properties of the permalloy films are improved by the addition of ammonium hydroxide to the chloride electrolyte that contains low concentrations of essential salts. Electrochemical deposition of the permalloy films from the chloride electrolyte with a ratio of $C_{Ni}/C_{Fe} = 4.26$ and a concentration of 0.004 mol/L Fe^{2+} allows for a $Ni_{81}Fe_{19}$ film to be produced at room temperature with a composition congruent with that of the electrolyte; furthermore, the above result demonstrates a relatively high rate of nickel deposition compared to that of iron.

Keywords: permalloy, electrochemical deposition, chloride electrolyte, ion charge.

Introduction

Studies on the electrochemical deposition of iron nickel alloys have been carried out over the years. After many observations, a low rate of deposition of nickel in relation to iron was established [1-9]. This effect was called anomalous deposition and is explained [1] by the concept of the effect of iron hydroxide on nickel deposition [2] or the formation of ions [3]. To circumvent the above effect and obtain the desired alloy composition, various electrolytes [4] have been proposed, including electrolytes with increased nickel content and various complex-forming additives [5]. Electrochemical deposition has also been conducted on substrates made from different materials [6], rotating cathodes [7] and porous substrates [8]. The electrolytes used are characterized by a wide range of nickel and iron

molar ratios from 0.1 to 50. However, there has been no definite connection between the composition of the electrolyte and the obtained film [9].

The charge of iron ions in the electrolyte changes [10], when the temperature changes. The charge of ions in the electrolyte depends not only on the temperature but also on the concentration of iron. A low concentration of iron, as is well known, leads to an increase in the electrolytic dissociation of salts. To determine the nature of the phenomena occurring in the electrolyte with a low concentration of the main salt component, a spectrophotometric study of chloride electrolytes and an evaluation of the deposition of NiFe films at room temperature were conducted.

1. Electrolyte spectrophotometry with NiCl₂, FeCl₂ and ammonium hydroxide

Spectrophotometric analyses of chloride electrolyte absorption with low concentrations of 0.064 mol/L NiCl₂ and 0.0037 mol/L FeCl₂ are investigated and described in the work of [17], which utilizes hydrochloric acid, caustic nitrate and isopropyl alcohol as additives. When observing the characteristic wavelengths of nickel (650 nm and 740 nm) and iron (960 nm), the additives cause small changes in absorbance. The main spectrum changes occur in a wavelength range of 330 nm - 450 nm, which corresponds to the dissociation of chlorine atoms.

The electrolytic dissociation of salts in a chloride electrolyte for electrochemical deposition of a NiFepermalloy was investigated in solutions with FeCl₂ 4H₂O (1.5 g) and NiCl₂ 6H₂O (6.6 g). Selected doses of salt were consistently dissolved in two liters of water, and then boric acid (50 g), saccharin (6 g) and ammonium hydroxide were added. The pH values were controlled: water - 7.36; nickel chloride solution - 6.65; iron chloride solution - 4.99; and a solution supplemented with boric acid - 4.38.

Figure 1 shows the absorption of the electrolytes with ammonium hydroxide in a wavelength range of 315 - 1150 nm obtained on a B-1100 spectrophotometer with a 1 cm ditch.

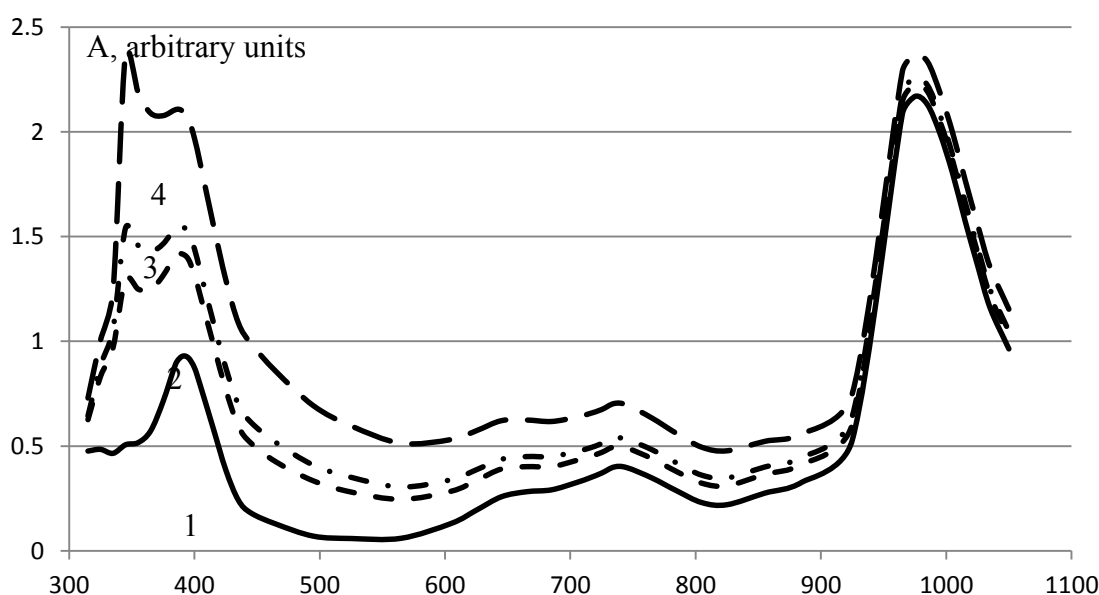


Figure 1. Absorption analysis of the electrolytes in a wavelength range from 315 - 1100 nm for the electrochemical deposition of permalloy with low concentrations of essential salts and supplemented with ammonium hydroxide: 1. Electrolyte containing: 3.3 g/L NiCl₂ 6H₂O, 0.75 g/L FeCl₂ 4H₂O, 25 g/L B₃OH₃, and 3 g/L saccharine, pH= 4.38; 2. Electrolyte 1 with a 0.0023 mol/L NH₄OH supplement, pH 5.77; 3. Electrolyte 1 with a 0.0047 mol/L NH₄OH supplement, pH 6.14; 4. Electrolyte 1 with a 0.0094 mol/L NH₄OH supplement, pH 6.44.

Ammonium hydroxide additives increase the pH of the solution as well as the absorption of all wavelengths of light, but these additives notably increase the absorption that occurs at a wavelength of 345 nm. After sitting for a day in the chloride electrolyte with low concentrations of nickel and iron and with the above additives, a gel-like

sediment layer forms near the bottom of the bath. After the top of the electrolyte merges, elemental microanalyses of the remaining dry residue are examined using energy dispersive X-ray spectroscopy with a Philips XL 40 instrument.

The sediment contains chlorine (60.79 at. %), iron (15.52 at. %) and nickel (23.69 at.%). The ratio of chlorine to iron and nickel is 1.55. These values correspond to the specific content of iron chloride and nickel chloride in the solution. The ratio of chlorine to iron and nickel is 2. The salts of nickel and iron form complex compounds with the boric acid and form a gel-like sediment near the bottom of the bath. This finding demonstrates the instability of the electrolyte over time. The electrolyte can only be used immediately after preparation and with continuous mixing.

2. Electrochemical deposition of NiFe films from a chloride electrolyte with low concentrations of the main salts, a variable nickel concentration and supplemented with ammonium hydroxide

Studies on the electrochemical deposition of permalloy films from chloride electrolytes with low concentrations of salts have shown that, without boric acid and saccharine additives, the deposition is extremely uneven, and a black sediment peels off. When hydrochloric acid is added to the chloride electrolyte with boric acid and saccharine, film deposition does not occur because the layer of nickel is poisoned. The addition of NH_4OH to the chloride electrolyte ensures that the permalloy films are obtained with the necessary composition at room temperature.

The electrolyte becomes cloudy and yellow during the process, but the film is deposited, despite the presence of small and then large bubbles and the formation of foam from the bubbles. A study was conducted on the relationship between the deposition rate, iron content and magnetic properties of permalloy films with metallic nickel on a silicon substrate by using a fixed iron content and a variable nickel content in a freshly produced chloride electrolyte. To reduce the formation of precipitates, the electrolyte was prepared before each deposition process and stirred during the deposition process by a magnetic stirrer.

Table 1. Parameters for the electrochemical deposition of a permalloy film from a low concentration of chloride electrolyte with NH_4OH additives at room temperature. C - composition of electrolyte for 2 litres H_2O of NiCl_2 – grams + NH_4OH – ml.

№ Sample	C	pH	I, mA	T, min	h, μ	V, nm/min	B, nWb	B/h	H, Oe	Fe, %
32	5,2	4,4	250	60	1,5	23	218	145	1,1	22
31	5,8	4,5	250	60	2,4	41	250	104	1,0	20,15
30	6,4 Γ	4,3	250	60	2,3	38	274	119	1,8	18,7
23	7,2	4,2	200	120	3	25	330	110	3	17,2
36	7,3	4,4	200	60	2,5	41	300	120	1,5	18,15
45	6,2+2	6,44	250	60	3,13	52	195	62,3	0,2	20,5
27	6,6+2	5,6	250	60	1,9	32	242	127	0,5	20,05
42	7,6+2	5,7	250	60	5	83	319	64	1,6	15,7
44	7,0+2	5,91	250	60	3,05	50	170	55,7	0,5	18,7

Figure 2 shows the correlation between the content of Ni/Fe atoms in the films and in the electrolyte, both without additives and with ammonium hydroxide supplements. The ratio of Ni/Fe atoms in the film is greater than the concentration ratio of Ni/Fe in the electrolyte. This finding means that the precipitation of nickel in relation to iron in a non-anomalous coordination with low selected concentrations of the two metals in the electrolyte is possible. By adding ammonium hydroxide to the electrolyte, the concentration of iron in the film increases but does not compare to the ratio of nickel and iron atoms in the electrolyte.

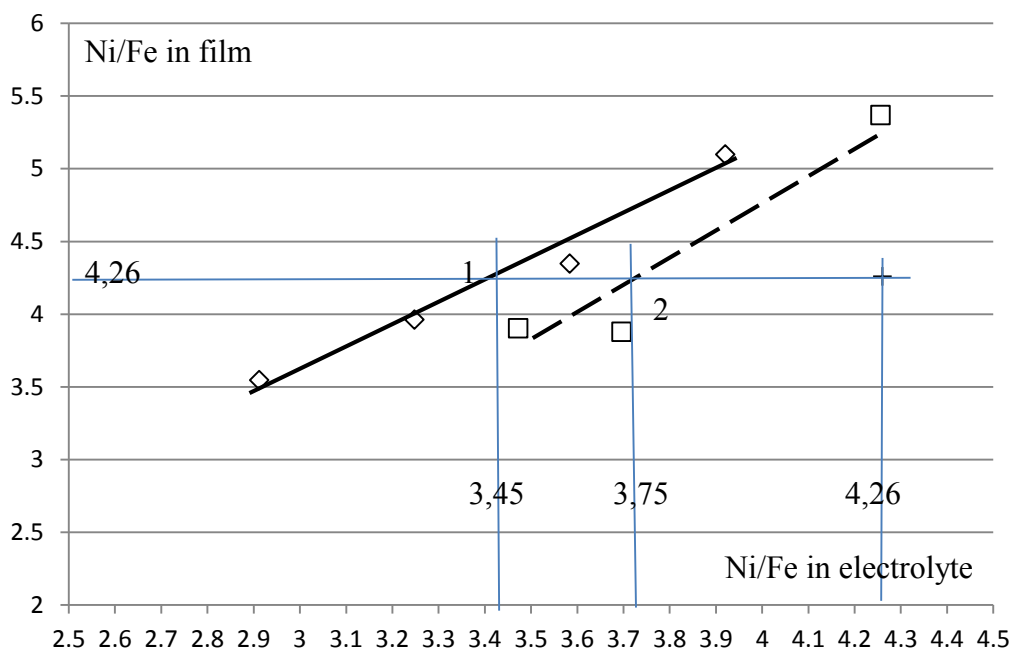


Figure 2. Film deposition rate of a NiFe alloy from a chloride electrolyte with 0.048 - 0.064 mol/L NiCl₂ and 0.015 mol/L FeCl₂.

The electrochemical deposition rate of NiFe films from a chloride electrolyte with a concentration of 0.048 - 0.064 mol/L NiCl₂ and 0.015 mol/L FeCl₂ is approximately 35 nm/min, and its dependence on the nickel content in the electrolyte is shown in Figure 3.

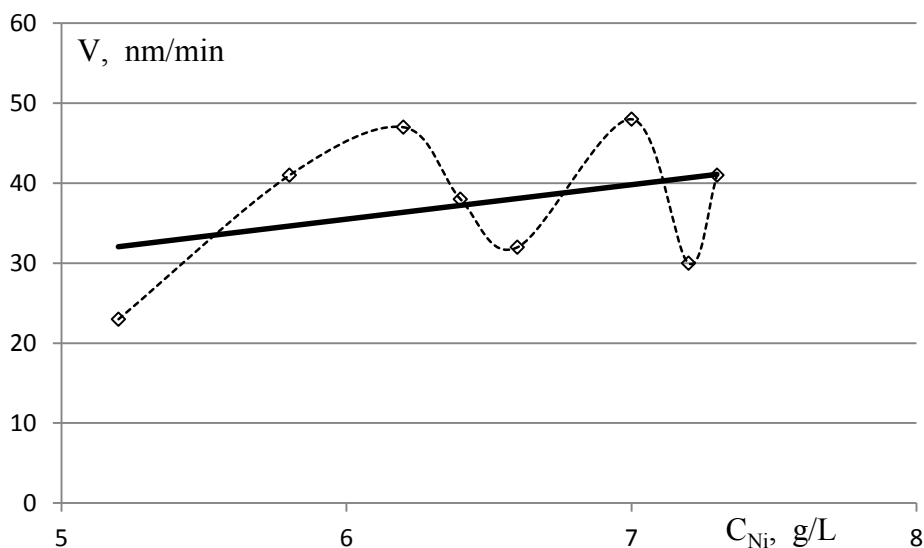


Figure 3. Film deposition rate of a NiFe alloy from a chloride electrolyte with 0.048 - 0.064 mol/L NiCl₂ and 0.015 mol/L FeCl₂.

The magnetization curves of films 23 and 45 from Table 2 are represented in Figure 4. The iron content in the No. 23 NiFe film is 17.2%, and in the No. 45 film, it is 20.5%. The thickness of the films is almost the same, with a value of 3 microns. The magnetic induction saturation in the No. 23 NiFe film (curve 4) is found to be 330 nWb, and that in the No. 45 film (curve 2) is 195 nWb; further, the coercive force in No. 23 is 3.0 Oe, and that in No. 45 is

0.2 Oe. When ammonium hydroxide is added to the chloride electrolyte, there is an improvement in the magnetic properties of the film. A coercive force of up to 0.2 Oe and growth of the derivative function of the magnetization - magnetic moment (curves 3 and 1) depend on the magnetic field in a range of up to 1 Oe. This property of deposited films is important for their application in magnetic field sensors.

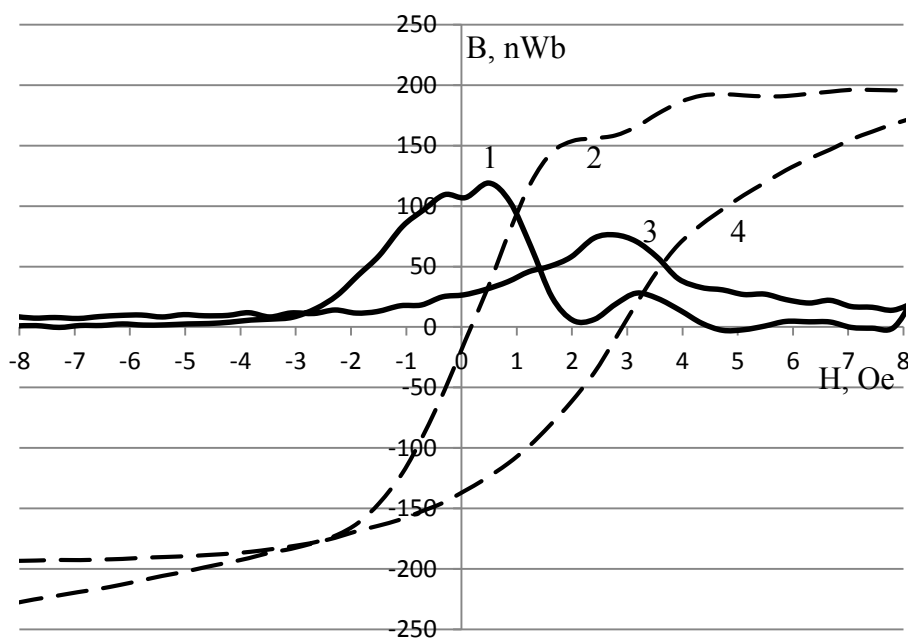


Figure 4. Magnetization curves for the permalloy films on the No. 23 (3, 4) and 45 (1, 2) plates.

3. Discussion of the results

FeCl_2 hydrolysis with a concentration of up to 1 mol/L is derived from thermodynamic calculations. The ions with a single positive charge (FeCl^+) predominate over the ions of Fe^{2+} with a positive charge of 2. Reducing the concentration of FeCl_2 allows the deposition of iron ions as Fe^{2+} , rather than as iron chloride ($\text{Fe}^{2+}\text{Cl}^+$), which alters the rate of deposition due to the size of the ion charge and creates a mixture of chlorine in the film.

Researchers for over 60 years have conducted evaluations of the electrochemical deposition of NiFe alloys and have observed preferential iron deposition in relation to the nickel content despite testing electrolyte compositions with a wide range of molar ratios of nickel and iron. None of the researchers linked the anomalous electrodeposition with the activity of the iron ions due to the existence of variable iron valence, for instance, two and three values for the charge of ions during the hydrolysis of iron salts.

The electrochemical deposition of NiFe alloy films from chloride electrolytes with low concentrations of the main salts at room temperature result in the preferential deposition of nickel, as opposed to anomalous deposition.

Adding ammonium hydroxide to a chloride electrolyte with a low concentration of basic NiFe salts reduces the formation of gas bubbles on the substrate. In a freshly prepared solution, the deposition process is normal at a rate of up to 60 nm/min. The magnetization curve shows improvement in the magnetic properties of the permalloy films: the coercive force decreases to 0.2 Oe, and the magnetic moment grows. This finding may be due to the action of nitrogen.

This work [11] shows that FeNiN films obtained by magnetron spraying of a $\text{Fe}_{20}\text{Ni}_{80}$ target in a N environment have high magneto soft properties. Inert nitrogen reacts with the nickel and iron, and it is possible to form magnetic variants, namely, Fe_4N and Fe_2N compounds. Nitrogen is present in the $\text{Fe}_{20}\text{Ni}_{80}$ films in small quantities and creates barriers at the boundaries of the pellets, which changes their domains and leads to changes in their magnetic properties.



Conclusion

Analysis of weak electrolyte solutions evaluating the deposition of the NiFe alloy shows that dilution not only increases the electrolytic salt dissociation but also increases the content of doubly charged iron ions compared to singly charged iron ions.

In diluted chloride electrolytes, the deposition of the NiFe alloy with a C_{Ni}/C_{Fe} ratio of 4.26 confirms the principle of the iron ion charge effect on the composition of the permalloy films.

Electrochemical deposition of the permalloy films from a chloride electrolyte with a ratio of $C_{Ni}/C_{Fe} = 4.26$ and with a concentration of 0.004 mol/L Fe^{2+} allows the films to be deposited at room temperature with a composition congruent to that of the electrolyte and bestows excellent magnetic properties [12-18].

Numerous studies on the electrochemical deposition of NiFe alloys have been conducted previously, but they have not allowed us to obtain a congruent concentration of NiFe alloy films during the electrochemical deposition process due to anomalous deposition.

This study establishes that congruent, non-anomalous deposition can be accomplished when the charges of the ions in the electrolyte are taken into account. This finding allows for the discovery of reproducible parameters to form films with a composition that uniquely corresponds to the specified composition of the electrolyte.

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