

RESEARCH ARTICLE

THE EFFECT OF ION CHARGE ON FERRIC CHLORIDE HYDROLYSIS DURING ELECTROCHEMICAL DEPOSITION OF NIFE ALLOY

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Abstract

A new phenomenon, i.e., complete ionization of ferric chloride, was discovered when the electrolyte when heated to 70°C. Abnormal deposition of NiFe alloy components was prevented due to ionization once the ions were changed from $(\text{Fe}^{2+}\text{Cl}^-)^+$ to Fe^{2+} . Maintaining a chloride electrolyte concentration ratio of Ni/Fe = 4.26 when adjusting the pH with hydrochloric acid results in congruent electrochemical deposition of iron concentrations on the order of 0.06 mol/l and films with the composition $\text{Ni}_{81}\text{Fe}_{19}$. Low concentration solutions increase salt dissociation and the content of two charged ions compared to that of one charged ions. A chloride and iron electrolyte concentration of 0.004 mol/l with Ni/Fe = 4.26 confirms that the charge of the iron ions influences the composition of the resulting permalloy films. Congruent electrodeposition of permalloy films produces films with a composition corresponding to the given composition of the electrolyte, while considering the charge of the iron ions. The idea of congruent alloy electrochemical deposition and electrochemical deposition is introduced based on the charge of ions in the electrolyte.

Keywords: permalloy, electrochemical deposition, chloride electrolyte, the charge of ions.

Introduction. Anomalous nickel-iron alloy plating

To obtain a nickel-iron alloy in [1], electrodeposition was conducted at 24°C and a pH of 3.1 with currents of 5, 10, and 20 mA/cm² under joint discharge of chloride ions in the cathode electrolyte with a total concentration

of iron and nickel (Fe + Ni) of 1 mol/l and a changing Fe/(Fe + Ni) ratio.

Preferential deposition of iron was observed, as shown in Figure 1. An increase in the iron content in the electrolyte led to an increase in the iron content of the alloy. The iron content in the alloy depends on the current density. The optimal results in terms of the appearance and coating with good current efficiency were obtained with an electrolyte containing 0.2 mol/l sodium citrate, which forms complexes with nickel and iron.

A review of the literature [1-54] shows that electrolytic deposition of nickel alloys of iron has been carried out for many years. Initially, the composition of the bath for electrolytic deposition of nickel-iron alloys, in particular Ni₈₀Fe₂₀ or permalloy, consisted of a simple mixture of sulfate or chloride nickel salts and iron. For example, a patent [2] was used to produce magnetic film memory devices via NiFe electrodeposition from an electrolyte containing 3 g/l Ni, 0.35 g/l Fe, and 0.35 g/l Cu without a chelating agent.

To circumvent the anomalous effects of an electrolyte with a much higher concentration of nickel, various additives and a complexing agent have been used to conduct depositions with a rotating cathode under alternating or pulsed direct currents and magnetic fields using solutions based on ionic liquids.

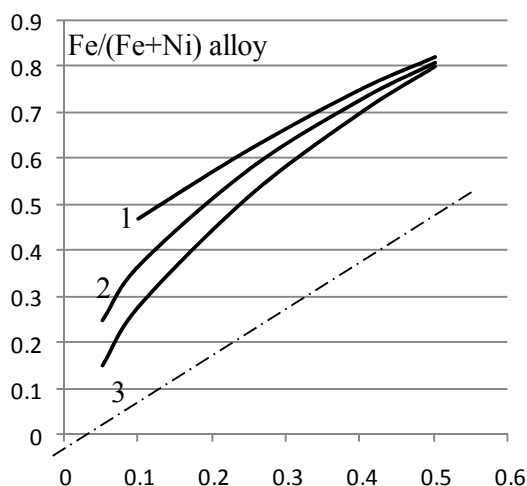


Figure 1. The dependence of the iron content in an alloy on the relative concentration of iron in a chloride solution for NiFe alloy electrodeposition. 1) $J = 5 \text{ mA/cm}^2$; 2) $J = 10 \text{ mA/cm}^2$; 3) $J = 20 \text{ mA/cm}^2$.

The applied electrolytes are characterized by a wide range of molar ratios of nickel and iron varying from 50 to 0.1. A one-to-one relationship between the electrolyte composition and the deposited film has not been established. The molar ratio is 4.26 for the Ni₈₁Fe₁₉ alloy. A study of the deposition process in a chloride electrolyte with a constant mole fraction of 4.26 was reported in 3 - 5. The film contained this alloy ratio of components.

The hydrolysis of ferric chloride is described in [6]

The interaction of salt ions with water leads to the formation of a weak electrolyte resulting from the hydrolysis of salt. Salt ions bind with water-generated ions, either H⁺ or OH⁻. According to Le Chatelier's principle,



a decrease in the concentration of the ions should lead to further disassociation of water molecules into ions. If an ion participates in the formation of ions from the electrolyte, then another ion accumulates in the solution, and the pH changes.

To strengthen salt hydrolysis, the solution is diluted and heated. According to the law of mass action, supplying one of the products of the hydrolysis to the solution decreases the hydrolysis of the salt. When a product of hydrolysis is removed, the hydrolysis of the salt is enhanced.

Ferric chloride partially hydrolyzes. Solutions of fully hydrolyzed ferrous chloride tetra hydrate $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ contain a sludge of ferrous hydroxide, $\text{Fe}(\text{OH})_2$, in the form of colloidal particles. The dissociation constants are $\text{FeCl}_2 - 1.2 \cdot 10^{-2}$ and $\text{Fe}(\text{OH})_2 - 1.3 \cdot 10^{-4}$.

Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ hydrolyses and dissociates completely. The dissociation constants are $\text{NiCl}_2 - 2.5 \cdot 10^9$ and nickel hydroxide $\text{Ni}(\text{OH})_2 - 2.5 \cdot 10^{-5}$.

Effect of hydroxide on the deposition of permalloy films

The anomalous character of the lower deposition rate deposition of nickel, which is more noble when compared to iron, is explained [1] on the basis of the influence of iron on the deposition of nickel, although this explanation has not been confirmed.

This concept has been seen in subsequent works. To circumvent the anomalous effect of electrolyte is injected high concentration of nickel, various additives, using solution based on ionic liquids. The process is performed on alternating or pulsed current in a magnetic field and with rotating cathode.

The applied electrolytes are characterized by a wide range of molar ratios of nickel to iron, i.e., from 50 to 0.1. However, a one-to-one correspondence between the composition of the electrolyte and the film has not been established.

In [7], an analysis of the solubility of $\text{Fe}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ and the dissociation constants of FeOH^+ and NiOH^+ led to the conclusion that to reduce the deposition rate of the more noble nickel, the inhibition mechanisms for the deposition of nickel substances containing no noble iron ions are invalid for NiFe alloy deposition, as shown in Figure 2.

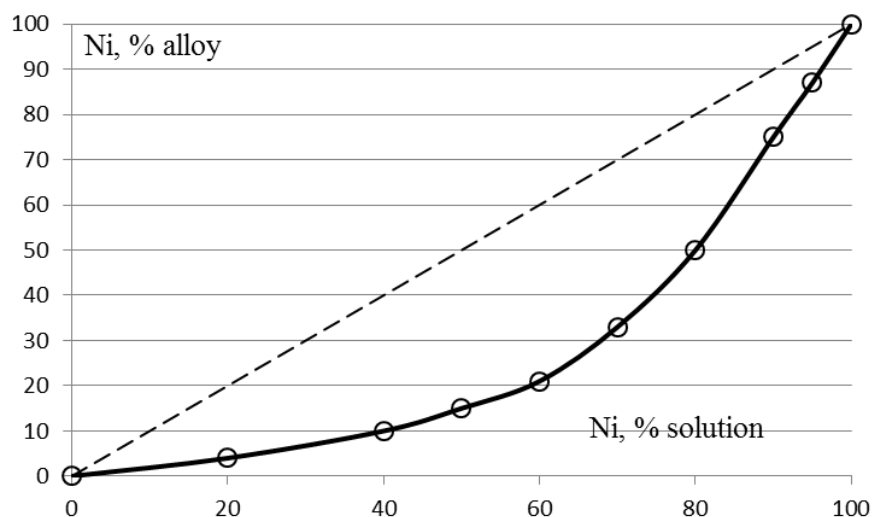


Figure 2. NiFe plating at a current density of 100 mA/cm² in sulfate electrolyte.

Measurements for the various current densities show an increase from 1 to 5 mA/cm² for a fivefold increase in the pH in the cathode layer. The concentration of ion metal hydroxides was 0.21 mol/l for Fe and 10⁻³ mol/l for Ni. These data do not explain or solve the problem of anomalous deposition.

It can be argued that the small dissociation constants of FeOH⁺ indicate loss of the iron hydroxide colloid state and an influence on the deposition process only as mechanical impurities.

Technique of permalloy films during electrochemical deposition of iron concentration in the order of 0.06 mol/l

For the deposition of permalloy Ni₈₁Fe₁₉, we used a chloride electrolyte. The addition of hydrochloric acid was regulated by the pH-1.5-3.5 electrolyte. Permalloy precipitates from the specified molar ratio electrolyte content of nickel and iron of 4.26 in an electrolytic volume of 2 liters with a graphite anode. A fixed cathode is used in the form of vertically arranged silicon wafers.

Rectangular areas of the permalloy films were obtained through the use of a photoresist mask on metallized layers using a NiCr Ni surface 100 mm diameter silicon wafer coated with a layer of SiO₂. The temperature of the electrolyte was 60 or 70°C due to heating by a submersible heater and mixing by a magnetic stirrer.

The main process parameters are maintained constant for the current density of 10-30 mA/cm² in the areas of the nickel cathode on the silicon wafer surface not covered by the photoresist.

This technique provides local permalloy films up to 40 microns thick without mechanical stress and with very good adhesion on silicon wafers.

The film thickness was measured using a Microsystems MSA-500 instrument. The composition of the films was studied using an X-ray Philips XL 40 micro analyzer. The magnetization of the films on the plates was determined by a MESA Analyzer-200.

Electrochemical depositing of NiFe alloy at 70°C

The results for the electrochemical deposition of permalloy in chloride electrolyte with a mole fraction Ni/Fe ratio equal to 4.26 as a function of temperature will allow the causes of abnormal deposition to be understood and ensure normal congruent deposition.

In [3], the electrochemical permalloy composition is shown to be strongly dependent on the temperature of the electrolyte.

This work obtained a very interesting composition dependence for the temperature for the electrolyte films with the following composition, in g/l: FeCl₂ 4H₂O-11; NiCl₂ 6H₂O-56; H₃BO₃-25; C₇H₅NaNO₃S-1.5; and HCl-2.7 ml/l. Holding 12 processes at the electrolyte temperature of 60°C and 70°C strongly modifies the iron content.

Figure 3 shows that the sequence of the processes and the current do not affect the composition, which is determined only by the temperature. The permalloy films deposited at an electrolyte temperature of 60°C contain 39.4% iron. The permalloy films deposited at an electrolyte temperature of 70°C contain 19.2% iron. Based on the results of the X-ray spectral analysis, for deposition in the same electrolyte, all current values showed a two-fold higher iron content at 60°C relative to that observed at 70°C.

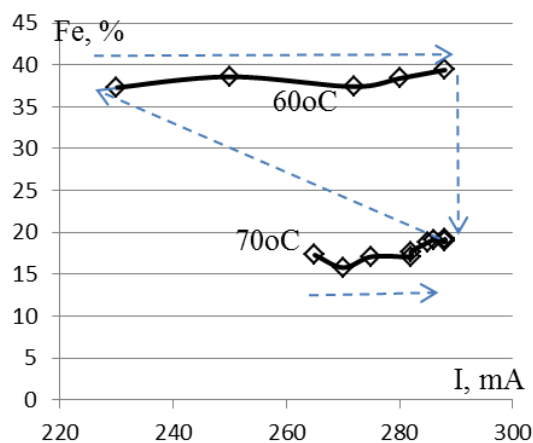


Figure 3. Iron content in permalloy films as a function of the current in a chloride electrolyte with a Ni/Fe ratio of 4.26 at 60°C and 70°C, pH = 1.9.

The film deposition speed of different compositions depending on the current has a slight dependence on the current magnitude at 275 mA, after increasing simultaneously. The electrochemical equivalent of permalloy deposition for the electrolyte has a single value for the films based on the growth rate for samples obtained at 60 and 70°C. However, the doubling of the iron content in the film at a lower temperature may be associated with the charge value of the iron ion.

Electrochemical equivalents for metals with double valence give a natural change in the deposition rate relative to their valence. When the current is determined by the electrochemical charge ions, ferric iron, nickel and

cobalt are precipitated 1.5 times slower than in the bivalent case.

Ionic balance in the hydrolysis of FeCl₂

[8] discusses the ionic equilibrium in the FeCl₂ electrolyte through thermodynamic calculations of equilibrium constants and considers adverse reactions as well as mass and charge balance equations, which are used to accompany the hydrometallurgical leaching process. Ion activity coefficients were calculated using the Bromley equation. In contrast with the generally accepted view of complete dissociation of salts in an electrolyte, partial dissociation was observed.

Distribution under standard conditions of FeCl₂ hydrolysis according to the concentration of the electrolyte: neutral molecules FeCl₂⁰, doubly charged ion Fe²⁺, singly charged ions (Fe²⁺Cl)⁺, and singly charged hydroxide (Fe²⁺OH)⁺.

When used for deposition of permalloy concentration FeCl₂ order 0.1 mol/l solution contains equal concentrations once charged ions (Fe²⁺Cl)⁺ and Fe²⁺ ions. While adding hydrochloric acid difference between these concentrations increased. The contents of the neutral molecules FeCl₂⁰ and hydroxide ions (Fe²⁺OH)⁺ is considerably smaller than the ions (Fe²⁺Cl)⁺ and Fe²⁺. For these calculations, the significant impact hydroxide (Fe²⁺OH)⁺ deposition should not have.

When heated electrolyte, increasing ionization and because the number of momentary ions (Fe²⁺Cl)⁺ or (Fe²⁺OH)⁺ can be less than the number of ions Fe²⁺. Neutral molecules become very little.

A new phenomenon full ionization of ferric chloride at a temperature of 70°C allows to interpreting the changes of the contents of iron in twice in the film, as a change in ion charge twice, from which deposition. At higher temperatures the electrolyte is ion Fe²⁺. Ion with a single charge it (Fe²⁺Cl)⁺. Around the cathode transfers one electron complex, iron deposition at the cathode and Cl⁻ ion excretion in the electrolyte with a change in pH of the electrolyte in the type field.

Based on the ratio of the electrolyte components, the mechanism of anomalous deposition changed from suppression of nickel iron hydroxide deposition to doubling the deposition rate of iron ions (FeCl)⁺ compared to that of multiply charged Fe²⁺. At 70°C, a concentration ratio change occurs due to full ionization of the singly charged ion (FeCl)⁺ and deposition of the electrolyte with multiply charged Fe²⁺, which corresponds to the normal, conventional idea of nickel-iron alloy deposition.

Reviewed explanation of the anomalous deposition of nickel-iron alloy based on the hydrolysis of ferric chloride not only explains why the phenomenon discovered 60 years ago, but also gives the solution to the problem of playing films in frequent reception of structure normal deposition. Due to the occurrence of the temperature regime of the 70°C and the composition of the electrolyte concentration ratio of chloride Ni/Fe = 4.26 in electrochemical obtained permalloy films Ni₈₁Fe₁₉. Numerous previous studies with a wide range of electrolyte composition had different relative content of ions (FeCl)⁺ and Fe²⁺, that conducted to a large spread in the whole film.

The electrochemical deposition of NiFe alloy films with chloride electrolyte containing low salt concentration 0.0037 mol/l

Examining NiFe alloy electrochemical deposition based on the charge of iron ions in the electrolyte with temperature change [1-7] allows for a new approach to creating the electrolyte. The charge of the ions in the electrolyte may depend not only on temperature but also on the concentration of iron. It is well known that reducing the concentration increases the electrolytic dissociation of salts. [8]

A study of solutions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ to ascertain electrolytic dissociation

Figure 4 shows the optical transmittance data at 495 nm and 975 nm at room temperature for a solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as the concentration of FeCl_2 varied from 0.00156 to 0.45 mol/l. Dilute electrolyte leads to increased bandwidth light. Since the concentration of FeCl_2 equal to 0.025 mol/l, there is a feature based on the spectrum at a wavelength of 975 nm. Electrolyte dilution leads to continuous uptake at this wavelength, corresponding ions of iron. At a wavelength of 495 associated with chlorine ion is a significant increase in bandwidth. Hence, as a result of electrolytic salt dissociation FeCl_2 begins education of the second charge of iron ion.

Weak electrolyte solutions for alloy deposition increase not only the dissociation of salts but also the content of doubly charged ions over that of singly charged ions.

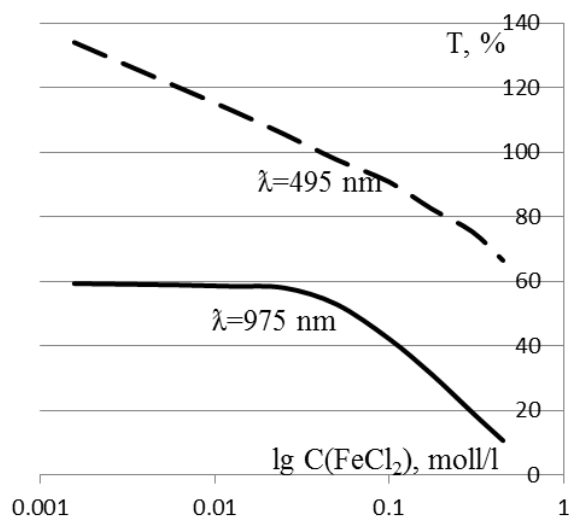


Figure 4. Transmission spectra of solutions at 975 nm and 495 nm as the concentration of FeCl_2 varied from 0.00156 to 0.45 mol/l.

Figure 5 shows the optical transmittance spectra at room temperature for an $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution at wavelengths of 495 nm and 975 nm as the FeCl_2 concentration varied from 0.00156 mol/l to 0.45 mol/l. Dilute electrolyte concentrations lead to an increased width of the light absorption band. When the concentration of FeCl_2 is equal to 0.025 mol/l, a feature in the spectrum is observed at a wavelength of 975 nm. Electrolyte dilution leads

to a continuous intensity increase at this wavelength, which corresponds to the iron ion content. The band at a wavelength of 495 is associated with chlorine ions, and a significant increase in the width of this absorption band is observed. Hence, as a result of electrolytic salt dissociation, FeCl_2 begins to ionize the second charge of the iron ion.

The results of the study of simple electrolytes are mapped with ionic equilibrium in electrolytes FeCl_2 , obtained from the Bromley Equation [8].

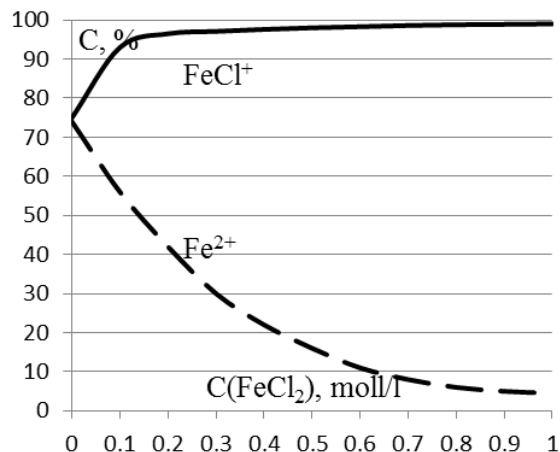


Figure 5. Distribution under standard conditions of FeCl_2 hydrolysis according to the concentration of the electrolyte: doubly charged Fe^{2+} ions and singly charged ions ($\text{Fe}^{2+}\text{Cl}^+$).

In a solution with a high concentration of FeCl_2 content one charging ions FeCl^+ prevails over the number two charging Fe^{2+} ions. By choosing a concentration of FeCl_2 must obtain a deposition of iron ions, Fe^{2+} rather than ferric chloride FeCl^+ , which creates in perceptible film admixture of chlorine and changes the speed due to the magnitude of the electric charge.

The electrochemical deposition of NiFe alloy films with chloride electrolyte containing low concentration of basic salts

In works [3-5], complete dissociation of ferric chloride is achieved by heating the electrolyte to a temperature of 60-70°C.

Electrochemical deposition of films of $\text{Ni}_{81}\text{Fe}_{19}$ with a low concentration of impurities in the electrolyte, i.e., mol/l: Ni-0.046 and Fe-0.01, at room temperature (19-25°C) improves the accuracy of the film composition and enhances the magnetic properties.

In a solution with a high concentration of FeCl_2 , the singly-charged FeCl^+ ions dominate when compared to the doubly charged Fe^{2+} ions. By choosing a concentration of FeCl_2 to obtain a deposition of Fe^{2+} iron ions rather than ferric chloride FeCl^+ , a precipitable film admixture of chlorine is created, which changes the deposition rate due to the magnitude of the electric charge.

An electrodepositing process must have equal Ni^{2+} ions and iron ions, Fe^{2+} . Iron chloride ($\text{Fe}^{2+}\text{Cl}^+$) creates a precipitable film admixture of chlorine, and for the largest current, it increases the speed of iron electrodepositing compared to that of the doubly charged iron ions. The choice of the concentration of FeCl_2 should result in a

preferential film content of iron ions, i.e., Fe^{2+} rather than iron chloride ($\text{Fe}^{2+}\text{Cl}^+$).

For different iron ion contents, the deposition from electrolytes with FeCl_2 occurs differently. When a current density of 4 mA/cm^2 is used for deposition on molybdenum foil, the dependence of the iron content in the films on the concentration of salt in the electrolyte was obtained, as shown in Figure 6. A study on the composition of the films was conducted using a *PhilipsXL 40* X-ray microanalyzer.

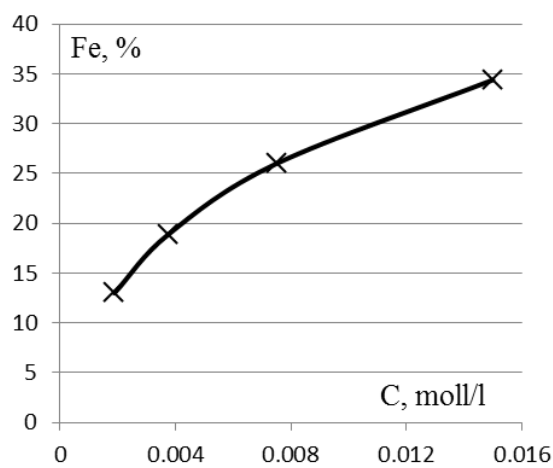


Figure 6. Iron content in the NiFe alloy films electrochemically deposited from a chloride electrolyte with concentrations NiCl_2 of 0.064 mol/l and FeCl_2 0.015 mol/l and 2, 4 and 8 times dilutions.

On the content of iron in permalloy films by diluting chloride electrolyte, it should be that films with permalloy $\text{Fe}_{19}\text{Ni}_{81}$ are obtained by simple electrochemical chloride electrolyte with the attitude of the $\text{Ni/Fe} = 4.26$ and concentrations of Fe^{+2} - 0.004 mol/l . Consequently, at these concentrations of chlorides of nickel and iron in molten nickel and iron ions charges Ni^{2+} , Fe^{2+} have same amount on cathode discharge two.

Electrochemical deposition of permalloy films with varying degrees of nickel electrolyte

The change in the sedimentation rate, iron and magnetic properties of permalloy films with a constant content of iron and variable content of nickel in chloride electrolyte on a silicon substrate was examined.

The electrolyte composition had the following specified concentrations: mol/l : NiCl_2 - 0.0016 ; FeCl_2 - 0.00037 ; H_3BO_3 - 0.404 ; $\text{C}_7\text{H}_5\text{NaNO}_3\text{S}$ - 0.0146 , NH_4OH - 0.0047 . The films were held at a temperature of $22 \pm 3^\circ\text{C}$ and $\text{pH} = 6.0 \pm 0.5$.

The analysis of the results presented in Figure 7 shows that when the chloride hydrate content of nickel in the electrolyte was 7.6 g and 1.5 g of ferric chloride hydrate was present, the corresponding ratio of nickel and iron was 4.26 , and the iron content in the film was less than 19% . The deposition mainly resulted in nickel.

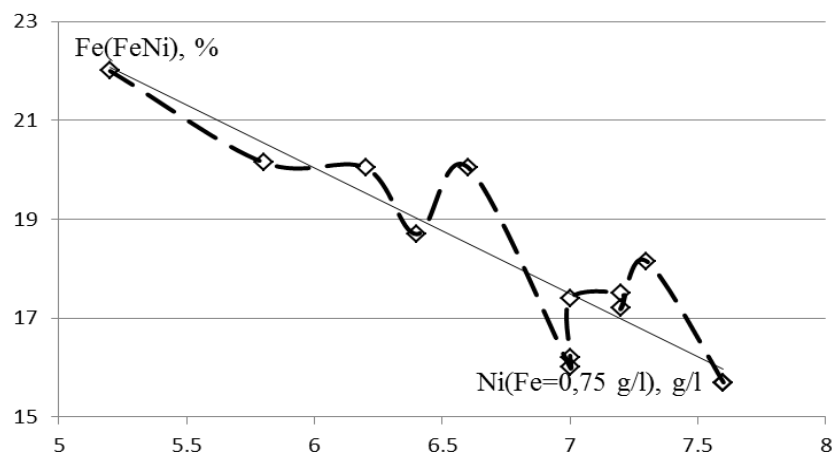


Figure 7. The iron content in the NiFe alloy films in a chloride electrolyte with concentrations of NiCl_2 of 0.048-0.064 mol/l and FeCl_2 of 0.0037 mol/l.

The content of nickel in the electrolyte must be reduced because a higher speed compared to that for the deposition of nickel iron occurs due to the higher electrochemical potential of nickel, which is more noble. An iron content of 19% is obtained by reducing the concentration of nickel in the electrolyte to 16%.

The magnetic properties of the thin films are presented in Figure 8, which shows a comparison of the magnetization for two plates. NiFe film "1" contains 20.4% Fe and NiFe film "2" contains 18.7% Fe. The magnetic properties of the permalloy films are enhanced with the addition of an ammonia chloride electrolyte. The coercivity decreases and increases the magnetization. Electrolyte 1 containing 3.3 g nickel chloride hydrate and 1.5 g ferric chloride hydrate with ammonia additive 1 ml/l resulted in the optimal magnetic permalloy films.

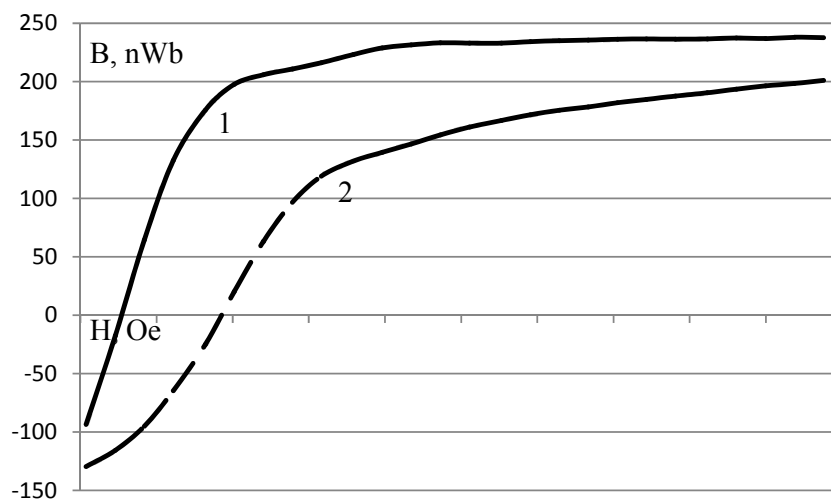


Figure 8. Magnetization curves of permalloy films derived from a chloride electrolyte with a low concentration containing (Ni)-3.3 g/l (0.016 mol/l) and (Fe)-0.75 g/l (0.0037 mol/l) "30" and with an additive in an electrolyte

with low concentrations of Ni-3.1 g/l (0.014 mol/l) and Fe-0.75 g/l (0.0037 mol/l) of a "28" ammonia solution 1 ml/l (NH₃-0.0047 mol/l).

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The effect of the temperature of the electrolyte on the ability to obtain permalloy films containing 19% iron is presented for selected concentrations of iron in solution in Figure 9. At low concentrations of nickel and iron chlorides, the room temperature deposition rate is significantly less than that at higher concentrations and 70°C.

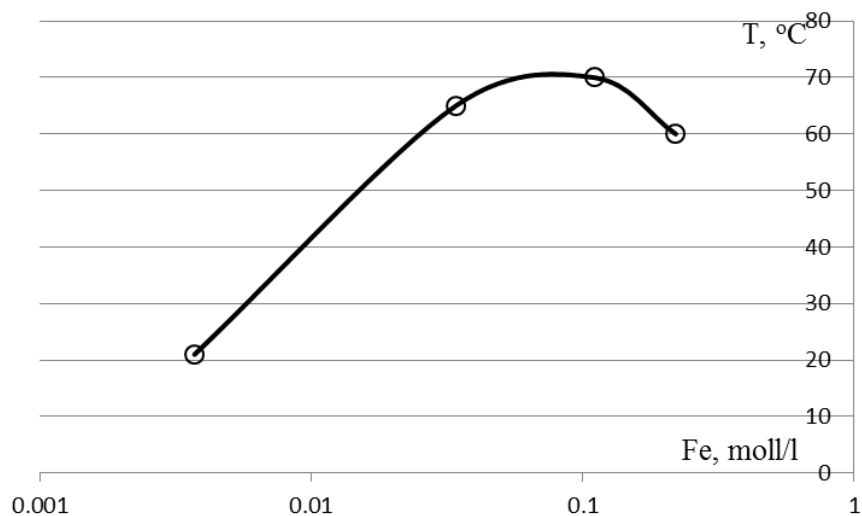


Figure 9. Electrochemical deposition of FeNi alloy films containing 19% iron from electrolytes with concentrations of Fe of 0.0037 mol/l at a temperature point, 0.034 mol/l at a temperature of 65°C, 0.11 mol/l at a temperature of 70°C, and 0.22 mol/l at a temperature of 60°C.

Conclusion

When an electrolyte is heated, ionization increases, and because the quantity of $(\text{Fe}^{2+}\text{Cl})^+$ ions can be less than that of Fe^{2+} ions, the number of neutral molecules becomes very small. The results for the composition of permalloy films elucidated a new phenomenon, i.e., full ionization of ferric chloride into Fe^{2+} ions in an electrolyte at a temperature of 70°C.

The ratio of ion electrolyte components changes the anomalous deposition of nickel deposition via iron hydroxide suppression by doubling the deposition rate for singly charged iron ions $(\text{FeCl})^+$ compared with that of doubly charged Fe^{2+} . Deposition of an electrolyte with Fe^{2+} corresponds to the normal, generally accepted notion of deposition of nickel-iron alloy.

The explanation of the anomalous deposition of nickel-iron alloy based on the hydrolysis of ferric chloride not only explains why the phenomenon was discovered 60 years ago but also solves the problem of creating films with normal deposition structures. A temperature of 70°C and an electrolyte concentration ratio of Ni/Fe chloride of 4.26 in electrochemical deposition provide permalloy films of Ni₈₁Fe₁₉. Numerous previous studies with a wide range of electrolyte composition used different relative contents of ions to create a wide distribution in the whole



film.

The creation of permalloy films from dilute solutions with a concentration of iron 0.0037 mol/l increases the depletion of ferric chloride and the electrolytic content of doubly charged ions relative to singly charged ions. The use of dilute chloride electrolyte for NiFe deposition with a ratio of Ni/Fe = 4.26 confirms the principle that the charge of iron ions influences the composition of permalloy films. Chloride electrolytes laced with ammonia can be used for the deposition of permalloy films with good magnetic properties at room temperature.

The deposition process for permalloy films from an electrolyte with chemical additives should be called an electrochemical process. The concepts of congruent alloy electrochemical deposition and electrochemical deposition based on the charge of ions in an electrolyte have been introduced for the first time.

References

- [1] *Korovin N.V.* O katodnom processe pri elektroosajdenii splava jelezo-nikel // Journal neorganicheskoy khimii, 1957, T. 2, V. 9, pp. 2259-2263.
- [2] *J.M. Brownlow*, Method of making magnetic thin film device// Patent US 3480522, 1966.
- [3] *R.D. Tikhonov*, Electrodeposition of Ni-Fe Alloy for the Production of Integrated Microcircuits// Moscow, Electroplating & surface treatment, 2015, T. XXIII, №4, pp. 13-19.
- [4] *R.D. Tikhonov*, Normal Electrochemical Deposition of NiFe Films// Advances in Research, 2017, 11(2), P. 10.
- [5] *R.D. Tikhonov*, Influence of additives like saccharin and hydrochloric acid chloride electrolyte for electrochemical deposition of permalloy films// British Open Research Publication, British Open Journal of Chemical Sciences, V. 1, No. 1, 2017, pp. 1-5.
- [6] *Korovin N.V. Obtschay khimiy, M. Vyshay shkola.* 1998. P. 559.
- [7] *H. Nakano, M. Matsuno, S. Oue, M. Yano, Sh. Kobayashi, and H. Fukushima*, Mechanism of Anomalous Type Electrodeposition of Fe-Ni Alloys from Sulfate Solutions// The Japan Institute of Metals, Materials Transactions, 2004, Vol. 45, No. 11 pp. 3130 – 3135.
- [8] *Man-Seung Lee*, Use of the Bromley Equation for the Analysis of Ionic Equilibria in Mixed Ferric and Ferrous Chloride Solutions at 25°C, // Metallurgical and materials transactions B, 2006, V. 37B, pp. 173-179.
- [9] *I.W. Wolf*, Electrodeposition of Magnetic Materials// Journal of Applied Physics 1962, V.33(3), pp. 1152-1159.
- [10] *A. Brenner*, Electrodeposition of Alloys// Academic Press, New York, 1963, P. 621.
- [11] *H. Dahms and I.M. Croll*, The Anomalous Codeposition of Iron-Nickel Alloys// J. Electrochem. Soc., 1965, volume 112, issue 8, pp. 771-775.
- [12] *H.V. Venkatesetty*, Electrodeposition of Thin Magnetic Permalloy Films// J. Electrochem. Soc., 1970, V. 117, No. 3, pp. 403-407.
- [13] *J.V. Powers & L.T. Romankiw*, Patent US 3,652,442, 1972.
- [14] *E.E. Castellani, J.V. Powers & L.T. Romankiw*, Patent US 4,102,756, 1978.
- [15] *J. Horkans*, Effect of Plating Parameters on Electrodeposited NiFe// J. Electrochem. Soc.: Electrochemical Science and technology, 1981, V. 128, No. I, pp. 45-51.
- [16] *L.T. Romankiw*, Proc. Symp. on Electrodeposition Technology, Theory and Practice, The Electrochemical Society, NJ, 1987, V. 87, №8, pp. 105-107.
- [17] *S. Hessami and C.W. Tobias*, A Mathematical Model for Anomalous Codeposition of Nickel-Iron on a Rotating Disk Electrode// J. Electrochem. Soc. 1989, 136, pp. 3611–3616.
- [18] *N. Furukawa, M. Hanabusa, and T. Hayashi*, Electrodeposition of Ni-Fe alloys from sulfate, sulfate-chloride and chloride baths// The American Electroplaters and Surface Finishers Society, Inc. (AESF) The Proceedings of the 79th AESF Annual Technical Conference, 1992, pp. 583-586.
- [19] *M. Matlosz*, Competitive Adsorption Effects in the Electrodeposition of Iron-Nickel Alloys// J. Electrochem.



Soc., 1993, V. 140, No. 8, pp. 2272-2279.

- [20] *P.C. Andricacos and L.T. Romankiw*, Magnetically Soft Materials: Their Properties and Electrochemistry. Advances in Electrochemical Science and Engineering, editors: H. Gerischer, Ch.W. Tobias, 1994, P. 331.
- [21] *A.Thommes, W. Stark, W. Bacher*, Die galvanische Abscheidung von Eisen-Nickel in LIGA-Mikrostrukturen// Institut für Mikrostrukturtechnik, 1995, P. 95.
- [22] *Th.M. Harris, and J.St. Clair*, Testing the Role of Metal Hydrolysis in the Anomalous Electrodeposition of Ni-Fe Alloys// J. Electrochem. Soc. 1996, V. 143, I. 12, pp. 3918-3922.
- [23] *S.D. Leith, Sh. Ramli, D.T. Schwartz*, Characterization of Ni_xFe_{1-x} ($0.1 < x < 0.95$) Electrodeposition from a Family of Sulfamate-Chloride Electrolytes// Journal of the Electrochemical Society. 1999. V. 146, pp. 1431-1438.
- [24] *A. Afshar, A. G. Dolati, and M. Ghorbani*, Electrochemical characterization of the Ni-Fe alloy electrodeposition from chloride-citrate-glycolic acid solutions// Materials Chemistry and Physics, 2002, V. 77, pp. 352–358.
- [25] *Chin-Ming Chu*, The Effect of Complexing Agents on the Electrodeposition of Fe-Ni Powders// J. Chin. Inst. Chem. Engrs., 2003, V. 34, No. 6, pp. 689-695.
- [26] *M.C. Wurz, D. Dinulovic, H.H. Gatzert*, Investigation of permeability on electroplated and sputtered permalloy// Institute for Microtechnology Hanover University. Proc. 8th Int. Symposium on Materials, Processes and Devices, 206th Meet. Of The Electrochemical Society 2004, Honolulu, Hawaii, USA. P. 526.
- [27] *F.R. Bento, L.H. Mascaro*, Electrocrystallisation of Fe–Ni alloys from chloride electrolytes// Surface and Coatings Technology, 2006, V. 201, Is. 3–4, pp. 1752–1756.
- [28] *K. Smistrup, P.T. Tang, and P. Møller*, Pulse Reversal Permalloy Plating Process for MEMS Applications// copyright The Electrochemical Society ECS Transactions, 2007, 25, pp. 179-189.
- [29] *E. Beltowska-Lehman, P. Indyka*, Electrodeposition and characterization of thin magnetic Ni-Fe films on copper substrates// Archives of metallurgy and materials. 2008. V. 53, pp. 97-99.
- [30] *P. Fricoteaux and C. Rousse*, Influence of substrate, pH and magnetic field onto composition and current efficiency of electrodeposited Ni-Fe alloys// Journal of Electroanalytical Chemistry, 2008, V. 612, No. 1, pp. 9–14.
- [31] *M. Poroch-Seritan, S. Gutt, Gh. Gutt, M.M. Bobu, T. Severin*, Synthesis and characterization of nickel iron alloys by electrodeposition// Roznov pod Radhostem, Czech Republic, Metal 2010. 18.-20.5.2010. pp. 1-7.
- [32] *R. Abdel-Karim, Y. Reda, M. Muhammed, S. El-Raghy, M. Shoeib, and H. Ahmed*, Electrodeposition and Characterization of Nanocrystalline Ni-Fe Alloys// Journal of Nanomaterials, 2011, V. 2011, Article ID519274, P. 8.
- [33] *A.A. Frey, N.R.Wozniak, T.B. Nagi, M.P. Keller, J.M. Lunderberg, G.F. Peaslee, P.A. DeYoung, and J.R. Hampton*, Analysis of Electrodeposited Nickel-Iron Alloy Film Composition Using Particle-Induced X-Ray Emission// International Journal of Electrochemistry, V. 2011, Article ID 604395, 7 pages.
- [34] *Y.D. Yu, G.Y. Wei, J.W. Lou, L.X. Sun, L. Jiang and H.L. Ge*, Preparation of NiFe films by magnetic electroplating// Surface Engineering, 2012, V. 28, N. 1.
- [35] *V.V. Amelichev, I.E. Abanin, V.V. Aravin, D.V. Kostyuk, S.I. Kasatkin, A.A.Reznev, A.N. Saurov*, Rasvitie tehnologii magnitopoluprovodnicovykh microsistem // Izvestiy vuzov. Elektronika, no 4, 2015, pp. 505 – 510.
- [36] *Y. Cao, G. Y. Wei, H. L. Ge & X. F. Meng*, Study on preparation of NiFe films by galvanostatic electrodeposition, Surface Engineering, 2014, V.30, No.2, pp. 97-101.
- [37] *M. Moniruzzaman, K.M. Shorowordi, A. Ashrafui, and M.F.N. Taufique*, Fe-Ni alloy electrodeposition from simple and complex type sulfate electrolytes containing Ni/Fe ratio of 1 and 12// The Institution of Engineers, Bangladesh, Journal of Mechanical Engineering, 2014, 44(1), pp. 50-56.
- [38] *Nai-Chang Lo, Pei-Chen Chung, Wan-Jung Chuang, Sodio C.N. Hsu, I-Wen Sun, and Po-Yu Chenb*, Voltammetric Study and Electrodeposition of Ni(II)/Fe(II) in the Ionic Liquid 1-Butyl-1-Methylpyrrolidinium Dicyanamide// Journal of The Electrochemical Society, 2016, 163 (2), pp. 9-16.
- [39] *Yu.D. Gamburg, G. Zangari*, Theory and Practice of Metal Electrodeposition// Springer, 2011. P. 506.
- [40] *S.S. Kruglikov*, Osobnosti raspredeleniy skorosti osajdeniy metalov i splavov v processe formirovaniy electroosajdenykh sloev pri nanesenii pokrytiy na komponenty electronnykh ustroystv // Electroplating & surface treatment, 2017, T. XXV, №1, pp.41-54.



- [41] *T. Homma, M. Kunimoto, M. Sasaki, T. Hanai, M. Yanagisawa*, Surface enhanced Raman spectroscopy measurement of surface pH at the electrode during Ni electrodeposition reaction// Springer, Journal of Applied Electrochemistry, published on line: 14 December 2017.
- [42] *I. Tabakovic, J. Gong, S. Riemer and M. Kautzky*, Influence of Surface Roughness and Current Efficiency on n Gradients of Thin NiFe Films Obtained by Electrodeposition// J. Electrochem. Soc. 2015, 162(3): pp. 102-108
- [43] *R.S. Larson*, The Role of Homogeneous Chemical Kinetics in the Anomalous Codeposition of Binary Alloys// J. Electrochem. Soc. 2007 154(8): pp. 427-434
- [44] *Chi-Chang Hu*, The Inhibition of Anomalous Codeposition of Iron-Group Alloys Using Cyclic Voltammetry// J. Electrochem. Soc. 2002 149(11): pp. 615-622
- [45] *P. Tsay and Chi-Chang Hu*, Non-Anomalous Codeposition of Iron-Nickel Alloys Using Pulse-Reverse Electroplating Through Means of Experimental Strategies// J. Electrochem. Soc. 2002 149(10): pp. 492-497
- [46] *F. Wang, L. Li, Sh. Qiu, H. Wang*, Ferronickel preparation using Ni-Fe co-deposition process// Journal of Central South University, 26 January 2017.
- [47] *R.D. Tikhonov, A.A. Cheremisinov, S.S., Generalov, D.V. Gorelov, S.A. Polomoshnov, and Iu.V. Kazakov*, Poluchenie concentratorov magnitnogo poly s pomoshiu electrochemicheskogo osahzdeniy permalloy// Nano- i microsistemnay tehnika. 2015, N. 3, pp. 51-57.
- [48] *R.D. Tikhonov, S.A. Polomoshnov, D.V. Gorelov, Ju.V. Kazakov, V.V. Amelichev, N.N. Nikolaeva*, Soft magnetic Permalloy films by an electrochemical deposition received from chloride electrolyte// Oboronniy complex – nauchno-tehnicheskomu progressu Rossii, no 4, pp. 26 – 31, 2015.
- [49] *V.V. Amelichev, S.A. Polomoshnov, N.N. Nikolaeva, R.D. Tikhonov, M.A. Kupriyanova*, Electrochemical Deposition Process for Permalloy Films on Magneto-Semiconductor Microsystems// Semiconductors, 2017, T. 51, I. 13, pp. 1707 - 1708. Pleiades Publishing, Ltd.
- [50] *R.D. Tikhonov, S.A. Polomoshnov, D.V. Gorelov, Iu.V. Kazakov, and A.A. Cheremisinov*, Variirovanie magnitnich svoistv plenok permalloy // Nano- i microsistemnay tehnika. 2016. N. 9. pp. 563-568.
- [51] *R.D. Tikhonov*, Sposob electrochimicheskogo localnogo osajdeniy plenok permaloiy Ni₈₁Fe₁₉ dly integralnyh microsystem, Patent RF, 2623536, 2017.
- [52] *R.D. Tikhonov, and A.A. Cheremisinov*, Magnetization of Permalloy Films// Russian Microelectronics, Pleiades Publishing, Ltd., 2017, V. 46, No. 2, pp. 95–104.
- [53] *R.D. Tikhonov*, Magnitnyi datchik toka s plenochysv koncentratorom, Patent RF, 2656237, 2018.
- [54] *R.D. Tikhonov, S.A. Polomoshnov, V.V. Amelichev, N.N. Nikolaeva, D.V. Gorelov, Iu.V. Kazakov, N.P. Klinchikova, and Iu.S. Zybina*, Varyirovanie magnitnich svoistv plenok permalloy // Nano- i microsistemnay tehnika. 2018. No. 1. pp. 26-39.