Fe-Ni ALLOY ELECTRODEPOSITION FROM SIMPLE AND COMPLEX TYPE SULFATE ELECTROLYTES CONTAINING Ni/Fe RATIO OF 1 AND 12

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Abstract: *Iron-nickel (Fe-Ni) alloy electrodeposition has been conducted from simple and complex baths having Ni/Fe ratio of 1 and 12. The applied current density varies from 30 to 100 mA/cm^2. The coating composition, morphology and microhardness are measured and characterized by SEM/EDX and Shimadzu microhardness tester. The percentage of Ni in the coating increases with increasing current density and the Ni/Fe ratio of electrolytes which is supported by the alloy deposition principle. Fine grained and smooth coating without microcracking is obtained from the complex baths. Complexing agents are supposed to reduce the deposit stress developed during electrodeposition. Increase in Ni/Fe ratio in the bath as well as current density results in decreasing grain size of the deposits. High current density is believed to give rise to a high degree of adatoms at the electrode surface and high degree of adatoms decreases the grain size. Microhardness of the coating increases with the increase of bath Ni/Fe ratio as well as current density of electrodeposition.*

Keywords: *Anomalous electrodeposition, Fe-Ni alloy coating, Complex bath, 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[1]. 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[2]. The properties, the composition and the grain size of electrodeposited Fe-Ni alloys are strongly dependent on the electrolyte composition, applied current density, bath pH, temperature, agitation etc. Fe-Ni alloy electrodeposition exhibits the phenomenon of anomalous codeposition. This term introduced by Brenner[3] 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 Ni is inhibited while the deposition of Fe 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[4]. Fe-Ni alloys ranging in composition from Invar ($Ni_{36}Fe_{64}$) to Permalloy ($Ni_{81}Fe_{19}$) exhibit a spectrum of physical properties that have led to the widespread use of these materials in a variety of high technology applications[5-8].

In spite of the importance of Fe-Ni alloy electrodeposition, addition of complexing agents in the bath and their interactions with the plating parameters on the properties of electrodeposited Fe-Ni alloy has received little attention so far. Previous study shows the effects of complexing agents and current density on electrodeposition of Fe-Ni alloy[9]. In the present work, baths containing sulfate salts with Ni/Fe ratio of low and high value including complexing agent and current density have been studied systematically.

EXPERIMENTAL

Commercial copper (Cu) sheets were used as substrates in the experiment of this study. Platinum anodes were used for electrodeposition. Dimension of the Cu substrate was 50 mm x 15 mm x 1 mm. The Cu substrates were degreased, mechanically and electrochemically cleaned by maintaining polishing with emery papers, pickling, rinsing and acid dipping process. Electrodeposition was carried out in a laboratory type electrodeposition set-up consisting of a beaker, a D.C. power supply, cathode and anode electrodes. Two platinum anodes were used at equal distance on both sides of the cathode for uniform deposition on both sides of the cathode.

Both simple and complex baths were used. Analytical reagent grade chemicals and deionized water were used to prepare baths. Sulfate baths composing of $NiSO_4,7H_2O$; $FeSO_4,7H_2O$; H_3BO_3 and Na_2SO_4 in varying composition comprise the simple baths where Ni/Fe ratio was maintained 1 and 12. One complex bath was prepared by adding only ascorbic acid and another complex bath was prepared by adding ascorbic acid, saccharin and citric acid in the simple bath. Ni/Fe ratio of both complex baths was maintained 12. Details of the simple and complex bath compositions are shown in Table 1.

All depositions were carried out at room temperature and at current densities of 30, 50, 70 and 100 mA/cm^2. Each deposition was continued for a predetermined time period of 2 hours without any stirring action. Scanning Electron Microscopy (SEM) was used to study the morphology of Fe-Ni alloy coatings. Chemical composition of the deposit was determined by energy dispersive x-ray (EDX) analyzer. Microhardness indentations were imposed on the coating surface by using a Shimadzu Microhardness Tester. A load of 25 g was applied for 10 seconds on unetched specimen surface of Fe-Ni alloy coating.

Samples of Bath B-2 (at current density 100 mA/cm^2) were heat-treated in inert atmosphere for 40 minutes at the temperature range of 350^{0}C to 500^{0}C and then the effect of heat-treatment on the coating morphology and microhardness (VHN) was studied.

Table 1. Plating Bath composition for the electro-deposition of Fe-Ni alloy coating

Bath identification	Bath composition		Ni/Fe ratio
	Principal ingredients (g/L)	Complexing ingredients (g/L)	
B-1a (simple)	$NiSO_4$. 7 H_2O = 28.1 $FeSO_4$. 7 H_2O = 27.8 H_3BO_3 = 12.4	------	1
B-1b (simple)	$NiSO_4$.7 H_2O = 53.3 $FeSO_4$. 7 H_2O = 4.44 H_3BO_3 = 0.25 Na_2SO_4 = 49.7	------	12
B-2 (complex)		ascorbic acid = 4	
B-3 (complex)		ascorbic acid = 4 citric acid = 4 saccharine = 4	

RESULTS AND DISCUSSION

Chemical Analysis of the Deposit

Two simple and two complex baths were used in this study. Effect of bath Ni/Fe ratio concentration on coating can be obtained from baths B-1(a), B-1(b) whereas effect of complexing agents on coating at high Ni/Fe ratio can be obtained from baths B-2 and B-3 (Table 1).

Chemical analysis of the coatings was carried out by the SEM equipped with EDX. Fe-Ni films obtained at different current densities from baths with varying Ni/Fe ratio showed the variation of Ni content in it (Fig. 1). It was observed that at low Ni/Fe ratio (B-1a), the percentage of Ni in deposited layer was lower than that of the layer deposited from the high Ni/Fe ratio (B-1b, B-2 and B-3). It was also seen that the percentage of Ni in the deposited layer increased with increasing applied current density for all bath composition at high Ni/Fe ratio. Good deposition could not be obtained from the simple baths B-1(a) and B-1(b) at 30 mA/cm^2. Thus good quality deposition at low current density was only possible from complex baths.

Simple Bath-1(a) contains lower Ni/Fe ratio in its electrolyte composition than the other three baths. The highest Ni content in the deposit was measured as 11.09 wt% for bath B-1(a) at the current density of 100 mA/cm^2 while 92.29, 92.34 and 90.59 wt% Ni content was found for bath B-1(b), B-2 and B-3 respectively at the same current density. This is supported by the alloy deposition principle that an increase in the metal percentage (or ratio) of a parent metal in an alloy plating bath results in an increase in its percentage (or ratio) in the deposit[10]. Moreover, the electrolyte conductance increases as a result of addition of Na_2SO_4 in bath B-1(b), B-2, B-3 and consequently it significantly increased Ni^{2+} in the deposit if compared with bath B-1(a)[9]. Here, the minimum Ni content (67.94%) of coatings obtained from all baths containing Ni/Fe ratio 12 is higher than the maximum Ni content (11.09 %) of those obtained from bath containing Ni/Fe ratio 1.

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[11,12]. Again according to Brenner's definition of anomalous codeposition[3], the less noble metal (here Fe) is deposited preferentially and its percentage in the deposit become higher than that in electrolytes. Fe-Ni alloy electrodeposition is recognized as anomalous co-deposition but under some conditions of current density and temperature, Fe-Ni metals may also co-deposit in a normal fashion. Figure 2 shows the relation between % Ni (more noble metal) in the deposit and % Ni in the bath. The feature of this figure is that the composition points for the more noble metals, Ni, lie below the composition reference line, AB, which means that the less noble metal deposits preferentially under the test conditions in this study. Thus, Fe-Ni alloy shows anomalous electrodeposition in the test conditions of this study. Point C (corresponding to the complex bath B-3) is closer to the reference line, AB, than the other two composition points indicating that higher %Ni (more noble) in coatings deposited from complex bath than the simple baths. This concludes that addition the complexing agents suppresses the anomalous nature of the Fe-Ni alloy electrodeposition.

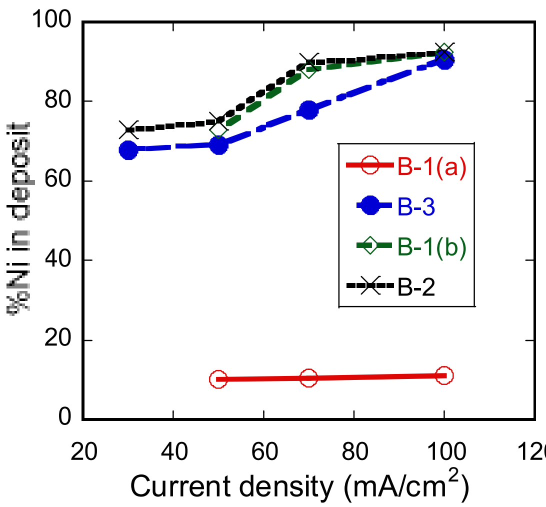

Figure 1. Effect of current density on %Ni in coating deposited from all the experimental baths.

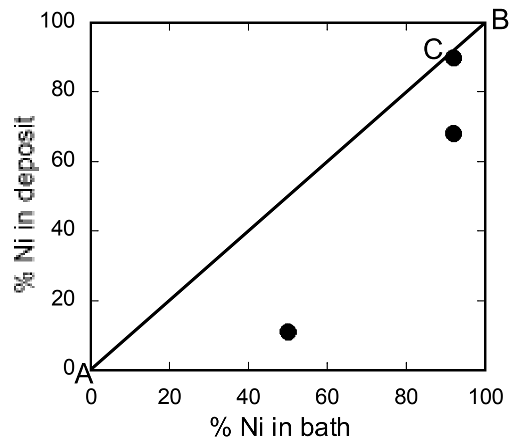

Figure 2. Relation between the composition of the deposit and the composition of the bath in Fe-Ni co-deposition from the baths under test.

Morphology of the Coating

The influence of bath composition with current density on the morphology of Fe-Ni coatings was evaluated by Scanning Electron Microscope (SEM). The topographies of Fe-Ni coatings were analyzed concerning their uniformity, grain size and the presence/absence of cracks.

SEM micrographs of Fe-Ni alloy coatings electrodeposited at current density of 70 mA/cm^2 both from simple and complex baths are shown in Fig. 3. Bath-1a and bath-1b are simple baths with electrolytes containing Ni/Fe ratio of 1 and 12 respectively. Grain size in Fig. 3a is ~ 6 μm and that in Fig. 3b is ~ 3 μm. Thus grain size decreased in coating obtained from bath having higher Ni/Fe ratio. Moreover, morphology of the Fe-Ni alloys obtained from the simple baths is characterized by the presence of sharp-line microcracks distributed over the deposits. The stress developed during electrodeposition is supposed to be attributed for the microcracks. On the contrary, microcracks could not be seen in the deposits obtained from complex baths (Fig. 3c and 3d).

Figures 4 and 5 show SEM images of Fe-Ni alloy coatings obtained from high Ni/Fe ratio complex baths B-2 and B-3 respectively at different current density. Grains of coatings obtained from bath B-2 containing only ascorbic acid as complexing agent are relatively smaller than those obtained from bath B-3 containing all three complexing agents. Grains are roughly spherical and average grain size decreases with increasing current density. Change in grain size is more prominent in coatings deposited from bath B-3 containing all three complexing agents. Thus structure of the Fe-Ni coatings is strongly influenced by current density. Myung et al.[13] reported similar observations to binary Fe-Ni thin films.

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[14]. 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[15]. From the SEM observations, it can be said that addition of complexing agent of 4.0 g/l ascorbic acid

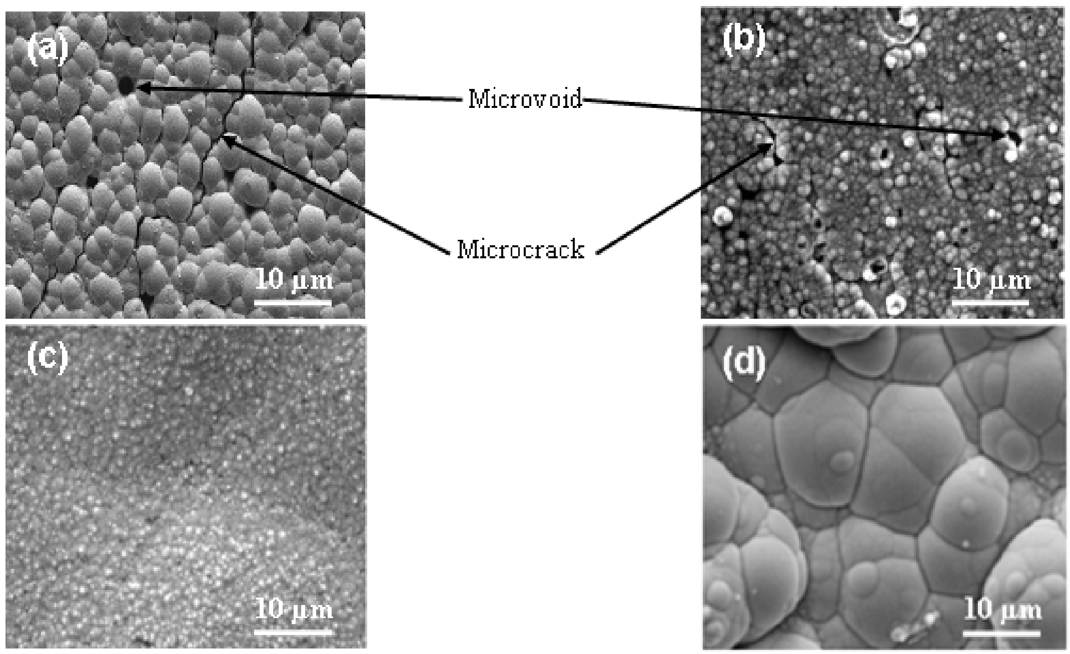

Figure 3. SEM micrographs of Fe-Ni alloy coatings electrodeposited at current density of 70 mA/cm^2 from (a) Bath-1(a), (b) Bath-1(b), (c) Bath-2 and (d) Bath-3

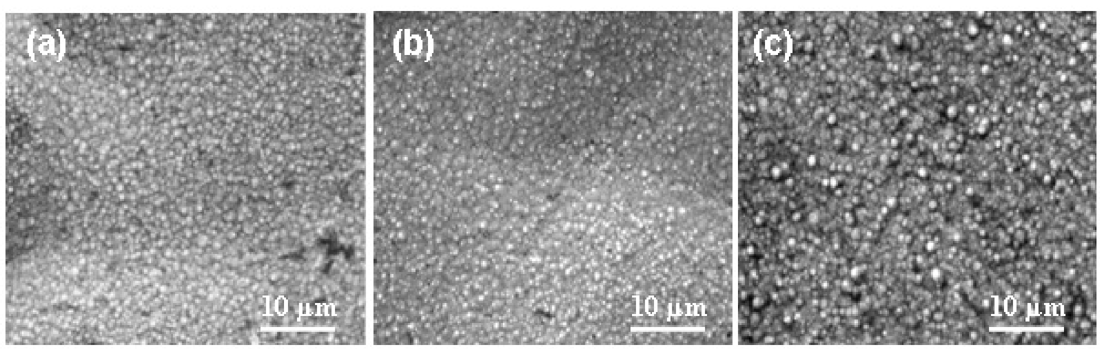

Figure 4. SEM micrographs of Fe-Ni alloy coatings electrodeposited from complex bath B-2 at current density of (a) 100 mA/cm^2 (b) 70 mA/cm^2 and (c) 30 mA/cm^2

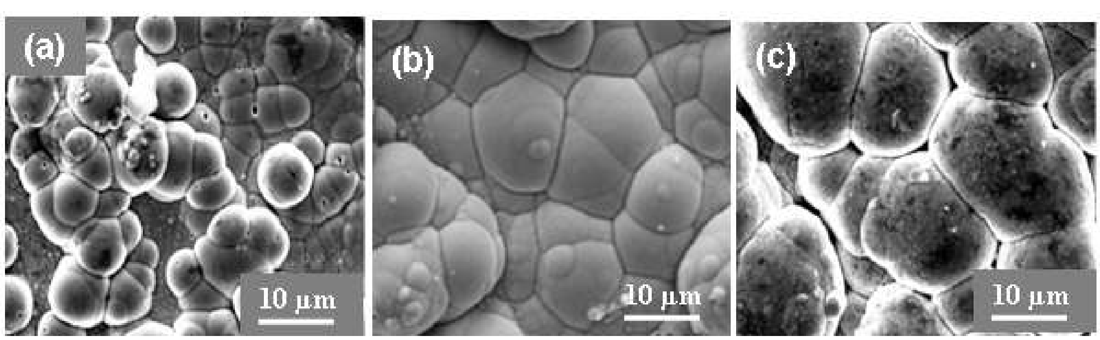

Figure 5. SEM micrographs of Fe-Ni alloy coatings electrodeposited from complex bath B-3 at current density of (a) 100 mA/cm^2 (b) 70 mA/cm^2 and (c) 30 mA/cm^2

increased nucleation rates that helped to form crack-free, uniform and fine grained structures as is seen in Fig. 3c whereas coarse grain morphology (Fig. 3d) is seen in deposit obtained from bath B-3. High surface diffusion rates, low population of adatoms and low over-potentials are believed to be predominant in case of bath B-3 containing all three complexing agents.

It is known that high current density give rise to a high degree of adatoms saturation at the electrode surface, and high degree of adatoms increases the crystallization and thus decreases the grain size. After heat treatment of the electrodeposited samples, the grain size was measured again. The average grain size increased after heat treatment than before. The grain size increment with annealing temperature is shown in Fig. 6.

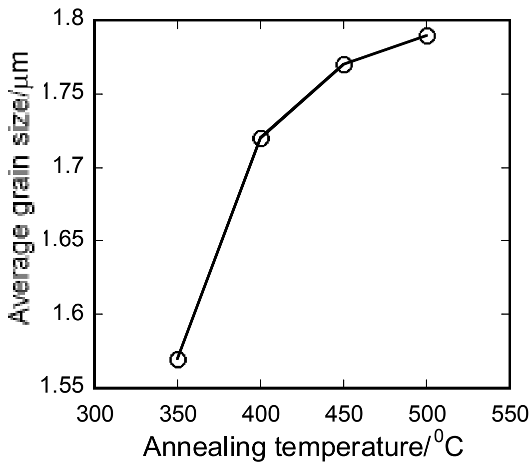

Figure 6. Effect of annealing temperature on average grain size in coating deposited from bath B-2 at current density of 100 mA/cm^2

Microhardness of the Coating

Vickers Hardness Number (VHN) of the deposits was evaluated by microhardness testing using a Shimadzu microhardness machine. It was found that the hardness of Fe-Ni alloy deposited from high Ni/Fe ratio containing bath was higher than the alloy deposited from the low Ni/Fe ratio containing bath. It is reported that Ni is harder than Fe[16]. As Ni percentage in the alloy deposited from high Ni/Fe ratio was higher (Fig. 1), it yielded high hardness. Figure 7a showed microhardness of the coatings deposited from complex bath B-2 as a function of applied current density in the deposition process. Microhardness increased with increasing current density as %Ni in the deposit increased with increasing current density. Increasing annealing temperature results the decrease of VHN of the deposits (Fig. 7b). Annealing softens the coating. Before annealing the VHN of the coating deposited at 100 mA/cm^2 from bath B-2 was 778 and the same sample showed 270 VHN after annealing at 500^{0}C.

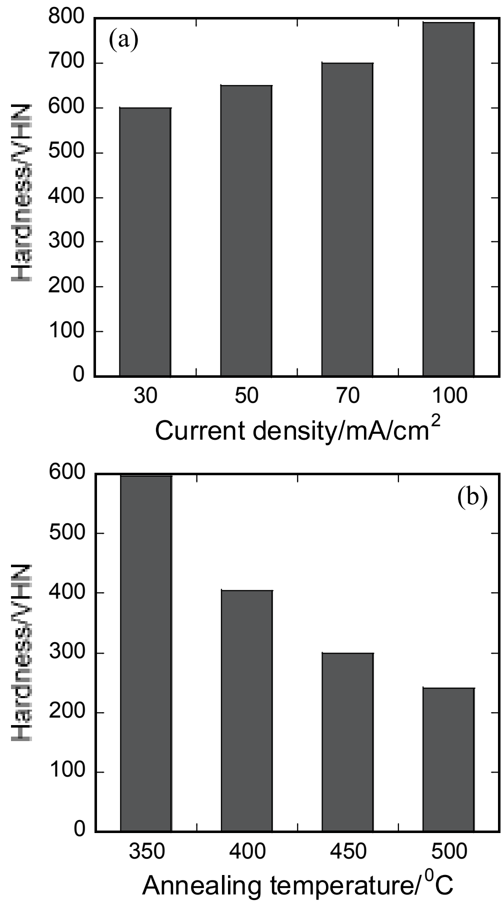

Figure 7. Microhardness as a function of (a) current density and (b) annealing temperature of the coating obtained from bath B-2 (current density of 100 mA/cm^2)

CONCLUSIONS

Electrodeposition of Fe-Ni thin films has been carried out on copper substrate under various electrodeposition conditions from simple as well as complex baths. The Ni/Fe ratio in bath composition with current density is considered as varying parameters in this work. The conclusions drawn from the study are:

- The percentage of Ni in the Fe-Ni alloy coating deposited from electrolytes containing high Ni/Fe ratio is higher than that of the coating deposited from low Ni/Fe ratio and the percentage of Ni into the coating increases with increasing current density. This is supported by the alloy deposition principle.

- The morphology of the Fe-Ni films obtained from simple baths is characterized by non-smooth surface with presence of microcracks onto it. On the contrary, coatings from complex baths are fine-grained with smooth surfaces which may be attributed to the addition of complexing agents as they act as stress reliever.
- Increase in Ni/Fe ratio in the bath as well as current density decrease grain size of the deposits. High current density is believed to give rise to a high degree of adatoms saturation at the electrode surface and high degree of adatoms decreases the grain size.
- Percentage Ni and hence VHN of the coating increase with increasing Ni/Fe ratio and current density. With increasing annealing temperature, VHN decreases as the grain size along with softening of the samples increases.

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