

Preparation of Ni Films using Solid/Liquid Hybrid Electroplating Method

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Electroplating is one of the important fabrication methods to obtain magnetic films commercially, and we have reported many soft magnetic films electroplated from water-based plating baths (liquid baths). Recently, we reported Ni films using gel-based plating baths (solid baths) to reduce waste after electroplating, considering the recent trend of raising environmental awareness. Expecting the spread of the application possibilities of the gel plating method, the present study focuses on solid/liquid hybrid plating, a combination of solid and liquid plating, and investigates the film's qualities and magnetic properties. In the investigations for single baths, the plating rates of both baths (liquid and solid baths) showed almost the same value, up to 10 min of plating time. The saturation magnetizations for both baths are also nearly the same. In the case of the hybrid baths, although no interaction was observed with the film's appearance, the saturation magnetization for the solid bath is slightly lower than that for the liquid bath. The decrease in the saturation magnetization is often observed when water decomposition becomes the dominant reaction on the cathode surface instead of metal ions' reduction; these results indicate that the hybrid bath process differs from the single bath process in Ni reduction. Although further study is required for the reduction process, the present study finds that ferromagnetic Ni films can be prepared by hybrid plating.

Keywords : electroplating, gel electrolytes, soft magnetic films, Ni films

1. Introduction

Typical fabrication processes for soft magnetic films, such as electroplating and electroless plating methods, are preferable over dry processes due to the simplicity of the equipment, and there are many reports on electro-deposited soft magnetic films from now on. Fe-Ni and Fe-Co alloys are well-known as excellent soft magnetic materials, and their electroplated films have been widely studied [1-7]. We have also employed the electroplating method using water-based plating baths (liquid baths) to obtain soft magnetic films and reported their good soft magnetic properties [8-11].

In recent years, environmental awareness has increased, and we need to consider the reduction in the environmental impact of manufacturing processes. Waste re-

duction is one of the efforts to reduce the environmental impact of electroplating. Therefore, our recent study focuses on gel-plating. Itagaki *et al.* studied partial Ni deposition on a Cu substrate using an organic gel electrolyte [12]. This method allows coating only selected areas, making it suitable for repairing damaged regions of the film as well as for surface patterning. They reported that gel-plating enables accurate and straightforward patterning without masking, while requiring only a small amount of electrolyte. Their report suggests a significant waste reduction and motivated us to apply gel-plating for the preparation of magnetic films. From their report, we recently reported a preparation method of soft magnetic Ni films using gel-based plating baths (solid baths) and concluded that gel-plating is one of the attractive fabrication processes of magnetic films [13].

We consider that a gel-plating method is a unique fabrication method for films. For example, we can directly obtain Fe and Ni films by a single plating process using two solid-plating baths with different bath compositions for Fe and Ni. To enhance the application fields of gel-plating methods, we proposed a solid/liquid hybrid electroplating method to prepare soft magnetic Ni films

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and investigated the film's qualities and magnetic properties in the present study.

2. Experimental Procedures

2.1. Electroplating Baths

Table 1 shows the bath conditions. First, the weights of each reagent were measured based on Table 1, and the measured reagents were placed in a beaker. We added distilled water into the beaker to adjust the mass to 50 g. The solution (distilled water with the reagents) was stirred at 50°C. After stirring enough, the solution was divided into two baths (described as baths #1 and #2). 2 mass% of gelatin was added into bath #1 and then stirred again at 50°C for ten minutes.

Figure 1 shows a jig used in this study for electroplating. After 10 min-stirring, we poured the solution of bath #1 into the jig and cooled the jig with the solution in a refrigerator for 120 minutes to gel (solidify) the plating bath. After cooling, the solution of bath #2 (liquid bath) was placed on top of the gel electrolyte (solid bath). This paper describes the combined bath as a “solid/liquid hybrid-plating bath.”

2.2. Electroplating

We electroplated Ni films using a DC-current power supply. Before pouring the solution of bath #1 as mentioned in Section 2.1, we placed the Ni plate (20 mm×5 mm×0.5 mm) as an anode and the Cu one (20 mm×5 mm×0.5 mm) as a substrate with a gap of 25 mm. Table 2 shows electroplating conditions. We electroplated

Table 1. Bath conditions.

Reagents	Concentration (g/L)
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	100
Glycine	15
NaCl	2
Sodium naphthalene tri-sulfonate	2

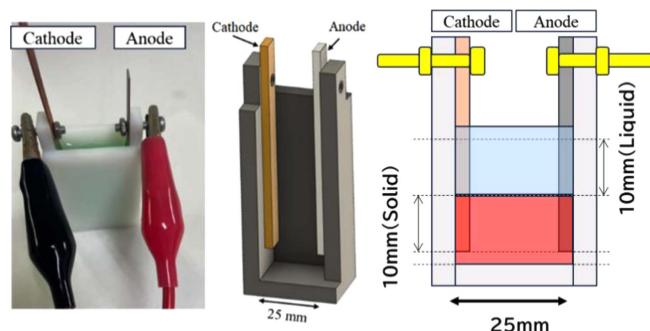


Fig. 1. (Color online) Jig for electroplating.

Table 2. Plating conditions.

Conditions	Values
Plating time t	3–15 min
Current density j	10 mA/cm ²

Ni film from a solid-bath on the lower side of the Cu plate and from a liquid-one on the upper side.

2.3. Measurements

The hysteresis loops were measured with a vibrating sample magnetometer (VSM), and the maximum applied field was approximately 1.5 MA/m. To discuss the crystalline structure of the films, X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Rigaku, Miniflex600-DX) with Cu-K α radiation.

3. Results and Discussion

3.1. Plating from a solid or liquid single bath

As a first step, we electroplated Ni films from liquid and solid single baths to obtain comparative data for the later discussion related to the hybrid plating. Fig. 2 shows the schematic representation of the bath in the jig. In this experiment, the inside of the jig was filled with only (i) liquid or (ii) solid baths.

Figure 3 shows the weight of Ni films plated from (i) a liquid-only bath and (ii) a solid-only one as a function of plating time. As shown in Fig. 3, the weight of both Ni films increased linearly with an increase in the plating time, up to ten minutes, and the 15-minute-plated film for the solid-only bath did not increase proportionally. In this study, as we did not cool the baths (not keep the baths at a constant low temperature), long-time plating (> 10 min) tends to increase bath temperature by the joule heating

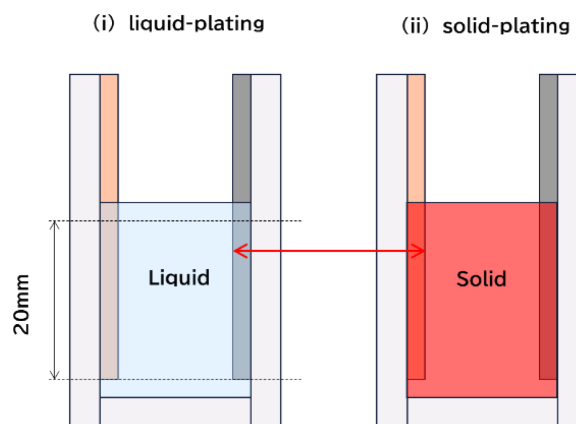


Fig. 2. (Color online) Schematic representation of the bath in the jig.

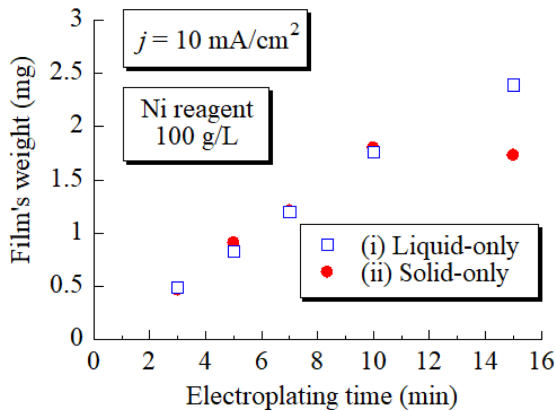


Fig. 3. (Color online) Weight of Ni films plated from (i) a liquid-only bath and (ii) a solid-only one as a function of plating time.

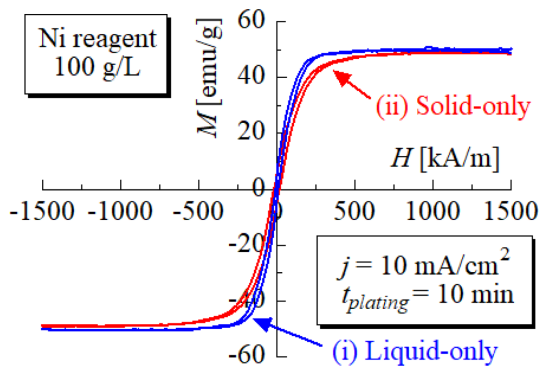


Fig. 4. (Color online) Hysteresis loops of Ni films plated from (i) a liquid-only bath and (ii) a solid-only one.

(current flow) and decompose the gel electrolyte. Since no gel decomposition was observed for up to ten minutes, we employed ten minutes as plating time in the following experiments.

Figure 4 shows the hysteresis loops of Ni films plated from (i) a liquid-only bath and (ii) a solid-only one. As shown in Fig. 4, since we could confirm that almost the same loop for both Ni films was obtained, we moved to investigate hybrid plating as the next step.

3.2. Plating from a hybrid bath

Figure 5 shows a photograph of Ni films electroplated from (i) liquid-only, (ii) solid-only, and (iii) hybrid baths. As shown in Fig. 5, the film's appearance (metallic luster) for the solid baths was less than that for the liquid ones. This result suggests that the effect of the brightener (Sodium naphthalene tri-sulfonate) is different between the liquid and solid baths. Improving the appearance of the gel-plated film (finding another brightener for gel-plating) is one of the future works.

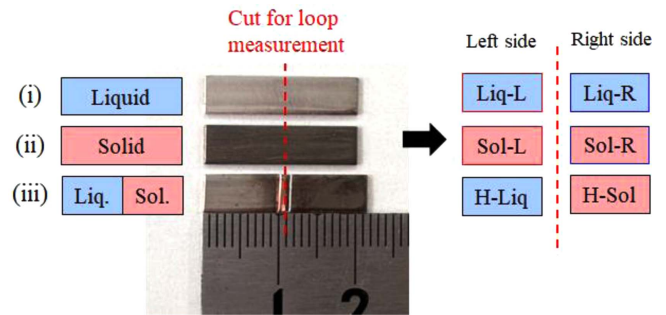
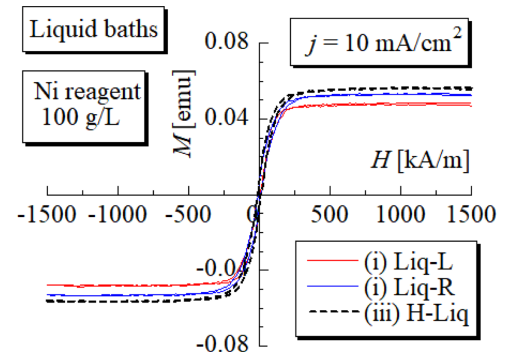
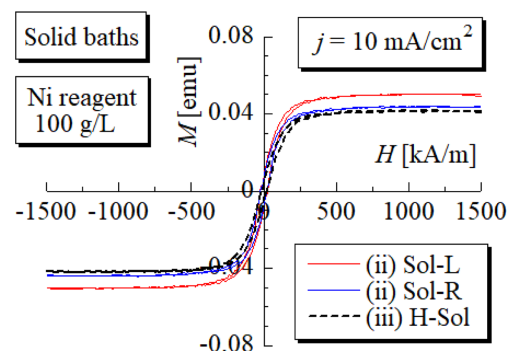


Fig. 5. (Color online) Photographs of Ni films plated from single baths and hybrid bath.

For measurement of the hysteresis loops, we cut the Ni films plated on Cu substrate at the center and separated the two Ni films, described as Liq-L (L: Left), Liq-R (R: Right), Sol-L, Sol-R, H-Liq, and H-Sol. Fig. 6 shows the hysteresis loops of the separated Ni films for (a) liquid baths and (b) solid baths. We obtained the weight of the Ni film by measuring the weight after electroplating (Ni plated film + Cu sub.) and subtracting the weight of the Cu substrate measured before electroplating. Since we could not measure the Cu substrates after the half-cut for



(a) Ni films plated from liquid parts



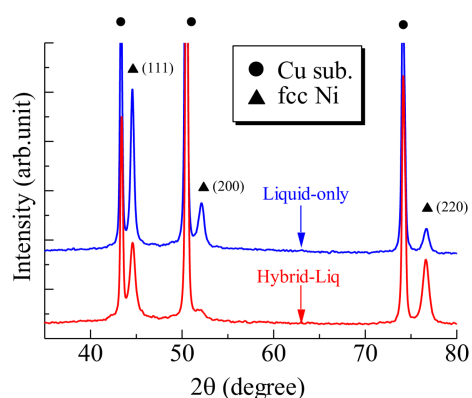
(b) Ni films plated from solid parts

Fig. 6. (Color online) Hysteresis loops of Ni films (a) Ni films plated from liquid parts (b) Ni films plated from solid parts.

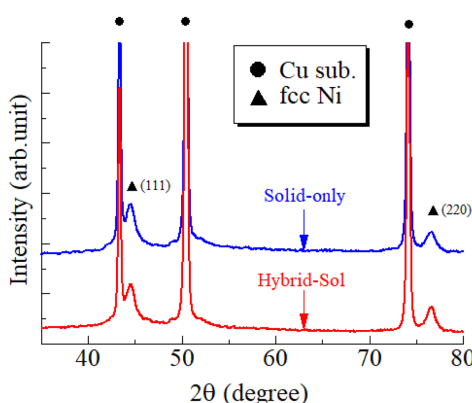
the hybrid plating, separating the weights of H-Sol and H-Liq was difficult. Therefore, the vertical axis of Fig. 6 is shown in emu (not shown in emu/g).

Focusing on the maximum magnetic moment, $M_{\max}$, for H-Liq and H-Sol, although we expected the same values between H-Liq and H-Sol from the results of Figs. 3–4, a slight difference was observed; $M_{\max}$ for H-Sol was slightly lower than that for H-Liq. If there is no interaction between the solid and liquid parts in the hybrid plating, we can predict that $M_{\max}$ for H-Liq should show the same value as Liq-L (or Liq-R). However, the $M_{\max}$ for H-Liq was slightly higher than Liq-R and Liq-L, as shown in Fig. 6(a). Additionally, $M_{\max}$ for H-Sol was slightly lower than Sol-R (or Sol-L). The fact that the $M_{\max}$ value of H-Liq (or H-Sol) was higher (or lower) than the predicted value implies that the hybridization of the baths affects the plating process.

To discuss the structural properties of the films, we obtained XRD patterns. Fig. 7 shows (a) the XRD patterns of the films prepared from liquid parts (Liq-L and H-Liq) and (b) those for solid ones (Sol-L and H-Sol).



(a) Ni films plated from liquid parts



(b) Ni films plated from solid parts

Fig. 7. (Color online) XRD patterns of Ni films (a) Ni films plated from liquid parts (b) Ni films plated from solid parts.

Sol). As shown in Fig. 7(b), the patterns for Sol-L and H-Sol were almost the same, indicating that hybridization of the baths did not affect the crystal structure of the gel-part-plated films. On the other hand, the patterns for Liq-L and H-Liq (Fig. 7(b)) were slightly different, and the Ni film for H-Liq tended to orient in the fcc (220) plane. The change in the grain orientation suggests that the Ni ion reduction on the substrate was changed by the hybridization. Pangarov investigated preferred orientations in electro-deposited metals and reported that the orientation axes of metals can be predicted by overpotential, which is the potential difference between a half-reaction's thermodynamically-determined reduction potential and the experimentally-observed potential [14]. From Pangarov's theory, there is a possibility of a change in the overpotential due to the hybridization in the liquid parts.

From this study, we found that ferromagnetic Ni films could be obtained from a hybrid plating bath and concluded that further investigations of the reduction process of Ni ions on the substrate in the hybrid baths are important for us.

4. Conclusions

The present study investigates solid/liquid hybrid electroplating for magnetic Ni films. The results are summarized as follows.

(1) In single baths (liquid-only and gel-only baths), the plate film's weight increased linearly with an increase in the plating time up to 10 minutes. For gel plating, a plating time exceeding 10 minutes tended to decompose the gel electrolyte, as we consider that the decomposition is attributed to the rising bath temperature generated by the current during plating (Joule heating).

(2) The hysteresis loops of the films prepared from the single baths were almost the same.

(3) In a hybrid bath, slight differences in the saturation magnetic moment were observed compared to the expected values from the result for single baths. The differences suggest that the hybridization of the baths affects the plating process, and further investigation is needed.

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