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Effects of bath composition and current density on the electrodeposition of Fe-Ni alloy on copper substrate and the property of deposited alloy

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Abstract

One simple and six complex baths are used to electrodeposit Fe-Ni alloy coating on copper substrate. All baths contain the same 1.04 Ni/Fe ratio. In addition to $NiSO_4.7H_2O$, $FeSO_4.7H_2O$, H_3BO_3 used in simple bath, the complex baths contain Ascorbic acid, Saccharin and Citric acid in different ratios. Electrodepositions have been carried out in the bath pH and constant current density range of 1 - 2.6 and 20 - 140 mA/cm^2, respectively. Anomalous nature of Fe-Ni alloy electrodeposition is suppressed in the complex baths. Microhardness as well as corrosion resistance of coating increased with increasing %Ni content in the deposit. The morphology of the Fe-Ni films obtained from simple baths is characterized by coarse-grained, non-smooth surface with presence of microcracks onto it. Coatings from complex baths are fine-grained with smooth surfaces.

Keywords: Electrodeposition; Fe-Ni alloy coating; Anomalous; Current density.

Introduction

Alloy electrodeposition technologies can extend tremendously the potential of electrochemical deposition processes to provide coatings that require unique mechanical, chemical and physical properties (Landolt, 2002). There has been a great research interest in the development and characterization of iron-nickel (Fe-Ni) thin films due to their operational capacity, economic interest and unique properties (Li *et al.,* 2003). The properties, the composition and the grain size of electrodeposited Fe-Ni alloys are strongly dependent on the electrolyte composition and the deposition parameters i.e. bath pH, temperature, applied current density and agitation. Fe-Ni electrodeposition exhibits the phenomenon of anomalous codeposition. This term introduced by Brenner is being used to describe the preferential deposition of the less noble metal, Fe, to the more noble metal, Ni. In other words, the reduction of nickel is inhibited while the deposition of iron is enhanced when compared with their individual deposition rates. Thus electrodeposition of Fe-Ni alloys has attracted considerable attention because of its special characteristic nature and wide range of unique properties. An important feature of the Fe-Ni alloy system is its structural evolution, with a change from bcc for the Fe-rich alloy to fcc for the alloy with higher Ni content (Abrikosov *et al.,* 1995).

Although there are several explanations of the anomalous phenomenon of Fe-Ni electrodeposition but the mechanism is not yet well understood. Moreover, the effects of addition of complexing agents in the bath and their interactions with the plating parameters on the properties of electrodeposited Fe-Ni alloy have received little attention so far. In the present Fe-Ni alloy electroplating system, the electrolytic composition including complexing agent and current density are investigated systemically, what, to our knowledge, has not yet been studied.

Materials and methods

Commercial copper sheets of 50 mm x 15mm x 1 mm were used as substrates (cathode) and platinum foil of 35 mm x 15 mm x 0.4 mm was used as anode in the investigation. The copper substrates were degreased by rinsing with detergent, mechanically and electrochemically cleaned by maintaining polishing with emery papers, pickling, rinsing and acid dipping process. Analytical reagent grade chemicals and deionized water were used to prepare the baths. One simple and six complex baths containing the same Ni/Fe ratio of 1.04 in each bath were used to electrodeposit Fe-Ni alloy. Bath compositions are shown in Table I. All depositions were carried

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out at room temperature and at constant current densities e.g. 20, 30, 40, 50, 60, 70, 100, 120 and 140 mA/cm². Each deposition was continued for a predetermined time period of 2 hours and without any stirring action.

Chemical analysis of the deposit was carried out by the conventional wet method. Microhardness indentations were imposed on the coating surface by using a Shimadzu Microhardness Tester. A load of 50 g was applied for 10 seconds on unetched specimen surface of Fe-Ni alloy coating. The two diagonals of the indentation after removal of the load were measured using Scanning Electron Microscope (SEM) and the Vicker Hardness Number (VHN) was calculated from the conventional conversion table. SEM was used to study the morphology of Fe-Ni alloy coatings. The Salt Immersion Corrosion Test was adopted to measure the corrosion resistance of Fe-Ni films on copper substrate. The immersion test was performed at room temperature using a solution of 5% NaCl and sections of Fe-Ni films were used as test samples. The test samples were weighed and recorded and then immersed in the prepared fresh salt water solution and they were kept there for 48 hours. When the test time was completed the samples were taken out of NaCl solution. After rinsing with tap water and drying with acetone, weight of the samples was taken. The difference in initial and final weight was the measure of weight loss which indicates the amount of corrosion occurred in the test. The expression mg/dm²/day (mdd) was used to express the corrosion rate of the samples.

**Results and discussion**

Electrodeposition of Fe-Ni alloy coating

Electrodeposition was performed at room temperature with no agitation where current density had been varied from 50 to 120 mA/cm² for simple bath and from 20 to 140 mA/cm² for the complex baths. Effect of combined complexing agents on coating can be obtained from baths C-1, C-2 and C-3 whereas that of individual complexing agent on coating can be obtained from baths C-4, C-5 and C-6. Good deposits were obtained from simple bath S-1 in the pH ranges of 1.9 - 2.6 and from complex baths in the pH ranges of 1.0 - 1.85. Bath pH for good deposit is found to be related to current density. Fig. 1 shows a representative good deposit obtained from bath C-1 and it was tested to measure its properties.

Fig. 1. Uniform, adherent and bright coating obtained from bath C-1

Chemical analysis of the deposit

Chemical analysis of the coatings was carried out by the conventional wet method. Percentage Ni in the deposit as a function of applied current density is shown in Fig. 2. Neglecting a small deviation, an increase of %Ni in the deposit with increasing applied current density is observed for simple bath while the reverse trend is seen for complex
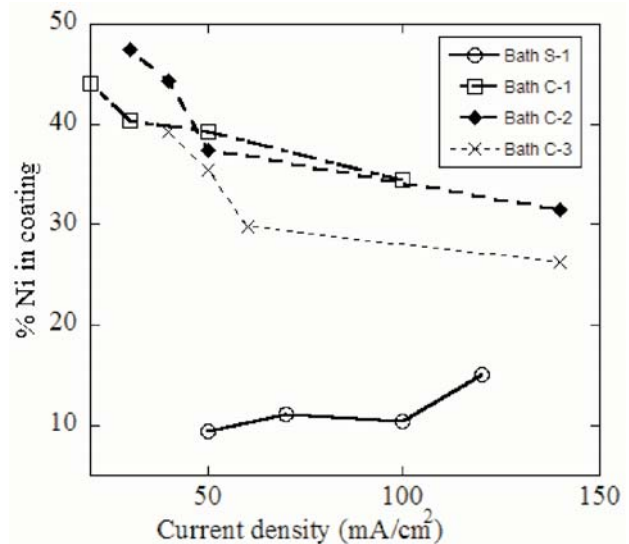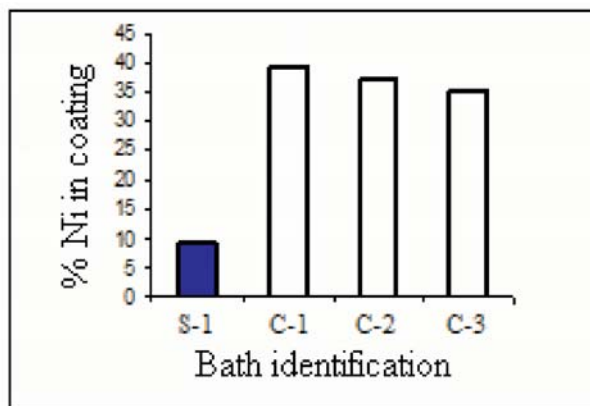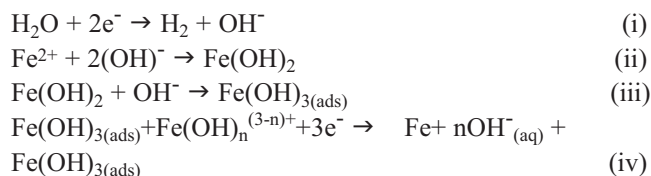

Fig. 2. Effect of current density on %Ni in coating deposited from simple and complex baths. Ni/Fe ratio of all the baths is 1.04

baths.The minimum Ni content (26.19%) of coatings obtained from all complex baths is higher than the maximum Ni content (15.11%) of coating obtained from the simple bath although the Ni/Fe ratio in all the baths is 1.04. Figure 3 shows the %Ni in the coating deposited from simple bath S-1 and complex baths C-1, C-2 and C-3 at the same current density of 50 mA/cm2. Higher %Ni in coatings deposited from complex baths than from simple bath is observed. The standard electrode potential for reduction of pure Ni^{2+} (-0.257 V) is relatively more positive than that of Fe^{2+} (-0.447 V). According to normal deposition theory, an element with a higher positive standard electrode potential is expected to deposit preferentially than the one with a less positive standard electrode potential (Abu-Krisha *et al.*, 2006). Again according to Brenner's definition of anomalous codeposition (Brenner, 1963), the less noble metal (here Fe) is deposited preferentially and its percentage in the deposit become higher than that in electrolytes. Higher %Ni (more noble) in coatings deposited from complex baths than the simple bath concludes that addition of the complexing agents suppresses the anomalous nature of the Fe-Ni alloy electrodeposition.
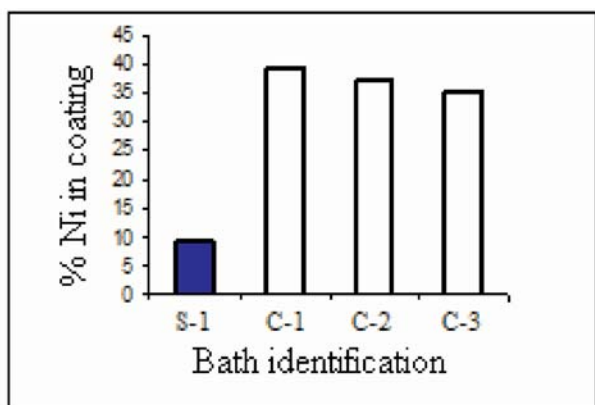
Fig. 3. Percentage Ni deposited from simple bath S-1 and complex baths C-1, C-2 and C-3. All depositions were carried on at 50 mA/cm^2

Effect of different complexing agents on %Ni in the deposit is shown in Fig. 4. Addition of ascorbic acid and citric acid shows a major impact (bath C-5) to increase %Ni in the deposit than addition of saccharin with citric acid (bath C-6) or only with citric acid in the bath C-4. Ascorbic acid prevents oxidation of ferrous to ferric ions (Matulis *et al.*, 1964) in the bath and thus the Ni content of the films was higher. The reaction mechanism may be proposed as following (Shull *et al.*, 1993):

$$H_2O + 2e^- \rightarrow H_2 + OH^- \qquad (i)$$
$$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2 \qquad (ii)$$
$$Fe(OH)_2 + OH^- \rightarrow Fe(OH)_{3(ads)} \qquad (iii)$$
$$Fe(OH)_{3(ads)} + Fe(OH)_n^{(3-n)+} + 3e^- \rightarrow \quad Fe + nOH^-_{(aq)} +$$
$$Fe(OH)_{3(ads)} \qquad (iv)$$

Fig. 4. Effect of complexing agent on % Ni in coating deposited from complex baths C-4, C-5 and C-6. All depositions were carried on at 30 mA/cm^2

According to these reactions, if $Fe(OH)_2$ is inhibited to convert to $Fe(OH)_3$, then $Fe(OH)_3$ was not able to act as a positive catalyst to produce Fe. So, inhibition of ferrous to ferric ions might increase the Ni content of the coatings obtained from bath C-5 by reducing Fe content of the deposited films. Saccharin increases the Ni content of the films. Citric acid increases the side reaction rate (Popov *et al.*, 1993) that decreases the alloy current efficiency due to the increase of the hydrogen ions adsorption which consequently might decrease the Ni content in coatings.

Microhardness of the coating

Vickers Hardness Number (VHN) of the deposits was evaluated by microhardness testing using a Shimadzu Microhardness Machine. Fig. 5 shows microhardness of the coatings deposited from various baths as a function of %Ni in the coatings. Microhardness is increased with increasing %Ni in the coating formed in all the cases. Maximum VHN of the film deposited from the simple bath S-1 is 120.2 and the same deposited from the complex bath C-2 is 172. Even the maximum value of microhardness the coating obtained from the simple bath falls below the minimum value of that obtained from the complex baths. So, complexing agent increased the % Ni as well as VHN of the deposited films.
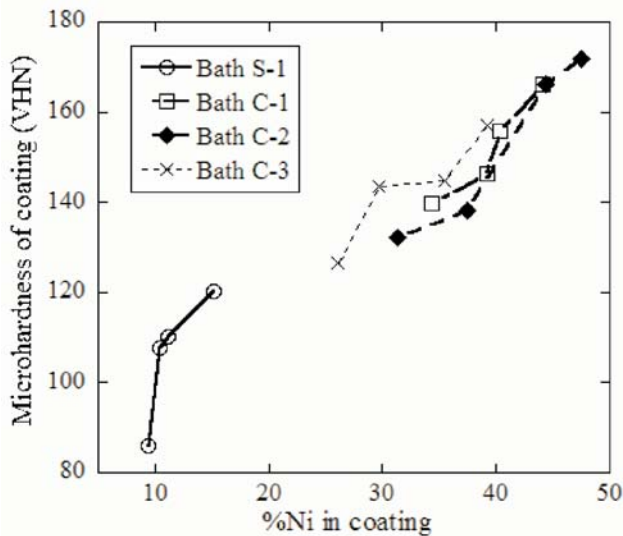
Fig. 5. Effect of % Ni in coating on its microhardness

Morphology of the coating

The influence of current density and bath composition on the morphology of Fe-Ni coatings was evaluated by SEM. The topographies of Fe-Ni coatings were analyzed concerning their uniformity, porosity and the presence of cracks. Fig. 6 shows SEM images of Fe-Ni alloy coatings obtained from simple bath S-1 and complex bath C-2 at two different current densities of 50 mA/cm^2 and 100 mA/cm^2. In case of the coatings deposited from bath S-1 [Fig. 6(a), 6(b)], grains are roughly spherical and the average grain size decreased with increasing current density. Thus structure of the Fe-Ni coatings is strongly influenced by current density. Myung *et al.* (2004) reported similar observations to binary Fe-Ni thin films. It is known that high current density gives rise to a high degree of adatoms saturation at the electrode surface and high degree of adatoms decreases the grain size. Elezovi *et al*. (2005) reported that the stress changes in the Fe-Ni films on varying deposition current density might be attributed to the changes of the average grain sizes. As the average grain size decreases with increasing current density, the deposit stress may be increased. Thus morphology of the Fe-Ni alloys is characterized by the presence of microcracks. In this study, stressed films at high current density revealed the presence of sharp line microcracks distributed over the deposits [Fig. 6 (b)].
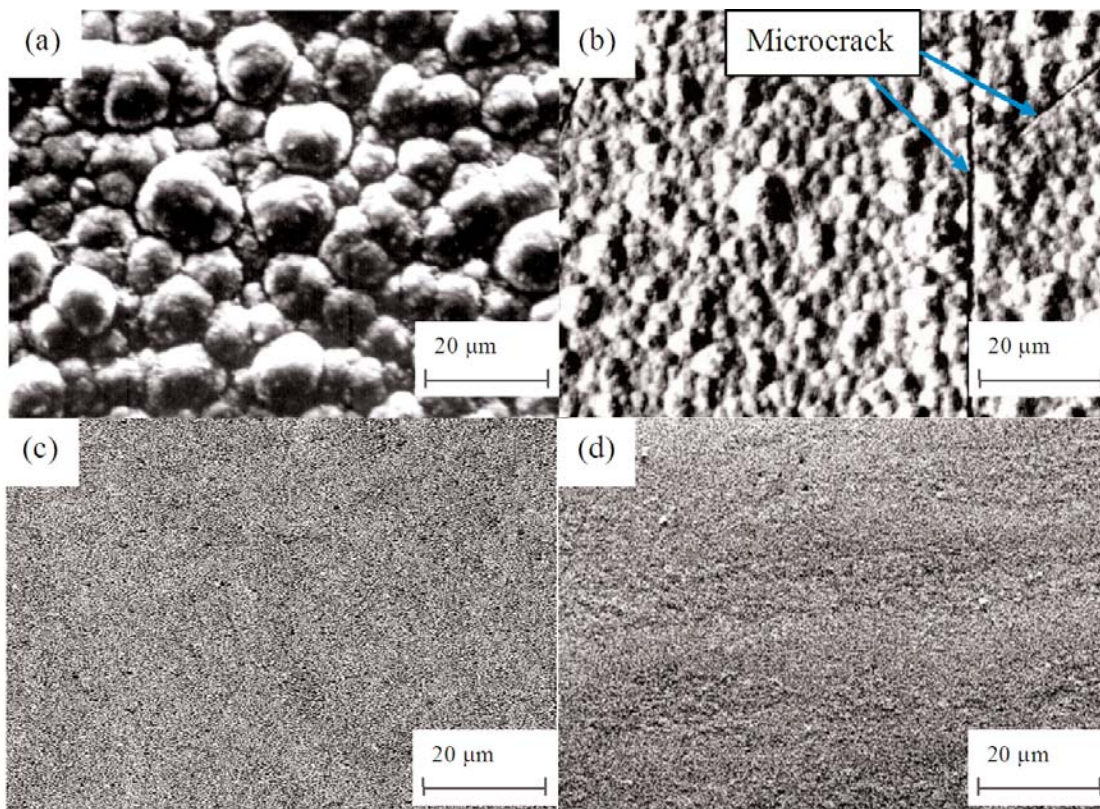

Fig. 6. SEM images of the deposit obtained from simple bath S-1 at current density of (a) 50 mA/cm^2, (b) 100 mA/cm^2 and from complex bath C-2 at current density of (c) 50 mA/cm^2, (d) 100 mA/cm^2

Morphology of the deposits can be controlled by using electrolytes containing complexing agent/agents with proper compositions. For complexing agent, the crystallization of the electrodeposited layer is very important since it influences directly the structure of the deposit and therefore its properties (Marder *et al.,* 2004). Crystallization occurs either by the buildup of old crystals or by the formation and growth of new ones. These two processes are in competition and can be influenced by different factors. High surface diffusion rates, low population of adatoms and low over-potentials are factors enhancing the buildup of old crystals. On the contrary, low surface diffusion rates, high population of adatoms and high over-potentials on the surface enhance the creation of new nuclei (Ebrahimi *et al.*, 2003). From the SEM observations, it can be said that addition of complexing agent of 2.0 g/l ascorbic acid, 3.0 g/l saccharin and 4.2 g/l citric acid in bath C-2 increased nucleation rates that helped form crack-free, uniform and fine grained structures as is seen in Fig. 6(c) and 6(d). As reported in the previous section, microhardness of coarse grained coating obtained from simple bath S-1 was lower than that of crack-free, uniform and fine grained deposits obtained from complex baths. Thus

microhardness of the coatings is in well agreement with their morphology.

With the presence of only citric acid as complexing agent in bath C-4, the film was highly porous [Fig. 7(a)] probably due to the hydrogen bubbles formed during co-deposition. Deposits obtained from the combined presence of citric acid and ascorbic acid in the bath C-5 displayed a few but large pores [Fig. 7(b)]. Addition of saccharin with citric acid into the bath C-6 resulted in smooth, bright deposit with a little porosity of small sizes in it [Fig. 7(c)]. Saccharin, as a leveling agent, might reduce H_2 evolution causing less porous, fine grained smooth deposit. However, a more detailed study concerning the mechanism of saccharin as a leveling agent should be carried out to reach a final conclusion.

Corrosion of Fe-Ni coating

Salt immersion corrosion test was conducted in the present study and the corrosion rate was expressed in $mg/dm^2/day$ (mdd). Effect of %Ni in the deposit on its corrosion rate is shown in Fig. 8. Decreasing corrosion rate with increase in %Ni in the deposits is observed. If a protective NiO layer is
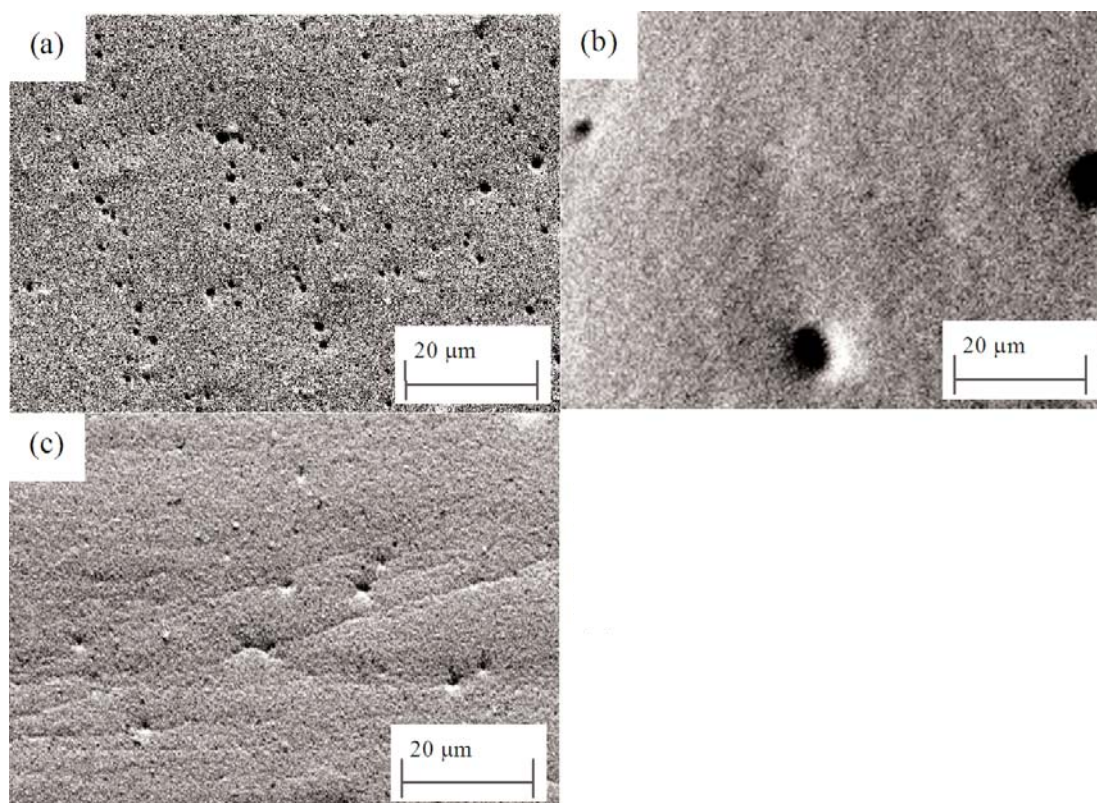

Fig. 7. SEM images of the deposit obtained at a current density of 30 mA/cm² from baths (a) C-4 (b) C-5 and (c) C-6

formed at the surface, the coating corrosion rate is decreased. At lower % Ni at the surface, the coating is no longer able to form NiO scale in corrosive environment. As a result, corrosion rate of Fe-Ni thin films is increased. Fig. 9 clears the effect of different complexing agents on the corrosion resistance of Fe-Ni thin film. The three coatings were deposited from the three different baths C-4, C-5 and C-6 at a same current density of 30 mA/cm^2. The coating deposited from bath C-5 containing ascorbic acid and citric acid shows better corrosion resistance than that deposited from bath C-6 containing saccharin and citric acid or from bath C-4 con-

taining only citric acid as complexing agent. Ascorbic acid and citric acid provide higher Ni content (32.13%) in coating than the other two combinations of complexing agents in baths C-4 and C-6. The film deposited with composition of 47.52 wt% Ni (bath C-2) showed the best corrosion resistance (Fig. 8).

After the salt water immersion test, the extent of corrosion was also evaluated qualitatively by visual inspection of the corroded samples. Photograph of the corroded samples for simple and complex baths at different parameters are shown in Fig. 10. The coating deposited from simple bath corroded
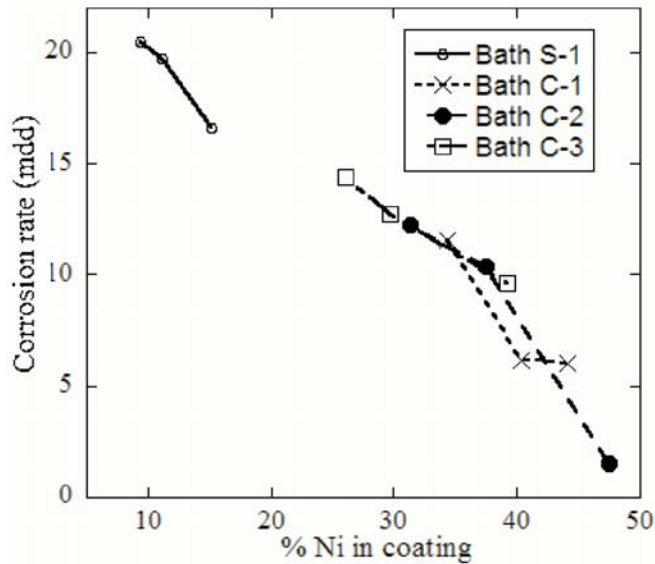

Fig. 8. Corrosion of Fe-Ni coating as a function of % Ni in coating
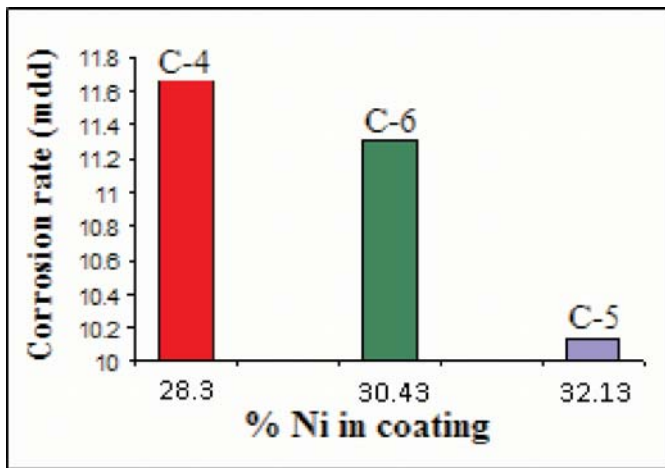

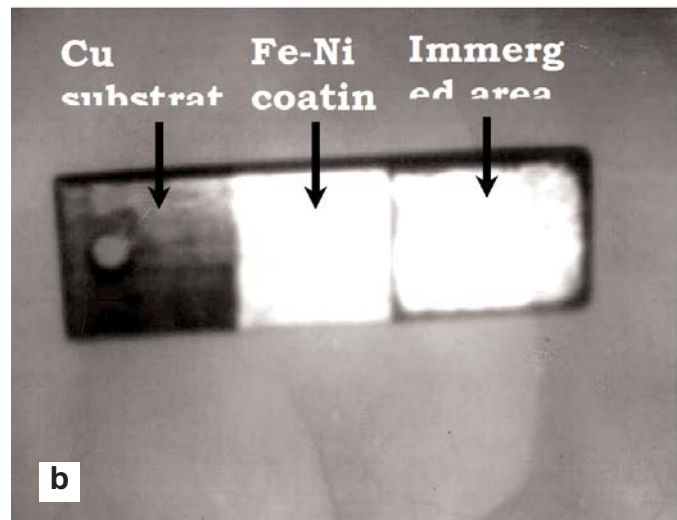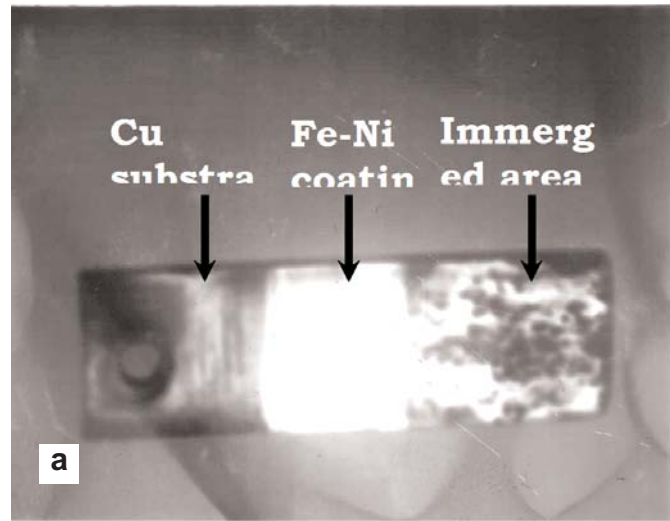Fig. 9. Effect of individual complexing agent on the corrosion rate of Fe-Ni coating

Fig. 10. Photograph of corroded samples obtained from (a) bath S-1 at current density of 120 mA/cm^2 and (b) bath C-2 at current density of 50 mA/cm^2

Table I. Simple and complex bath compositions

Simple Bath identification	Bath concentration (g/l)		Ni/Fe ratio
S-1	$NiSO_4. 7 H_2O$	: 28.1	
	$FeSO_4. 7 H_2O$	: 27.8	1.04
	H_3BO_3	: 12.4	

Complex bath identification	Principal ingredients (g/l)		Complexing ingredients (g/l)			Ni/Fe ratio
			Ascorbic acid	Saccharin	Citric acid	
C-1	$NiSO_4.7H_2O$	: 28.1	1.5	1.5	2.1	
C-2	$FeSO_4.7H_2O$	: 27.8	2.0	3.0	4.2	
C-3	H_3BO_3	: 12.4	3.0	4.5	8.4	1.04
C-4	Na_2SO_4	: 49.7	—	—	4.2	
C-5	H_2SO_4	: 9.8	2.0	—	4.2	
C-6			—	3.0	4.2	

and almost the entire coating disappeared after 48 hours of immersion as is seen in Fig. 10(a) whereas for the coatings deposited from complex baths, the progress of corrosion was much lower as shown in Fig. 10(b).

Conclusion

One simple and six complex baths have been considered to electrodeposit Fe-Ni alloy coating on copper substrate. All electrolytic baths contain the same 1.04 Ni/Fe ratio. The conclusions drawn from the study are:

1. Addition of ascorbic acid, saccharin, citric acid as complexing agents in the plating bath suppresses the anomalous nature of Fe-Ni alloy electrodeposition.

2. Microhardness as well as corrosion resistance of Fe-Ni alloy coating increased with increasing %Ni content in the deposit.

3. The morphology of the Fe-Ni films obtained from simple bath is characterized by coarse-grained, non-smooth surface with presence of microcracks onto it. On the contrary, coatings from complex baths are fine-grained with smooth surfaces.

Acknowledgement

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