

# Soft magnetic properties of Electrodeposited Fe-Ni Films Prepared in Citric Acid Based Bath

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Electrodeposited Fe-Ni films are widely used in device applications. However, there is a growing awareness of the toxicity of the plating bath containing boric acid. In order to avoid boric acid in the deposition process, we have employed a citric acid based bath for electrodeposition of Fe-Ni films and investigated the effect of the acid content in the bath on the structural and magnetic properties of the deposited films. It is found that the Fe content of the film depends largely on the acid concentration and low coercivity values of less than 30 A/m are realized when the Fe content of the film is around 22 at.%. This magnetic softness is attainable in a wide film thickness range between 20 and 120  $\mu\text{m}$ . Our process exhibits a relatively high cathode efficiency of above 55 %. Furthermore, a high deposition rate of 170  $\mu\text{m}/\text{h}$  is obtained without sacrificing the magnetic softness of the film by increasing the current density during the deposition. From these results, we conclude that the citric acid based bath is an environmentally friendlier plating bath ideal for mass-production of magnetically soft Fe-Ni films.

**Index Terms**— Soft magnetic material, Electrodeposition, Permalloy, Film

## I. INTRODUCTION

Fe-Ni alloys exhibit good soft magnetic properties such as low coercivity and high permeability and have been applied in a range of electric devices for the purpose of shielding and converging magnetic flux. Both the magnetocrystalline anisotropy and magnetostriction constants become nearly zero at an alloy composition of  $\text{Fe}_{22}\text{Ni}_{78}$  and thus, this alloy is well-known for its excellent soft magnetic properties [1]. The Fe-Ni films in the electric device applications are commonly prepared by electrodeposition because of the high economic viability of the process as well as the simplicity of fabrication equipment.

Currently, the commonly used plating bath for the Fe-Ni films contains boric acid for the purpose of controlling pH of the bath. Although the boric acid plays an important role in the plating process of Ni and Fe films [2,3], the waste bath containing boron is harmful and thus, restricted by the regulation of environmental protection in Japan [4]. Doi *et al.* reported that a plating bath containing citric acid is effective in obtaining fine crystalline Ni films free of texture effects by plating [5,6]. It is well known that fine crystal structures are effective in realizing good soft magnetic properties due to the exchange softening effect [7-10]. Therefore, Fe-Ni films prepared by electroplating using citric acid instead of the harmful boric acid could be a potential candidate for the substitution of the boric acid based bath in the plating process of soft magnetic Fe-Ni films. In this report, in order to clarify the potential of the citric acid based bath, we have investigated the structural and magnetic properties of electrodeposited Fe-Ni films prepared from a plating bath containing citric acid.

## II. EXPERIMENTAL PROCEDURES

### A. Preparation of electrodeposited Fe-Ni films

The base electrolyte of the plating bath contained the following: 275 g/L of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 35 g/L of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 50 g/L of NaCl and 5 g/L of  $\text{C}_7\text{H}_4\text{NNaO}_3\text{S} \cdot 2\text{H}_2\text{O}$ . We added 0-300 g/L of citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) to the above-mentioned plating bath. pH in the bath was not adjusted (approximately 2.2). Anode and cathode used were 500  $\mu\text{m}$  thick Ni and Cu plates, respectively. The Fe-Ni films were electrodeposited on the Cu plate. The deposition was typically performed on a plating area of 75  $\text{mm}^2$  under a dc current density of 2.0  $\text{mA}/\text{mm}^2$  for a deposition time of 10 min. The bath temperature was 50  $^\circ\text{C}$ .

### B. Measurements

The thickness and dc-hysteresis loops of the electrodeposited Fe-Ni films were measured with a micrometer (Mitutoyo CPM15-25MJ) and a B-H tracer (Riken Denshi BHS-40) operated at a field sweep rate of 50 mHz, respectively. The maximum excitation field of approximately 4000 A/m was used for the B-H measurements and the coercivity was determined from the loop. The compositions and crystal structures of the films were analyzed by EDX (Hitachi High-technologies S-3000) and XRD (Rigaku Rint 2000), respectively. The thickness and the composition of each 75  $\text{mm}^2$ -film were determined by averaging the values obtained for approximately every 7  $\text{mm}^2$  (12 points) and 9  $\text{mm}^2$  (9 points), respectively. All measurements were carried out for the Fe-Ni films in an as-deposited state.

## III. RESULTS AND DISCUSSION

Figure 1 shows the changes in the coercivity and Fe content

in the electrodeposited Fe-Ni films as a function of the content of citric acid in plating bath. As shown in Fig.1, the Fe content increases from 18 to 50 at.% with increasing the content of citric acid from 0 to 100 g/L. The coercivity shows a dramatic decrease from 380 to 20 A/m with increasing the citric acid content from 0 to 30 g/L followed by a moderate increase in the higher acid concentrations. Both the Fe content and the coercivity are approximately 50 at.% and 70 A/m and are almost constant for the acid concentrations higher than 100 g/L.

In order to clarify the effect of Fe content on the coercivity, the coercivity results in Fig. 1 are replotted in Fig. 2 as a function of Fe content. It is clear that the lowest coercivity value is obtained around 22 at.% of Fe, the well-known composition where both the magnetocrystalline anisotropy and the magnetostriction constants become nearly zero. Thus, the dramatic improvement of the magnetic softness observed in the acid concentration range between 0 and 30 g/L is readily understood by the induced change in Fe content. The low coercivity less than 30 A/m is due to the realization of the required composition in the film, i.e. Fe<sub>22</sub>Ni<sub>78</sub>.

The coercivity of the films in Fig. 2 remains relatively low even with a high Fe of around 50 at.% despite the fact that the intrinsic magnetocrystalline anisotropy of the films is expected to be high. In order to understand this behavior, we investigated the structure of the films. Figure 3 shows XRD patterns of the films prepared at various concentrations of citric acid. It is evident on these diffraction patterns that line broadening and a shift of the diffraction angle to the lower angle side take place when the acid concentration is high. The shift of the diffraction angle reflects the effect of Fe content on the lattice parameter of Fe-Ni alloys while the line broadening indicates that higher acid concentrations are effective in reducing the grain size. Since the effective magnetocrystalline anisotropy could be reduced by grain refinement, the relatively low coercivity values at a high Fe of around 50 at.% is attributable to the grain refinement effect.

From these results, we found that the Fe-Ni films with relatively low coercivity could be obtained in a wide Fe content range between 20 and 50 at.%.

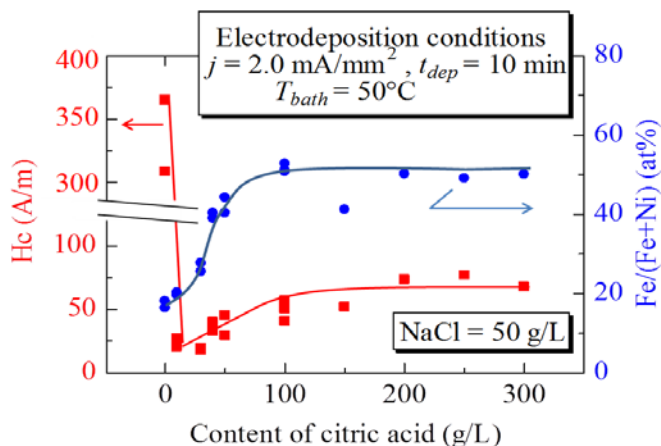


Fig.1 Changes in the coercivity and Fe content in deposited Fe-Ni films as a function of citric acid content in plating bath.

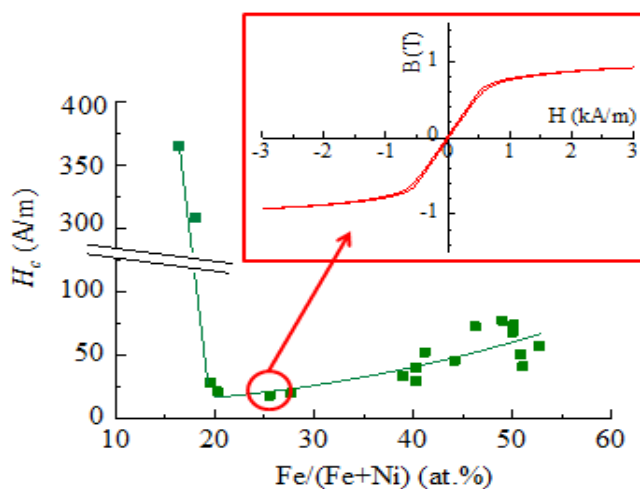


Fig.2 Relationship between the coercivity and Fe content (replot of the results in Fig. 1). The inset shows a typical B-H loop of the film with low coercivity.

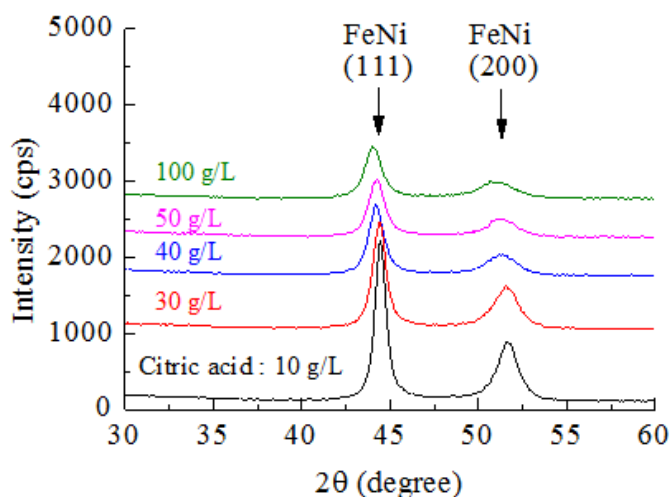


Fig.3 XRD patterns of the films prepared with various contents of citric acid. All the films shown were deposited under the same conditions (a dc current density of 2.0 mA/mm<sup>2</sup>, a deposition time of 10 min, a bath temperature of 50 °C and a plating area of 75 mm<sup>2</sup>).

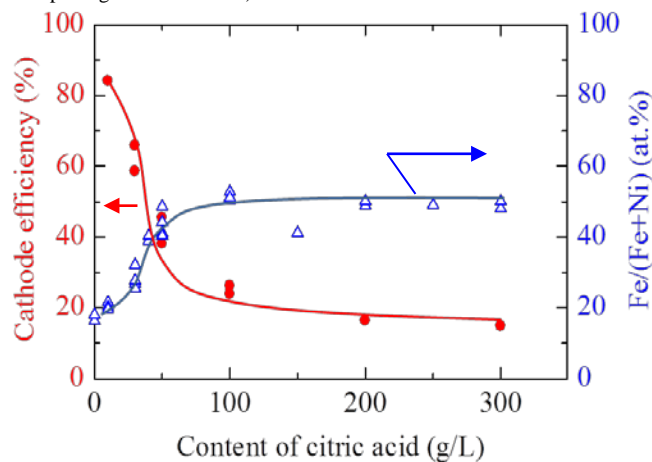


Fig.4 Changes in cathode efficiency and Fe content as a function of the citric acid content in the plating bath. The cathode efficiency was obtained from the actual and theoretical weights of the electrodeposited Fe-Ni films. The theoretical weight was calculated by Faraday's law based on the alloy composition of the film.

High deposition rate has an advantage in mass production because required film thickness could be obtained in a short deposition time. Since the deposition rate for the plating process in an aqua bath is often limited by generation of hydrogen, the cathode efficiency is one of the most important parameters for realization of high-rate electric plating. Hence, we investigated the cathode efficiency by comparing the experimental and theoretical film mass; the cathode efficiency is defined by the actual weight of electrodeposited Fe-Ni film divided by the theoretical weight as per Faraday's law. Figure 4 shows the cathode efficiency as a function of citric acid content in the plating bath. The film compositions are also shown in Fig. 4. It is clear that the cathode efficiency shows a tendency to decrease with increasing the content of citric acid whereas the Fe content exhibits an opposite trend. It is worth mentioning here that the cathode efficiency remains a high value above 55% with 20-30 g/L of citric acid where the ideal film composition of  $\text{Fe}_{22}\text{Ni}_{78}$  is realized. According to previous reports on the Fe-Ni films prepared in a boric acid based bath, the cathode efficiency at Fe content of around 22 at.% was approximately 60 % [11-13]. Consequently, it is confirmed that the cathode efficiency for our citric acid based bath is comparable to that in the boric acid based bath.

Figure 5 shows the changes in the film thickness and the coercivity for the electrodeposited Fe-Ni films as a function of deposition time. In addition to a current density ( $j$ ) of 2.0 mA/mm<sup>2</sup>,  $j = 1.3$  and 2.7 mA/mm<sup>2</sup> were also used in the deposition process. As shown in Fig. 5, the film thickness increases proportionately with deposition time for all the three current densities. However, the coercivity at each current density appears almost unaffected by the deposition time up to 40 min, although the coercivity values of the films deposited at  $j = 1.3$  mA/mm<sup>2</sup> are clearly higher than those for the higher current densities. We have confirmed that the Fe content in the film at  $j = 1.3$  mA/mm<sup>2</sup> is slightly higher than the ideal alloy composition and the poorer magnetic softness for  $j = 1.3$  mA/mm<sup>2</sup> can be explained by this compositional effect. The deposition rates, which were calculated by the slope of the linear fitting lines, were 85  $\mu\text{m/h}$  for 1.3 mA/mm<sup>2</sup>, 137  $\mu\text{m/h}$  for 2.0 mA/mm<sup>2</sup> and 176  $\mu\text{m/h}$  for 2.7 mA/mm<sup>2</sup>. This indicates that the deposition rate is enhanced in proportion to the current density.

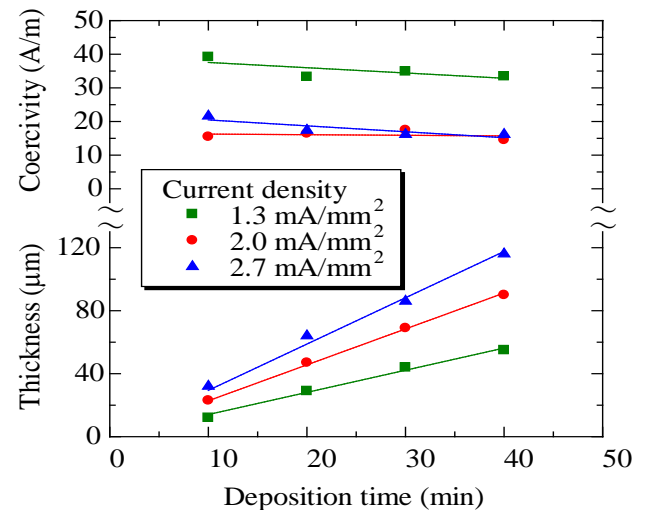


Fig.5 Changes in film thickness and Fe content for the electrodeposited Fe-Ni films as a function of deposition time.

#### IV. CONCLUSION

In this report, we have investigated the structural and magnetic properties of electrodeposited Fe-Ni films prepared from a citric acid based bath. The obtained results are summarized as follows:

- (1) Fe-Ni films with a low coercivity of less than 30 A/m could be obtained around 22 at.% of Fe.
- (2) Fe content was increased with increasing the content of citric acid from approximately 18 at.% to 50 at.%
- (3) Cathode efficiency was reduced from 80 % to 18 % with increasing the content of citric acid
- (4) A high deposition rate of 170  $\mu\text{m/h}$  could be obtained without deterioration of good soft magnetic property of the film
- (5) Fe-Ni films with a low coercivity value of 20 A/m were obtained in a wide thickness range of 20 to 120  $\mu\text{m}$ .

From above-mentioned results, we conclude that the citric acid based bath is an ideal plating bath for obtaining Fe-Ni films with good soft magnetic properties.

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