# Electrodeposited Fe-Ni films prepared in a citric-acid-based bath with different pH values

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**We plated Fe-Ni films from a citric-acid-based plating bath and evaluated the effect of pH value in the bath on the magnetic properties and the productivities of the films. In this study, the pH value of the bath was controlled from 0.5 to 3.6 by the addition of hydrochloric acid or sodium citrate. The electrodeposited Fe-Ni film with the Fe content of approximately 22 at.% prepared at high pH (> 3) tends to show large coercivity (> 100 A/m), rough surface and relatively high cathode efficiency (> 70 %) whereas the films prepared at low pH (< 1) tend to show low coercivities (< 50 A/m), smooth surfaces and low cathode efficiencies (< 60 %). The $Fe_{22}Ni_{78}$ film prepared from the bath without the pH adjuster of a hydrochloric acid or a sodium citrate shows low coercivity of 25 A/m, smooth surface and relatively high cathode efficiency of 65 %. Since low coercivity, smooth surface and high cathode efficiency are important factors for mass-producing Fe-Ni films, we concluded that a citric-acid-based bath with pH range from 1 to 3 is suitable for electrodeposition of soft magnetic Fe-Ni films.**

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

## I. Introduction

Fe-Ni alloys have good soft magnetic properties and their films have been applied into electric devices for the purpose of shielding and converging magnetic flux. For mass-producing Fe-Ni films used in electric devices, chemical processes such as electrodeposition methods are preferred over physical processes such as sputtering methods since the chemical processes have high economic viability of the process and the simplicity of fabrication equipment. There have been many reports on electrodeposited Fe-Ni films, and good soft magnetic properties of the films have been obtained [1-3]. Recently, we have prepared Fe-Ni films in a citric-acid-based bath and reported that the films have good soft magnetic properties [4]. Although we have not adjusted the pH value of the plating bath in the previous report, it is well known that pH values affect various properties of deposited films such as surface morphologies, chemical compositions and magnetic properties [5-10]. We, therefore, have investigated the effect of pH value on the coercivity, surface morphology, compositions and cathode efficiencies of Fe-Ni films prepared in a citric-acid-based plating bath.

## II. Experimental Procedures

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

We plated the Fe-Ni films using direct current in the galvanostatic mode. The contents of electrolyte are shown in Table 1. Hydrochloric acid and sodium citrate were used as pH adjuster and we changed the pH value from 0.5 to 3.6 by using the pH adjuster. Conditions of the electroplating are shown in Table 2. 500 μm thick and 5 mm wide Ni and Cu plates were used as the anode and the cathode electrodes, respectively. The distance between the electrodes was set at 25 mm and Fe-Ni films were deposited on the Cu plate. The current density and the deposition time were controlled by a computer-aided dc current source. The bath temperature was kept at 50 °C during the plating.

TABLE I
ELECTROLYTE IN THE PLATING BATH

| Components | Concentration |
|---|---|
| $NiSO_4 \cdot 6H_2O$ | 275 g/L |
| $FeSO_4 \cdot 7H_2O$ | 35 g/L |
| NaCl | 50 g/L |
| $C_7H_4NNaO_3S \cdot 2H_2O$ | 5 g/L |
| Citric acid ($C_6H_8O_7 \cdot H_2O$) | 30 g/L |

TABLE II
ELECTROPLATING CONDITIONS.

| Condition | Value |
|---|---|
| pH | 0.5 -3.6 |
| Bath temperature | 50 °C |
| Current density | 2.0 mA/mm$^2$ |
| Deposition Time | 10 min |

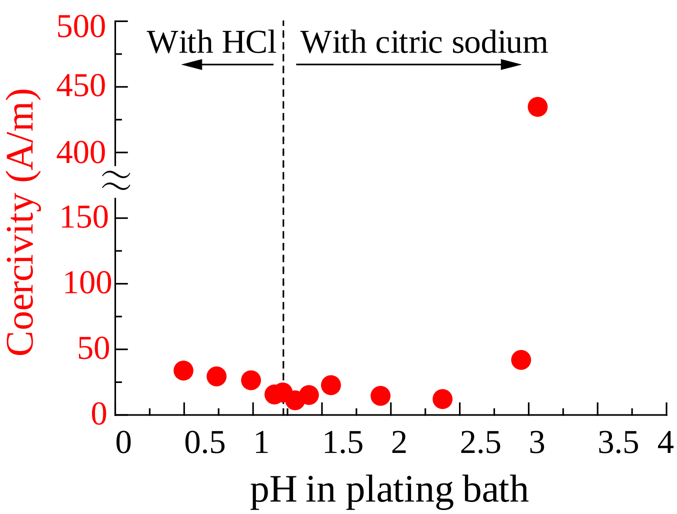
### B. Measurements

The dc-hysteresis loops of the electrodeposited Fe-Ni films were measured with a B-H tracer (Riken Denshi BHS-40) operated at a field sweep rate of 50 mHz. The maximum excitation field of approximately 4 kA/m was used for the B-H measurements and the coercivity was determined from the loop. The surface morphology and compositions of the films were analyzed by means of SEM-EDX (Hitachi High-technologies S-3000). The composition of 75 mm$^2$-films was determined by averaging the values obtained for approximately every 9 mm$^2$ (9 points). The cathode efficiency is calculated from the actual weight of the electrodeposited Fe-Ni film and the theoretical weight obtained by Faraday's law. The theoretical weight was obtained from the evaluated composition of the film.

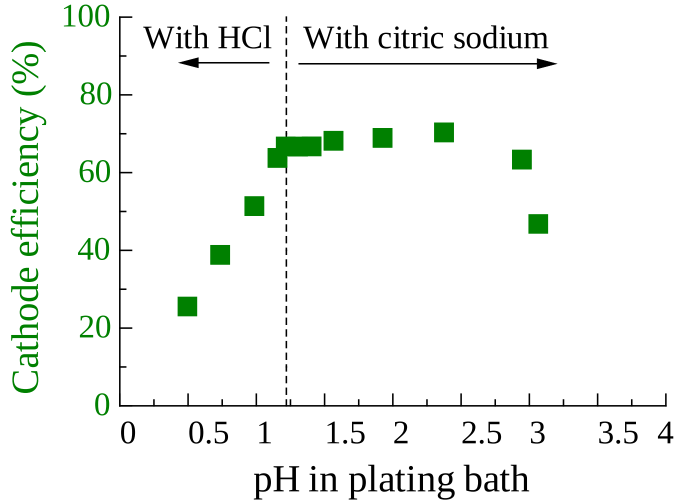
## III. Results and Discussion

For mass-production of Fe-Ni films, good soft magnetic properties, smooth surface and high productivities are important factors. In order to confirm the effect of pH value in the plating bath on the soft magnetic properties and the productivities, we evaluated the coercivity and the cathode efficiency of the electrodeposited Fe-Ni films. Figure 1 shows (a) the coercivity and (b) the cathode efficiency in the electrodeposited Fe-Ni films as a function of the pH value in the plating bath. The coercivity shows a slight decrease from 40 to 25 A/m with increasing the pH value from 0.5 to 1.2 followed by an increase in the pH value. A large coercivity value of over 400 A/m was observed in the film prepared at pH of 3.1 and small coercivity values were obtained in the films prepared at pH range from 1.2 to 2.5. We confirmed that the lower pH values of less than 2.5 are suitable for obtaining the Fe-Ni films with good soft magnetic property. In contrast to the result for coercivity, the cathode efficiency shows an increase from 25 to 65 % with increasing the pH value from 0.5 to 1.2 followed by a rapid decrease around pH of 3. Since high cathode efficiency enables us to obtain Fe-Ni films in a short deposition time, we found that a low pH value of less than 1.0 is not suitable for mass-productive Fe-Ni films.

As shown in Fig. 1(a), the large coercivity was observed in the Fe-Ni film prepared at pH of 3.1. In order to clarify the origins of the large coercivity, we evaluated the compositions of the films with low and high coercivity values. As a result, the evaluated compositions for pH of 1.2 and 3.1 were $Fe_{22}Ni_{78}$ and $Fe_{59}Ni_{41}$, respectively. It is well-known that $Fe_{22}Ni_{78}$ alloy has excellent soft magnetic properties since the magnetocrystalline anisotropy and magnetostriction constants become nearly zero. Thus, a reason for the large coercivity in the high pH bath is understood by the change in the Fe content in the film from the required composition of $Fe_{22}Ni_{78}$.




(a) Coercivity




(b) Cathode efficiency

Fig.1 Changes in (a) the coercivity and (b) the cathode efficiency of the electrodeposited films as a function of pH value in the plating bath.

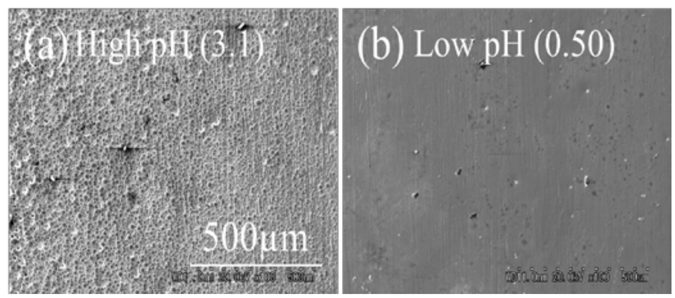



Fig.2 Surface morphologies of the films prepared at pH of (a) 3.1 and (b) 0.5.

Figure 2 shows surface morphology of the film prepared at a high pH of 3.1. The result for the film prepared at a low pH of 0.5 is also shown in Fig. 2. As shown in Fig. 2, the film prepared at high pH has a rough surface compared with the surface for the film prepared at low pH. In general, soft magnetic properties of films with a smooth surface are better than those for films with a rough surface since smooth surface doesn't prevent domain wall movement during magnetization. Therefore, we considered that the rough surface is another reason for the large coercivity.

Two reasons for the large coercivity were suggested in the above-mentioned results. In order to clarify the dominant factor for the large coercivity, we fabricated the films with controlled Fe content. The Fe content in the film was controlled around 22 at.% by adjusting the content of the $FeSO_4{\cdot}7H_2O$ and the citric acid. Figure 3 shows (a) the coercivity and (b) the cathode efficiency in the electrodeposited Fe-Ni films with controlled Fe content as a function of the pH value in the plating bath. All films appear to fall within the Fe content range from 21 to 30 at.%. As shown in Fig. 3, the coercivity increases slightly with increasing the pH value from 1.0 to 2.7, and a large coercivity of over 100 A/m was observed in the film prepared at pH of over 3.5. In the pH range from 0.5 to 2.5, the cathode efficiency shows almost the same tendency as the film without controlled Fe content shown in Fig. 1(b). However, a different tendency was observed in the higher pH region (> 2.5). We already have confirmed that the Fe content in the film affects cathode efficiency and that Fe-Ni films with a high Fe content have low cathode efficiency [4]. Judging from our previous results, the different tendency in the high pH region is explained by the change in Fe content in the film. Although we reduced the Fe content of the film prepared in the higher pH region, a large coercivity was still observed as well as the result in Fig. 1(a), suggesting the effect of the surface roughness. Hence, we observed the surface morphology of the film. Figure 4 shows surface morphology of the film (a) with controlled Fe content film prepared at pH of 3.6. The result for the film (b) without controlled Fe content prepared at pH of 3.1 is also shown in Fig. 4. As shown in Fig. 4, the film with controlled Fe content still shows a rough surface as well as the result for the film without controlled Fe content.

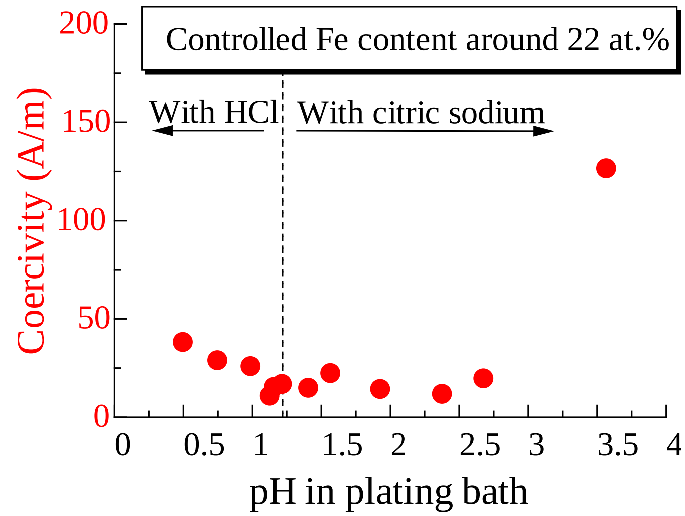
Generally, coercivities of Fe-Ni thin films show values lager than those for Fe-Ni thick films since the boundary states, such as roughness of the substrate, affect the soft magnetic properties of the films. In order to confirm the effect of the thickness on the coercivity, we evaluated the coercivity of the films with various thickness. Figure 5 shows the coercivity as a function of the thickness of the film prepared in the baths with various pH values of 0.5, 1.25 and 3.5. As show in Fig.5, the coercivity decreases with increasing film thickness. The coercivity of the films prepared in the bath with high pH is obviously lager than those for the films prepared in the baths with low pH.

From these results, we found that pH from 1 to 3 is a suitable range to obtain the Fe-Ni films from a citric-acid-based bath since the films have low coercivities and relatively high cathode efficiencies.

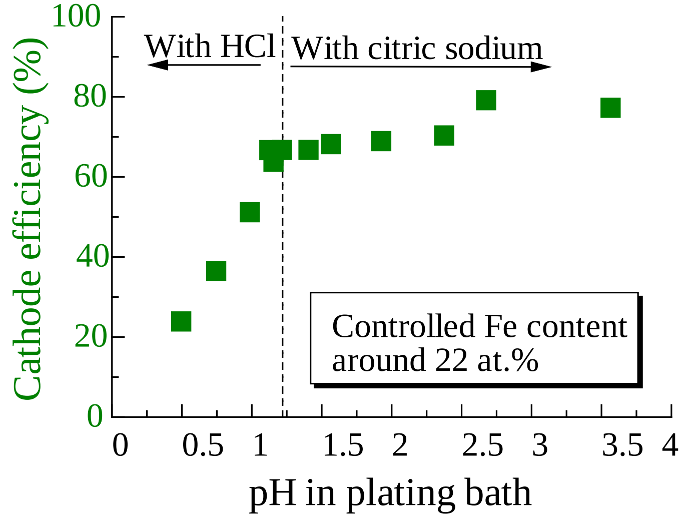
## IV. Conclusion

In this report, Fe-Ni films were prepared in a citric-acid-based plating bath and the effect of pH in the bath on coercivity, surface morphology, composition and cathode efficiency was evaluated. The obtained results are summarized as follows:

(1) Plating baths with low pH show low cathode efficiencies and they are not suitable for mass-productive Fe-Ni films.
(2) Fe-Ni film prepared at high pH has a rough surface and a high coercivity.
(3) For preparation of Fe-Ni films with good soft magnetic properties and high productivity, a suitable pH range is from 1 to 3.




(a) Coercivity




(b) Cathode efficiency

Fig.3 (a) the coercivity and (b) the cathode efficiency of the electrodeposited films with controlled Fe content as a function of pH value in the plating bath.

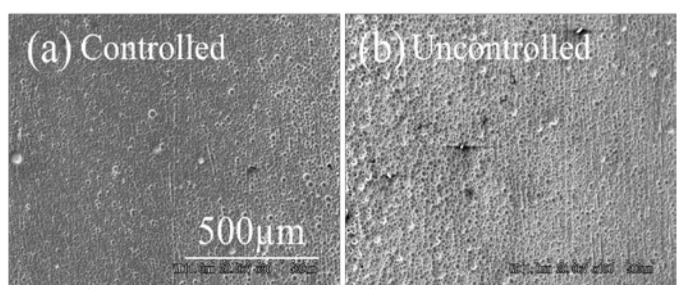



Fig.4 Surface morphologies of the Fe-Ni films with or without controlled Fe content prepared at high pH. The Fe contents of the films were controlled around 22 at.% by the change in the contents of the $FeSO_4 \cdot 7H_2O$ and the citric acid.

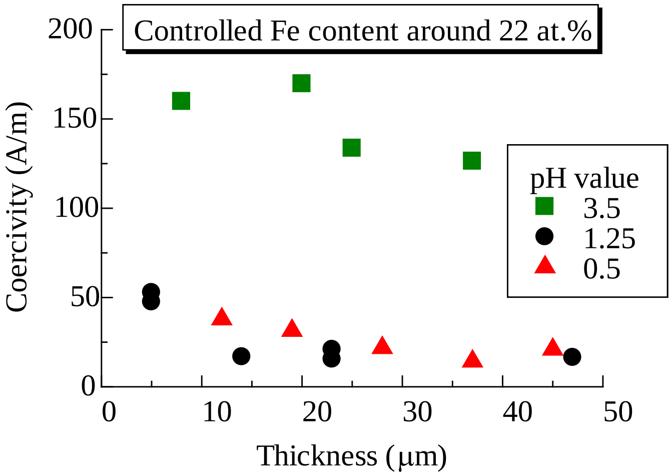



Fig. 5 Change in the coercivity as a function of the thickness of the film prepared in the baths with various pH values. The Fe contents of the films were controlled around 22 at.% by the change in the contents of the $FeSO_4 \cdot 7H_2O$ and the citric acid.

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