Mechanism of the Electrochemical Deposition of a CoNiFe Alloy

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

Original Research Article

ABSTRACT

Heating the chloride electrolyte to a temperature of 70°C ensures the normal codeposition of the components of the CoNiFe alloy as a result of the discharge of single-charged iron and cobalt species $(Fe^{2+}Cl^-)^+$ and $(Co^{2+}Cl^-)^+$, respectively and double-charged Ni^{2+} ions at a high cathode current density. The chloride electrolyte obtained with filtration and pH correction by hydrochloric acid provides the electrochemical deposition of CoNiFe films with a $C_{Co}:C_{Ni}:C_{Fe}$ ratio of 1:1:1. The mechanism of the abnormal deposition of Co, Fe and Ni occurs due to the incomplete ionization of atoms and differences in ion mobility. Based on the experimental results of CoNiFe films, an electrochemical deposition mechanism is proposed. In contrast to the well-known in the literature, the phenomena occurring in the volume of electrolyte, including transmission of ions, with the determining effect is the mobility and formation of positive ions on the anode. CoNiFe films are produced without mechanical stresses, with a uniform structure and with high magnetic parameters without a high burn temperature. Electrochemical deposition when the charge of ions in the electrolyte is taken into account allows to obtaining a reproducible electrochemical deposition of CoNiFe films.

Keywords: CoNiFe films; electrochemical deposition; chloride electrolyte; filtration; abnormal deposition of Co, Fe and Ni; transfer of ions; ion charge.

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1. INTRODUCTION

The electrochemical coating of CoNiFe is used in many areas of technology: To reduce corrosion and wear, to fabricate magnetic devices, to create electro catalytic materials.

Compared to "dry" processes, electrochemical deposition gives a smoother coating with fewer defects and allows you to increase the thickness of films without mechanical stresses, if necessary.

The electrochemical deposition of iron, nickel and cobalt exploits these electrolyte metals as bivalent ions, in accordance with the valence of the metal that forms salts. However, electrolytic dissociation and hydrolysis ionize atoms in accordance with the energy levels of salt in water.

This paper provides the results of the study of the electrochemical deposition of the CoNiFe triple system from a chloride electrolyte, with specified equimolar concentrations of Co, Ni and Fe (Co:Ni:Fe ratio of 1:1:1) at 70°C, and considers the experience of the congruent deposition of a NiFe permalloy [1-5]. The aim of the study is to determine the effect of the mass transfer of ions in the electrolyte on the electrochemical deposition mechanism of the CoNiFe alloy.

2. POLARIZING ELECTROLYTES OF COBALT, NICKEL AND IRON SULFIDES

The mechanism of the electrodeposition of nickel, iron and their mixture with a sulfide electrolyte was investigated in the work [6]. As shown in Fig. 1, the potential for nickel recovery at -0.75 V is more positive than that for iron at -0.92 V and that for a mixed solution at -0.88 V, i.e., has an intermediate value. During joint discharge, there is an abnormal phenomenon; the rate of the recovery of nickel ions is much lower than that of iron. Polarization curves with a large current have no saturation. It is believed that in the electrical quenching of nickel, the inhibitory effect is exerted by the absorption of iron hydroxides.
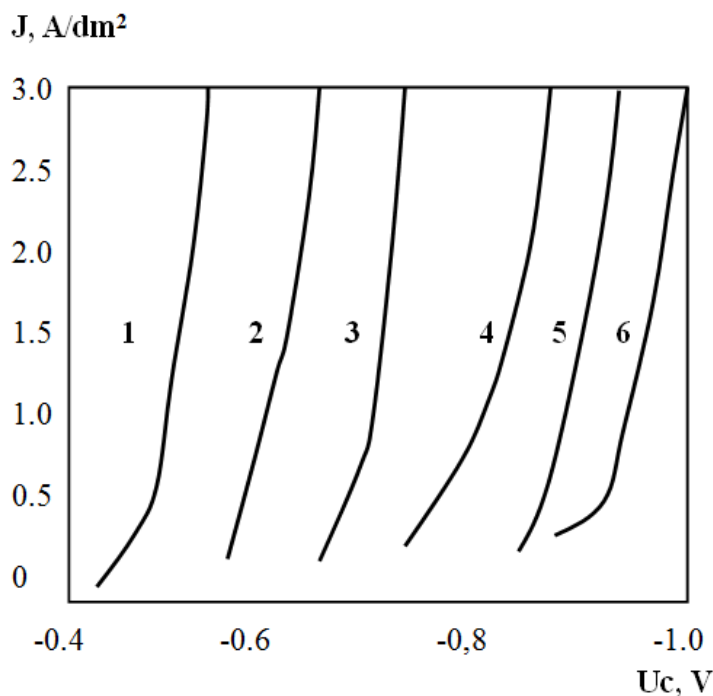

Fig. 1. Polarization curves obtained for electrodeposited cobalt, nickel and iron at a pH of 1.9 with the addition of 30 g/l boric acid to the solution: 1. $CoSO_4$, 4. $NiSO_4$, 6. $FeSO_4$, 5. mixed $NiSO_4$ and $FeSO_4$ at 25°C; 2. $NiSO_4$ at 95°C; 3. $FeSO_4$ at 95°C

The rate of the joint recovery of nickel and iron ions has an average value between separate values and is not aggregated. At temperatures over 90 degrees Celsius, the recovery rate of nickel ions is higher than that of iron ions. The polarization curves show that the potential for nickel recovery is at -0.59 V, which is more positive than that of iron, at -0.7 V. The recovery potential ratio is not the cause of abnormal deposition at high temperatures for normal preeminent nickel deposition, as evidenced by the deposition of NiFe films obtained in an autoclave at temperatures of up to 120°C from a sulfate electrolyte with 30 g/l boric acid.

The kinetics of the electrode processes [7] considers the polarization curves as overexertion—a shift in the electrode's potential from a thermodynamic equilibrium value. The leaking current disturbs the thermodynamic equilibrium. Due to different factors acting at different speeds, different types of overexertion are distinguished.

Overexertion creates a voltage threshold that determines the transition from the small current values of the cathode due to a potential barrier at the edge of the phase section to the rapid increase in the electrode current. Observations of interactions occurring at the electric double layer near the cathode do not consider the existence of ions with different charges and mobility's in the electrolyte volume, mass transfer, or the mixing and viscosity of the electrolyte. These phenomena determine the volume properties of the electrolyte.

Iron, cobalt and nickel are virtually insoluble in water. The existence of metal ions in water is due to their presence in the form of salts. The deposition of metals on the cathode is accompanied by the discharge of the ion and the destruction of the salt molecule. This process creates a layer of residues of molecules near the cathode, which changes the composition of the electrolyte.

3. PARTIAL ION CURRENTS

The magnitude of the potential difference between the cathode and the anode determines the intensity of the electric field in the electrolyte, the speed of movement of the ions and the density of the current at each point. The amount of current in each part of the area between the cathode and the anode is a constant value due to the continuity of the current. The deposition of

ions on the cathode fixes the composition of the current.

In an electrolyte containing the three components $CoCl_2$, $NiCl_2$, and $FeCl_2$, the difference between the charge of the ions and their mobility determines the difference in the partial density of the current for each component in the form of single-charged ions.

$$J = q \; E_+ [(n \; u)\langle(FeCl)^+\rangle + (n \; u)\langle(CoCl)^+\rangle + (n \; u)\langle(NiCl)^+\rangle]$$

A mathematical model has been developed [8] that describes the electrodeposition of the nanometer multilayered magnetic-sensitive structures of FeCoNiCu/Cu. Changes in precipitation are calculated based on the partial currents of two valence ions during the pulsed deposition performed on the rotating cathode.

4. ELECTROCHEMICAL DEPOSITION OF CoNiFe FILMS

CoNiFe films are deposited with a 1:1:1 ratio of $CoCl_2$ $6H_2O$:$FeCl_2$ $4H_2O$:$NiCl_2$ $6H_2O$ at 0.5 mole/l. The electrolytes added include 20 g/l boric acid (H_3BO_3), 1.5 g/l sodium hydrate ($C_7H_4NaNO_3S$), and 3 ml/l acid salt. A film from the specified electrolyte is deposited in an electrochemical cell with a galvanic bath volume of 2 liters and a graphite anode. The cathode's nickel ring electrode comes into contact around the perimeter with a metallized silicon plate located vertically in the rig.

Areas of film with a diameter of 8 cm (54 cm^2) were obtained on the metallized layers of NiCr, and a Ni surface of a silicon plate with a diameter of 100 mm was covered with a layer of SiO_2.

The electrolyte had a temperature of 70°C due to heating by a submersible heater and was mixed with a magnetic mixer. The main parameter of the process, the force of the current, was maintained constantly when setting the current density from 5 to 20 mA/cm^2 in the deposition area on the silicon plate.

Electrolytes with Co, Ni and Fe concentrations of 0.476 mol/l gave [9] a 180 mA deposition film with a composition of $Co_{32}Ni_{61.5}Fe_{6.5}$ (1 process - $Co_{29,52}Ni_{64,16}Fe_{6.32}$; 2 processes - $Co_{34,16}Ni_{58,83}Fe_{6.5}$). When deposited at 250 mA, the composition of the $Co_{18,61}Ni_{76,9}Fe_{4.48}$ film changed after electrolyte filtration in the next process to $Co_{45.5}Ni_{44,1}Fe_{10,4}$. Thus, electrolyte

filtration significantly changes the content in the solution of electroactive ions, which are deposited on the substrate. When deposited at a current of 500 mA, the composition of the film was $Co_{57.8}Ni_{17.1}Fe_{25.1}$; at 750 mA, it was $Co_{48,04}Ni_{8,4}Fe_{43.55}$; and at a current of 1000 mA, the film composition was $Co_{32}Ni_{61.5}Fe_{6.5}$.

The dependence of the composition of the CoNiFe films on the current density at the cathode during electrochemical deposition was investigated.

The relative content of the Co, Ni and Fe components in the film shown in Fig. 2 differs from the composition of the electrolyte with the same component content of 33.3% and varies greatly depending on the density of the current. When the current density increases from 5 to 15 mA/cm^2 in the CoNiFe film, the iron content increases from 8.9% to 41.3% and with a current density of 20 mA/cm^2, the iron content remains at the same level of 42.35%. With an increase in the current density from 5 to 15 mA/cm^2 in the CoNiFe film, the nickel content decreases from 38.5% to 7.9% and with a current density of 20 mA/cm^2, the nickel content remains at the same level of 7.85%. The actual change in the iron and nickel content at a current density of 10 mA/cm^2 changes the cobalt content in the overall balance

to 60.8%. With a current density of 5, 15 and 20 mA/cm^2, the cobalt content values are similar, at 50.6, 50.8 and 49.8, respectively. The concentrations of the components are identical to those obtained during the deposition of the CoNiFe films with an electrolyte concentration of 0.476 mole/l; i.e., the results are repeated.

The composition of the films indicates that the density of the partial current of the cobalt ions has almost a constant value. The density of the partial current of the nickel ions decreases as the total current increases. The density of the partial current of the iron ions increases as the total current increases.

The growth rate of the CoNiFe films in Fig. 3 differs little in terms of the electrochemical deposition from chloride electrolytes with concentrations of each component being 0.0074, 0.08 and 0.5 mole/l, i.e., resulting in a difference of concentrations of 70 times. The growth rate of CoNiFe films increases as the current density increases but depends little on the concentration of the component. This result may be due to the limitation of the number of ions capable of discharge on the cathode. The growth rate of the CoNiFe films, calculated by Faraday's law, exceeds the experimental values by approximately two times.
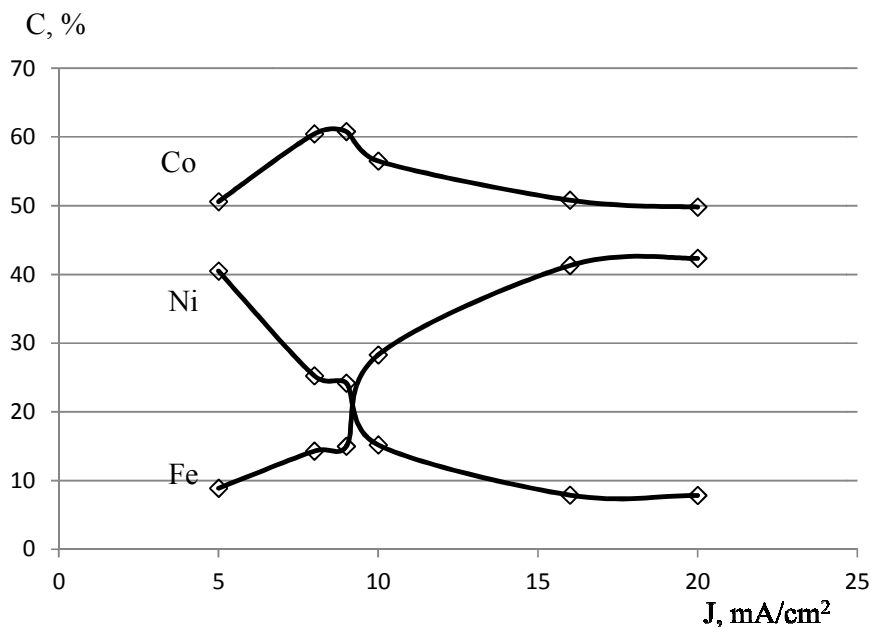

Fig. 2. The CoNiFe film component content depends on the current density derived from the chloride electrolyte with a 0.5 mole/l concentration
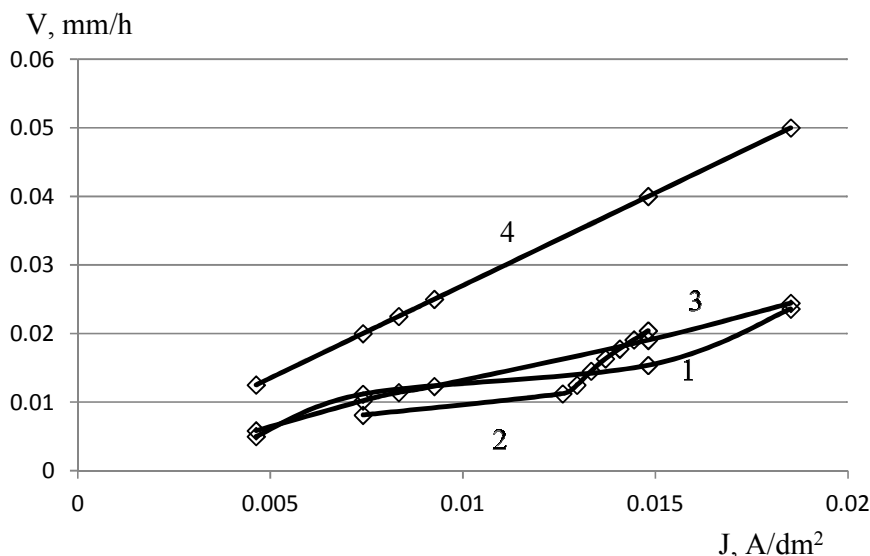
Fig. 3. Growth rate of CoNiFe films with respect to the current density of the J cathode experiment, which was performed with electrolytes with a concentration of each component of 0.0074 (3), 0.08 (2) and 0.5 (1) mole/l, as calculated by Faraday's law (4)

The mobility values of the ions are calculated by the weight of the film prepared by a deposition rate of 0.02 mm/h, by the content of the component in the film $Co_{50}Ni_8Fe_{42}$, and by the concentration of the salts in the 0.5 mole/l electrolyte, and the values are based on the magnitude of the intensity of the electric field in the electrolyte at 0.5 V/cm. For a square centimeter, the substrate surface was discharged in an hour to obtain 9.3×10^{18} single-charged cobalt ions, 7×10^{18} single-charged iron ions and 3×10^{18} double-charged nickel ions. The value of the partial current on the cathode is 0.41 mA/cm^2 for cobalt, 0.31 mA/cm^2 for iron, and 0.27 mA/cm^2 for nickel, and the general current is 0.99 mA/cm^2. The total current of the metal ions on the cathode is much smaller than the current of 15 mA/cm^2, which is set during the process.

When the ions are concentrated in the 0.5 mole/l electrolyte and their full ionization is achieved, the mobility values are 1.6×10^{-8} m^2/V s for the single-charged cobalt ion of CoCl, 1.28×10^{-8} m^2/V s for the single-charged iron ion of FeCl and 0.26×10^{-8} m^2/V s for the double-charged nickel ion of Ni. If we consider that the ions deposited on the cathode differ 15 times from the electrics, the mobility of the ions can be increased by an appropriate degree.

Fig. 4 shows the voltage dependence between the anode and the cathode on the density of the stabilized current of 5 ÷ 20 mA/cm^2 at equal concentrations of $CoCl_2$, $NiCl_2$ and $FeCl_2$ in the electrolyte.

The drop in the voltage in the electrode space of 3 cm changes almost linearly with an increase in the current density from 5 to 20 mA/cm^2; i.e., the electrolyte conductivity determines the passage of the current in the working mode. A current density of 16 mA/cm^2 enables electrochemical deposition from the chloride electrolyte with the same concentrations of each component, 1. 0.5, 2. 0.08, and 3. 0.0074 mole/l at electrode voltage 2 V, 3.5 V and 5.5 V by reducing the number of ions in the electrolyte.

5. DISCUSSION OF RESULTS

The choice of current density used to obtain the desired composition of films is widely used in electrochemical deposition. The mechanism of the influence of the cathode current density on the composition of the resulting alloys is not defined.

One can ask the following: why does the composition of the CoNiFe film in our experiment depend on the density of the current, and at a high current density, why does the composition cease to change?
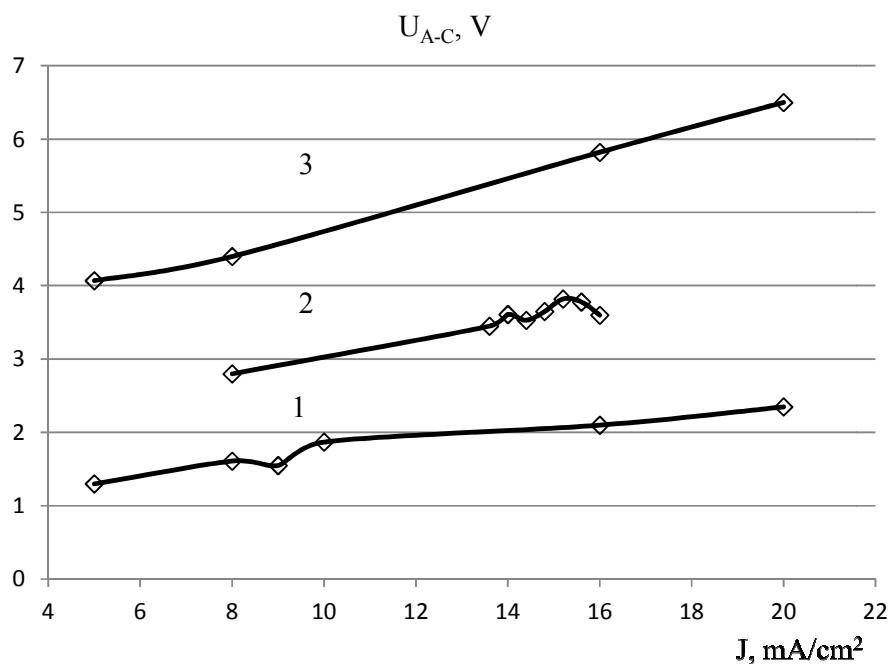
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U_{A-C}, V

Fig. 4. Voltage between the anode and the cathode depending on the current density of 5 ÷ 20 mA/cm² with CoCl₂, NiCl₂ and FeCl₂ in a chloride electrolyte, at concentrations of 0.5, 0.08, and 0.0074 mole/l, respectively

Here are some of the specifics of the processes. The resistance of the electrolyte in the electrode space is crucial for the ion conduction of dissolved salts.
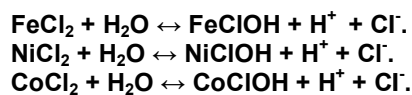
The total current of the ions discharged on the cathode is much smaller than the current that is set during the process. This difference is due to the large current of ions that do not participate in deposition.

The nickel ions deposited on the cathode are formed on the anode at a high concentration and have little mobility. Iron ions are formed on the anode at a low concentration and have mobility due to the many ions of nickel. Cobalt ions are formed on the anode at a medium concentration but have greater mobility than iron atoms. These are the ions that are involved in the electrochemical reaction occurring during metal deposition. It is possible that such ions are hydroxide species formed by the hydrolysis of CoClOH, NiClOH and FeClOH.

Current leakage is a continuous process, and the discharge of positive ions on the cathode should be accompanied by the formation of positive ions

on the anode. The rate of deposition practically does not depend on the concentration of salts but depends on the density of the current, i.e., the number of positive ions created on the anode and discharged on the cathode. The mobility of active ions varies according to the different natures of the salts.

The experimental features of electrochemical deposition are described by a sequence of chemical and electrochemical reactions. The dissolution of cobalt, nickel and iron chlorides is accompanied by a hydrolysis reaction.

$$FeCl_2 + H_2O \leftrightarrow FeClOH + H^+ + Cl^-.$$
$$NiCl_2 + H_2O \leftrightarrow NiClOH + H^+ + Cl^-.$$
$$CoCl_2 + H_2O \leftrightarrow CoClOH + H^+ + Cl^-.$$

On the anode, there is an electrochemical reaction, and in accordance with the size of the current and the potentials of ionization, positive ions with different concentrations are formed. At the nickel anode, chlorine dissolves the electrode when produced.

Graphite anodes are successfully used [10] in the electrolysis of chloride salt solutions (17) and

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the anode potential at them is low (23). The products of the destruction of graphite anodes do not contaminate the cathode metal. On graphite anodes, chlorine is released.

$$FeOH^+ + H^+ + Cl_2 \uparrow.$$
$$NiOH^+ + H^+ + Cl_2 \uparrow.$$
$$CoOH^+ + H^+ + Cl_2 \uparrow.$$
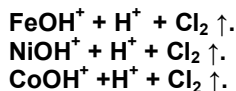
Under the influence of the electric field in the electrolyte, there is a drift in the positive ions of the metal hydroxides from the anode to the cathode at a speed determined by the magnitude of the mobility of the ions and the tension of the electric field.

On the cathode, there is an electrochemical reaction of metal discharge from hydroxide species and the formation of water molecules.

$$FeOH^+ + e^- + H^+ = Fe + H_2O.$$
$$NiOH^+ + e^- + H^+ = Ni + H_2O.$$
$$CoOH^+ + e^- + H^+ = Co + H_2O.$$
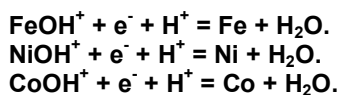
6. COMPARISON OF CONIFE'S PROPOSED ELECTROCHEMICAL DEPOSITION MECHANISM WITH DATA FROM THE LITERATURE

An article on the electrochemical deposition of nickel from a chloride electrolyte [11] indicates that the main obstacle to accelerating the processes of electron-withdrawing metals and alloys is the low speed of the mass transfer of reagents to the surface of the cathode.

This study [12] explored the electron-withdrawing mechanism of nickel, iron and their mixture in a sulfide electrolyte. During joint discharge, there is an abnormal phenomenon in which the rate of recovery of nickel ions is much lower than that of iron ions. It is believed that during the electrical quenching of nickel, the inhibitory effect is exerted by the absorption of iron hydroxide.

In book [13], the process of the electrochemical deposition of alloys is considered to be an electrochemical reaction on the cathode, and the anode is seen as an element for circuit closure, which can be soluble or insoluble. It is indicated that in all electrical deposition processes, one or two electrons are transported across the boundary of the electrode/solution section, with the formation of a metal phase. The following examples are given: the electrodeposition of zinc into low-carbon steel, the receipt of copper powder by electron-withdrawing copper from diluted acidified copper sulfate solutions, the galvanoplasty receipt of a nickel layer by depositing it from a neutral solution based on nickel sulfamate, and the formation of metallic lead on a lead battery anode when it is charged.

In book [14], electrochemical deposition is considered to exploit the electrochemical reaction of the anode (i.e., the return of electrons by the restorer). It is indicated that in the first place, the strongest restorers react at the anode (i.e., the substances that have the most negative potential).

In our experiment, according to the terminology adopted in the book, the current is not limited to the diffusion layer on the cathode and the transfer of electroactive ions is determined by the migration of ions at a large current of the background electrolyte.

Based on the experimental results of the CoNiFe films, a mechanism of electrochemical deposition is proposed, which differs from the well-known mechanism described in the literature, by considering the phenomena occurring in the volume of the electrolyte, mass transfer of ions, and considering the difference in their mobility and the formation of positive ions on the anode.

7. CONCLUSION

By the selection of a chloride electrolyte with a ratio of $C_{Co}/C_{Ni}/C_{Fe} = 1/1/1$, the development of an electrolyte preparation technology and a deposition process performed at 70°C have produced films with a high-quality structure, variable compositions and good magnetic properties.

The proposed new mechanism of the electrochemical deposition process to fabricate CoNiFe films from a chloride electrolyte considers the phenomena occurring in the volume of the electrolyte, including mass transfer of ions, with the determining effect being the mobility and the formation of positive ions on the anode makes it possible to improve the process of obtaining films with a given composition.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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