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Dependence of the Composition of Conife Films on the Electrolyte Concentration during Electrochemical Deposition

Tikhonov Russia*

Department of geophysicist, SMC Technological Center University, Moscow, Russia

Abstract

A study on electrochemical deposition in a triple-component CoNiFe system from a chloride electrolyte solution with equal concentrations of Co, Ni, and Fe was performed. The concentrations used were 0.48; 0.083; 0.00625 mol/l, and the temperature was 70°C. The relative content of the components in the film approached the composition of the electrolyte, though the concentration of each component was slightly decreased. The dependence of the composition of films on the current density is explained by concentration polarization.

Keywords

CoNiFe Films • Chloride Electrolyte • Partial Ion Current Balance

Introduction

Thin films of triple alloys consisting of the ferromagnetic metals Fe, Co and Ni have a high magnetization saturation, high magnetic permeability and low coercivity, and they are used in many areas, such as computers, read/write heads and Microelectromechanical Systems (MEMS). Electrochemical deposition is one of the most preferred methods for producing thin layers of alloy due to its simplicity, cost-effectiveness, versatility and relatively rapid deposition. A characteristic feature of the electrochemical deposition of CoNiFe films is the discrepancy between the fraction of elements in the electrolyte and in the film, which makes it difficult to obtain a film with the desired electrophysical properties [1]. This paper presents the results of a study on electrochemical deposition of a triple CoNiFe system from a chloride electrolyte solution with equivalent concentrations of Co, Ni, and Fe at 0.48, 0.083, and 0.00625 mol/l and a temperature of 70°C. The study of electrochemical deposition of CoNiFe alloys provides new insight into the mechanisms that determine the composition of the precipitated layers and their dependence on the composition of the electrolyte. Finding the composition of the electrolyte to obtain the desired composition of the precipitated film is a very time-consuming task. The decision on the composition of the electrolyte depends on the introduction of additives into the electrolyte that improve the mechanical properties, adhesion and morphology of the films. The conducted studies of congruent electrochemical deposition of the triple CoNiFe system with equal concentrations of components in the electrolyte allow us to approach finding a solution to the electrolyte composition problem that determines the composition of precipitated films of complex composition.

Electrochemical deposition of CoNiFe films

For the deposition of CoNiFe films, a chloride electrolyte solution containing three components, $CoCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, and $NiCl_2 \cdot 6H_2O$, was used, with the components in a 1:1:1 molar ratio; three concentrations were tested: 0.48, 0.083, and 0.00625 mol/l . Various additives were added to the electrolyte solution in the following concentrations: H_3BO_3 - 20 g/l, $C_7H_4NaNO_3S \cdot 2H_2O$ - 1.5 g/l, HCl - 3 ml/l. The film from the specified electrolyte was deposited in a galvanic bath with a volume of 2 liters and a graphite anode. A vertically-oriented metallized silicon wafer was used as the cathode. The distance between the anode and the cathode was 8 cm. Insoluble hydroxides were removed by filtration. An alloy film with a diameter of 8 cm was obtained on the metallized Ni surface of a 100 mm silicon wafer [2]. The electrolyte was heated by a submersible heater to 70°C and mixed with a magnetic stirrer. A constant current density of 3 to 40 mA/cm2 was maintained in the deposition area on the silicon wafer. As the concentration of $CoCl_2$, $NiCl_2$, and $FeCl_2$ salts in the electrolyte solution increased, the resistance of the solution decreased, and this resistance determined the amount of current passing between the anode and the cathode and the voltage that changed linearly with increasing current. At a current density of

***Address to correspondence:** Tikhonov Russia, Department of geophysicist, SMC Technological Center University, Moscow, Russia; E-mail: r.tichonov@tcen.ru*

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16 mA/cm2, the voltage between the anode and the cathode was 2 V, 3.5 V, and 5.5 V in the different electrolyte solutions.

With a difference in electrolyte concentrations of 77 times, the growth rate of CoNiFe films practically does not depend on the concentration of the electrolyte.

The growth rate of CoNiFe films increases with increasing current density and half the values calculated according to Faraday's law, i.e. the cathode current output is 0.5.

Electrolytes with Co, Ni, and Fe concentrations of 0.48 mol/l precipitated at a current density of 3.6 mA/cm2. The composition of the film was Co32Ni61,5Fe6,5. At a low current density, the composition of the film was characterized by a high nickel content and low iron and content.

When the current density of the CoNiFe film increased to 15 mA/cm2, the iron content rose to 41.3%, and at a current density of 20 mA/cm2, it remained approximately the same at 42.35%.

When the current density of the CoNiFe film increased to 15 mA/cm2, the nickel content decreased to 7.9%, and at a current density of 20 mA/cm2, it remained at the same level of 7.85%.

The actual change in the iron and nickel content at a current density of 10 mA/cm2 changed the relative cobalt content to 59%. At current densities of 15 and 20 mA/cm2, the cobalt content had similar values of 49 and 48%.

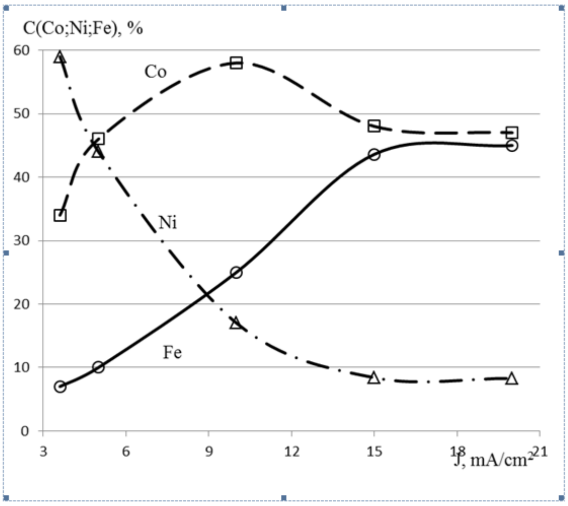

Figure 1. Dependence of the composition of films obtained from a three-component solution on the electric current density of 3.6 ÷ 20 mA/cm2. The solution contained CoCl2, NiCl2, and FeCl2 with each component at a concentration of 0.48 mol/l, and it also contained the following additives: H3BO3 - 20 g/l, C7H4NaNO3S•2H2O - 1.5 g/l, and HCl - 3 ml/l.

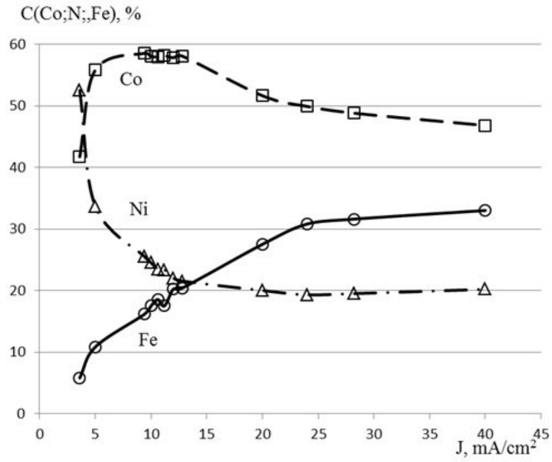

Figure 2. shows the relative contents of Co, Ni, and Fe in the film during deposition from the electrolyte solution when the concentration of each component was 0.083 mol/l. There is a weak dependence on the current density at a value of more than 25 mA/cm2; in the CoNiFe film, the nickel content is 19 - 22%, the iron content is 28 - 33%, and the cobalt content has a value of 55 - 47%. With a lower current density, the composition of the CoNiFe film varies greatly; the nickel content decreases from 57 to 19%, the iron content increases from 5 to 28%, and the cobalt content ranges from 42 - 55 - 48%.

(Figure 2) Dependence of the composition of films obtained from a three-component solution on the electric current density of 3.6 ÷ 40 mA/cm2. The solution contained CoCl2, NiCl2, FeCl2, and the concentration of each component was 0.083 mol/l. The solution included the following additives: boric acid, saccharin, hydrochloric acid. Comparison of the dependences on the current density of the composition of films obtained from a three-component solution of CoCl2, NiCl2, FeCl2 in which the concentration of the components was either 0.48 mol/l or 0.083 mol/l showed that the dependencies were similar. Increasing the current density led to a decrease in the nickel content and an increase in the iron content, and the predominant cobalt deposition persisted. Their dependence of the composition of the films on the current density was stable within a certain area.

At a current of more than 25 mA/cm2, the ratio of metal concentrations in the film to the metal concentrations in the electrolyte was 1.44 for cobalt, 0.97 for iron, and 0.54 for nickel, which is almost the same as the values at an electrolyte concentration of 0.48 moll/l, but closer to the concentrations in the electrolyte.

The relative contents of Co, Ni, and Fe in the film differ from the composition of the electrolyte and are highly dependent on the current density.

It is not possible to control the deposition with the current density to obtain a film composition equal to the composition of the electrolyte.

Electrochemical deposition of CoNiFe films was performed in an electrolyte solution in which the Co, Ni, Fe chloride concentrations were all 0.00625 moll/l. The solution also contained 30% hydrochloric acid (0.3 ml/l), and the temperature was 70°C.

Redeposition was carried out from the same electrolyte solution, but with the addition of saccharin and boric acid, the results are shown in (Table 1).

#	pH	U, V	I, mA	T, min	H, μ	V, nm/ min	Co, %	Ni, %	Fe, %	Electrolyte additive
1	2,62	6,8	500	30	4,34	145	42	13,5	44	
2	2,25	5,8	500	30	3,19	106	34	35	31	Saccharin 3 g/l
3	2,8	8,1	570	30	4,36	177	51	20	30	
4	2,2	8,55	570	30	5,31	145	45,3	17,8	36,9	boric acid 20 ml/l
5	2,35	7,75	534	30	4,5	150	44,5	24	31,5	Saccharin 1,5 g/l
6	2,7	10,4	610	10	1,9	190	35,9	29,7	33,6	
7	2,55	8,3	610	10	2,8	88	50,6	13,7	35,7	Saccharin 1,5 g/l; boric acid 20 ml/l

Table 1. Thickness and composition of CoNiFe films after electrochemical deposition from an electrolyte solution in which each component had a concentration of 0.00625 mol/l. The solution also contained added boric acid and saccharin.

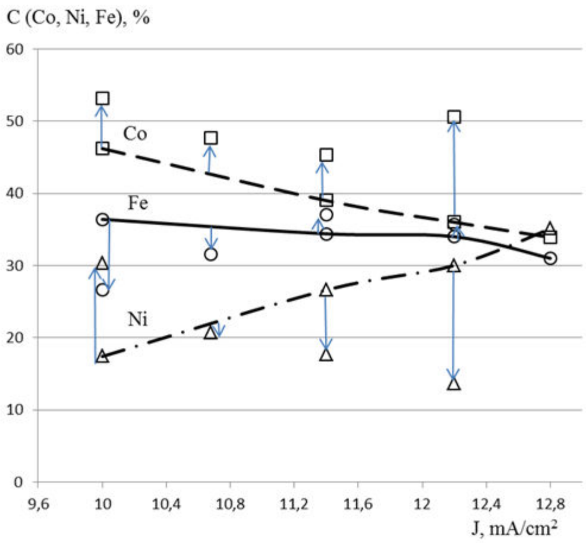

Figure 3. Dependence on the current density J in the range of 10 -12.8 mA/cm2 percentage of the components of films C(Co; Ni; Fe), obtained from an electrolyte with an equal 33% molar content of salts CoCl2, NiCl2, FeCl2, each with a concentration of 0.00625 mol/l.

Figure 3 shows the compositions of CoNiFe films without additives with markers connected by lines. The Co content is indicated by rectangular markers and a dashed line. The Ni content is indicated by triangular markers and a dotted line. The Fe content is indicated by round markers and a solid line. For the samples that contained additives to the electrolyte (saccharin at concentrations of 3 g/l (at 10 mA/cm2) and 1.5 g/l (at 10.7 mA/cm2) and boric acid at a concentration of 20 g/l (at 11.4 mA/cm2)), the composition values are presented in the form of individual points. Arrows indicate changes in the composition of films for the selected current in electrolyte solutions containing the appropriate additives. As seen in the figure, the compositions of the films depend on the current, and at a current density of 12.2 mA/cm2, the compositions of the metals in the CoNiFe films are close to 33% molar content of CoCl2, NiCl2, FeCl2 salts in the electrolyte, congruent electrochemical deposition of the triple-component CoNiFe alloy is observed. Additives to the electrolyte change the composition of the films and disrupt the congruence of deposition in various ways. Saccharin increases the content of Co and Ni and reduces the content of Fe. With a decrease in the additive from 3 to 1.5 g/l, the change in composition decreases. Boric acid at 20 g/l increases the content of Co and Fe and reduces the content of Ni. The simultaneous addition of saccharin (1.5 g/l) and boric acid (20 ml/l) increases the content of Co, slightly reduces the content of Ni and greatly reduces the content of Fe. The thickness of the concentrated films was measured using an MSA-500 microsystem analyzer. The study of the composition of the films was carried out using a PhilipsXL 40 energy dispersion X-ray microanalyzer.

Discussion

FeCoNi films were deposited by the electrochemical method from a sulfate chloride electrolyte , containing, moll / l: NiSO4• 0.34, NiCl2• 0.084, CoSO4 0.1, FeSO4 0.036, H3BO3 20 g / l, 2 g / l stabilizer, 4 g / l tartaric acid, 4 g / l bleach, 0.1 g / l wetting agent and tartaric acid additives. Optimum conditions for obtaining high-quality films of Fe15.6-20.6Co43.8-61.9Ni22.5-40 current density 4 A / dm2, temperature 40 °C, pH 2.3-3.2, tartaric acid concentration 8-12 g / l, molar Co2+ / Ni2+ ratio = 0.26-0.4. The composition of the film depends on the current density, electrolyte temperature, and pH. The ratio of the content of elements in the electrolyte and the film is observed - CRL for Fe, Co = 3, and for Ni = 0.5. Cobalt and iron precipitate with a concentration greater than in the electrolyte, and less nickel. For electrochemical deposition of iron, the abnormal deposition is characteristic. Iron is deposited more intensively than cobalt and nickel [3]. Cobalt is deposited more intensively than nickel. Estimating the deposition rate based on electrochemical potentials assumes a normal deposition of nickel, but there are many factors in the processes that determine metal deposition.

The concept of congruent electrochemical deposition determines the equality of the electrolyte and sludge compositions. The composition of CoNiFe films formed by electrochemical deposition depends on the temperature, pH, concentration and electrolyte composition . The congruence of deposition is achieved by deposition from electrolytes with low concentrations of components and without additives. The same is true of the congruent deposition of NiFe films .

The change in the electrode potential due to a change in the concentration of reagents in the electrode space during the passage of current is called concentration polarization [4]. Electrochemical reactions on the electrodes lead to a significant change in the concentrations of substances due to the slow diffusion of reagents or the removal of reaction products. The difference in the diffusion coefficients or mobility of the ions of the electrolyte component determines the balance of partial ionic currents and the content of the components in the film from the current density. The thickness of the layer deposited by the electrolyte during an electrochemical reaction -SISEER is fairly large, on the order of a millimeter. A layer of this thickness has a significant effect on the mass transfer of ions to the electrodes.

The formation of a layer with a changed composition in the cathode region of the electrolyte explains the dependence of the composition of the sediment on the mixing of the electrolyte that destroys the concentration polarization layer. The lower the concentration of the electrolyte is, the smaller the deviation of the composition of the films from the equilibrium state and the closer the composition of the films to the composition of the electrolyte. Therefore, congruent electrochemical deposition of CoNiFe alloy can be obtained only when the concentrations of the main components of the electrolyte are low and when boric acid and saccharin are not added [5].

Conclusion

The deposition of CoNiFe films was performed in a chloride electrolyte with a ratio of CCo:CNi:CFe = 1:1:1, and technology for preparing an electrolyte via filtration and performing deposition at a temperature of 70°C was developed. It was found that the desired 1:1:1 ratio of concentrations of the metals in the film was achieved at a current density of 12.5 mA/cm2 and a metal chloride concentration of 0.00625 mol/l. CoNiFe films are obtained reproducibly with minimal mechanical stresses and with good adhesion to the nickel sublayer during electrochemical deposition. The mechanistic study of the electrochemical deposition of a CoNiFe alloy as the electrolyte concentration changes resulted in congruent deposition of the three-component alloy. The use of congruent electrochemical deposition will simplify the choice of electrolyte composition for obtaining films with a complex composition.

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