Effect of Initial Ni Plating on the Structure and Hardness of Electrodeposited Ni–W Alloys with and without Annealing

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Ni–W alloys were electrodeposited onto steel sheets with an initial Ni plating. The electrodeposition was conducted in unagitated sulfate solution containing citric acid at pH 5 and 60°C under coulostatic (9.0 × 10^4 C·m⁻²) and galvanostatic (100–5 000 A·m⁻²) conditions. The effect of the initial Ni plating on the structure and hardness of the deposited Ni–W alloys was investigated before and after annealing. At all current densities and in the presence and absence of the Ni plating, Ni₄W and NiW were precipitated in the annealed deposits. Without initial Ni plating, the Ni in the deposits diffused into the steel substrate during annealing, increasing the W content near the steel substrate. Consequently, many large precipitates were found in that vicinity. With initial Ni plating, the Ni in the plating diffused into the Ni–W deposits during annealing, and the W content of the deposits decreased around the plated Ni. The precipitates in the Ni–W deposits with initial Ni plating were finer than those without initial Ni plating. Before annealing, the W content in the deposits was lower in the initially Ni-plated sheet than in the unplated sheet. During annealing, Ni diffused from the plated Ni to the Ni–W deposits, apparently repressing the formation of large Ni₄W and NiW precipitates. The fine, uniformly deposited Ni₄W and NiW precipitates increased the hardness of the deposited Ni–W alloys after annealing.

KEY WORDS: electrodeposition; Ni–W alloy; deposits; structure; hardness; annealing; Ni plating; precipitate.

1. Introduction

Nickel-plated steel sheets, which constitute battery cases and numerous other items, are likely to seize the plated layers and dies during press working. When hard Ni–W alloys with excellent abrasion resistance¹²) are coated onto Ni-plated steel sheets, steel sheet seizure is unlikely, and excellent consecutive press formability can be achieved. Annealing increases the hardness of the deposited Ni–W alloys, but the hardening mechanism is not clearly understood.³–⁸) Previously, we investigated the effect of annealing on the structure and hardness of deposited Ni–W alloys, and reported that the hardness increased regardless of alloy composition and the degree of increase particularly enhanced at W contents above 40 mass%.⁹) Moreover, the alloy composition that significantly changed the hardness also changed the structure of the deposits.⁹) To simplify the system, we previously deposited Ni–W alloys directly onto steel sheets without an initial Ni plating, and investigated the hardness and texture of the products. As the second step, the initial Ni plating was performed on steel sheets in the present study, and subsequently, we deposit the Ni–W alloys. The hardness and structure are investigated in annealed and non-annealed sheets.

2. Experimental

Prior to Ni–W alloy deposition, the steel sheets were Ni-plated under the conditions in Table 1. As the electrolytic solution, fixed amounts of high-grade NiSO₄·6H₂O...
(0.91 mol/L), NiCl₂·6H₂O (0.19 mol/L), and H₂BO₃ (0.49 mol/L) were dissolved in distilled deionized water. The pH was adjusted to 4.2 with sodium hydroxide. Electrodeposition was performed in unagitated solution under galvanostatic (500 A/m²) and coulostatic (3 × 10⁵ C/m²; target thickness = 4 μm) conditions at 40°C. The cathode and anode were composed of steel and nickel sheets, respectively (both of dimensions 3 × 3 cm²). After the initial Ni plating process, the steel sheets were washed with water and dried, and the Ni–W alloys were subsequently electrodeposited. The solution composition and electrolysis conditions of the electrodeposition are given in Table 2. To prepare this electrolytic solution, fixed amounts of high-grade Na₂WO₄·2H₂O (0.2 mol/L), NiSO₄·6H₂O (0.2 mol/L), C₆H₈O₇·2NH₃ (0.45 mol/L), and HCOONa (0.2 mol/L) were dissolved in distilled deionized water. The pH was adjusted to 5 with sulfuric acid. Electrodeposition was performed in unagitated solutions under galvanostatic (100–5 000 A/m²) and coulostatic (9 × 10⁵ C/m²; target thickness = 5 μm) conditions at 60°C. The anode substrates were (3 × 3) cm² stainless steel sheets (SUS304). The deposited films were experimentally quantified by dissolution. For this purpose, the Ni–W alloys were deposited directly onto the steel sheets without initial Ni plating, and the deposits were dissolved from the cathode using a mixture of nitric acid and hydrogen fluoride (HNO₃/HF = 1/1). The Ni and W contents were quantified by inductively coupled plasma spectrometry (ICP).

For annealing, the deposited Ni–W alloys were maintained at 700 ± 5°C for 15 min in an N₂ atmosphere, cooled to 200°C for 5 min and removed into air. The deposited Ni–W alloy structure was examined by X-ray diffraction. The Ni crystallite size in the deposits was calculated by Scherrer’s equation, using the half-width of the X-ray diffraction peak of the 111 reflection. The surfaces and cross-sectional morphologies of the deposits were determined from the secondary electron images and the backscattered electron images of a scanning electron microscopy (SEM) operated under an ultra-low accelerating voltage. The backscattered electron images were obtained by the EsB (Energy Selective Backscatter Electron Detector) and AsB (Angle Selective Backscattered Electron Detector). The hardness of the deposited Ni–W alloys was measured by nanoindentation on the surface and cross-section. The surface and cross-sectional hardness values were measured at > 30 points under a 10 mN load and at > 10 points under a 5 mN load, respectively. Both hardness values were obtained with 500 partitions and a step interval of 20 ms.

### Table 2. Solution composition and electrolysis conditions of Ni–W alloy deposition.

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Na₂WO₄·2H₂O (mol/L)</th>
<th>NiSO₄·6H₂O (mol/L)</th>
<th>C₆H₈O₇·2NH₃ (mol/L)</th>
<th>HCOONa (mol/L)</th>
<th>pH</th>
<th>Current density (A/m²)</th>
<th>Amount of charge (C/m²)</th>
<th>Temperature (°C)</th>
<th>Cathode</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating conditions</td>
<td>0.2</td>
<td>0.2</td>
<td>0.45</td>
<td>0.2</td>
<td>5</td>
<td>100–5 000</td>
<td>9.0 × 10⁵</td>
<td>60</td>
<td>Fe (3×3 cm²)</td>
<td>SUS304 (3×3 cm²)</td>
</tr>
</tbody>
</table>

3. Results

#### 3.1. Effect of Initial Ni Plating on the Structure of Deposited Ni–W Alloys

Figure 1 shows the X-ray diffraction patterns of the pre-annealed Ni–W alloys with various compositions deposited at each current density with and without initial Ni plating. Under 100, 200, 500, 1 000, and 3 000 A/m², the W contents in the deposits were 32.6, 37.1, 40.7, 45.2, and 44.9 mass%, respectively. Before annealing, the initial Ni plating scarcely affected the X-ray diffraction patterns. In both Ni-plated and
unplated samples, the diffraction patterns of the deposited Ni–W alloys revealed a single Ni phase, indicating the formation of W solution in the Ni. As the current density increased, the W content in the deposits increased and the diffraction patterns broadened, implying a significant decrease in crystal grain size. At W contents exceeding 44.9 mass% and current densities exceeding 1 000 A/m², halo patterns appeared in the diffraction spectra, characterizing the alloys as amorphous structures.

Figure 2 shows the X-ray diffraction patterns of the post-annealed Ni–W alloys with various compositions deposited at each current density with and without initial Ni plating. After annealing, all of the Ni–W alloys, both Ni-plated and unplated, and including those showing halo patterns before annealing, displayed sharp peaks of Ni. However, the unplated alloys deposited at 100 and 200 A/m² presented Ni₄W peaks, whereas those deposited at 500 to 3 000 A/m² presented peaks of Ni₅W and Ni₆W. In alloys initially plated with Ni, the Ni₄W peaks were attenuated and the Ni₆W peak was scarcely detected, except at 3 000 A/m². According to the equilibrium phase diagram of the Ni–W binary system,¹¹) Ni₄W and Ni₆W are the stable phases at W contents of 40.7–42.7 and 75.3–75.8 mass%, respectively. Therefore, in this study, the metallic compounds precipitated by annealing are expected from the equilibrium phase diagram of the Ni–W binary system, but Ni₅W and Ni₆W precipitation was suppressed by the initial Ni plating.

As shown in Figs. 1 and 2, the diffraction peaks shifted toward low diffraction angles as the W content increased in the deposits. The lattice constants of Ni were calculated from the shift of the main diffraction peak, corresponding to the shift of the 111 reflection of Ni to a lower angle. Figure 3 plots the lattice constant of Ni as a function of W content in the deposits. In the pre-annealed sample without initial Ni plating, the Ni lattice constant linearly increased with W content up to 40.7 mass%, consistent with Vegard’s law¹²) and with a previous study of Ni–W alloy deposited from ammoniacal citrate solution.¹³) In that study, the Ni lattice constant linearly increased with W content up to 36.7 mass%. At room temperature, the solid solubility limit of W in Ni is approximately 31 mass%,¹¹) lower than observed in the present study. The excess solution of W in Ni is attributed to the nonequilibrium phase formed by the electrodeposition. After annealing, the solution amount of W in Ni irregularly decreased as the Ni₅W and Ni₆W precipitated, disrupting the linear relationship between the Ni lattice constant and W contents in the deposits. The Ni lattice constants were smaller in the initially Ni-plated alloys than in the unplated samples (except at W contents approaching 45 mass%), and were further decreased by annealing. As indicated in Fig. 3, the W content in the deposits was smaller in the initially Ni-plated alloys than in the unplated samples. Furthermore, annealing should decrease the W content in the Ni solid solution, because it precipitates Ni₆W.

Figure 4 shows the relationship between the current density and the Ni crystallite size before and after annealing the
Ni–W alloys deposited at various current densities with and without initial Ni plating. Initial Ni plating scarcely affected the crystallite size of the Ni in the pre- and post-annealed deposits. In the pre-annealed samples, the Ni crystallite size decreased with increasing current density. The annealing process increased the Ni crystallite size of the deposits at all current densities.

3.2. Effect of Initial Ni Plating on the Morphology of Deposited Ni–W Alloys

Figure 5 shows the secondary electron images of the pre-annealed Ni–W alloy surfaces with various compositions deposited at each current density with and without initial Ni plating. Exposed edges of platelet crystals appeared in the deposits on the unplated samples obtained at 100 and 200 A/m². The boundaries between these platelet crystals were occupied by small granular crystals. At current densities exceeding 500 A/m², the platelet crystals disappeared, and the deposits were completely composed of small granular crystals, yielding a smooth surface. The morphologies of the deposits on the Ni-plated surfaces were similar to those on the unplated surfaces at 100 and 200 A/m², but significant differences were observed at 500 A/m². At this current density, the deposits on the Ni-plated surfaces assembled into small platelet crystals. At 1 000 and 3 000 A/m², the morphology of Ni–W deposits on the Ni-plated surfaces altered to small granular crystals and a smooth surface, as observed on the surface without initial Ni plating. However, on the Ni-plated surface, the granular crystals obtained at 1 000 and 3 000 A/m² were clustered into aggregates of size 1–2 μm, which was larger than that without initial Ni plating.

Figure 6 shows the backscattered electron images of the cross-sections of pre-annealed Ni–W alloys with various compositions, deposited at each current density with and without initial Ni plating. On the unplated surfaces obtained at 100 and 200 A/m², the deposits exhibit a columnar texture, presumably a field-oriented texture, in which specific planes preferentially orient toward the electric field during deposition. At higher current densities (500–3 000 A/m²), the deposits formed a layered texture. On the Ni-plated surfaces, the deposit morphologies were similar to those on the unplated surfaces at 100 and 200 A/m², but were columnar and layered at current densities of 500 A/m² and above 1 000 A/m², respectively. Thus, the initial Ni plating shifted the texture of the deposits toward layering at higher current densities. According to an EBSD orientation analysis of Ni, the layered deposits were composed of fine crystals. The layered texture might result from the fluctuating concentrations of W and Ni ions in the cathode vicinity during deposition. To test this idea, we analyzed the deposition behavior. Figure 7 plots the total current density versus the partial current densities of Ni and W during the Ni–W alloy deposition. Here, the total current density is the sum of the partial current densities of Ni and W deposition and hydrogen evolution. The total current density is a nonlinear function of the partial current density, indicating that the deposition rate is controlled by ion diffusion. The partial current density of W deviates from linearity at lower current density than the partial current density of Ni, suggesting that W ions are more diffusion-limited than Ni ions. Therefore, the layered texture of the deposits is attributed to fluctuating W ion concentration around the cathode. On the unplated
surfaces, the deposits developed a layered structure at lower current density, suggesting that the W ion concentration fluctuates more readily on these surfaces.

Figure 8 shows the secondary and backscattered electron images of the annealed Ni–W alloy surfaces with various compositions deposited at each current density with and without initial Ni plating. On the unplated surface, the platelet crystals deposited at 100 and 200 A/m² were decomposed into granular crystals, whereas at current densities exceeding 500 A/m², the deposits formed a smooth surface of fine granular crystals. As revealed in the backscattered electron images, W precipitates were present in all deposits, and their prevalence increased with current density. On the other hand, the deposits on the Ni-plated surfaces formed platelet crystals (in part) at 100 and 200 A/m², and large granular crystals at 500 A/m². When the current density increased to 1 000 and 3 000 A/m², a smooth layer of fine granular crystals was deposited. The backscattered electron images show similar tendencies in the Ni-plated and unplated cases. That is, all deposits under the various current densities comprised Ni₄W and NiW precipitates, whose density increased with current density. The surface morphologies of deposits on the Ni-plated and unplated surfaces differed under current densities of 500 A/m² or less. At 1 000 and 3 000 A/m², these differences appear to arise from differences in the pre-annealed surface morphology, as shown in Fig. 5. Generally, the precipitation after annealing was reduced on the Ni-plated surface.

Figure 9 shows the backscattered electron images of the cross-sections of annealed Ni–W alloys with various compositions deposited at each current density with and without initial Ni plating. Granular precipitates were formed under all current densities, but were smaller (in both size and amount) on the Ni-plated surfaces than on the unplated surfaces. At 3 000 A/m², the precipitates in the deposits concentrated around the steel substrate in the unplated sample, but formed in the upper region of the deposits on the Ni-plated sample.

### 3.3. Effect of Initial Ni Plating on the Hardness of Deposited Ni–W Alloys

Figure 10 shows the hardness of the Ni–W alloy surface with various compositions deposited at each current density with and without initial Ni plating. The initial Ni plating scarcely affected the hardness of the pre-annealed Ni–W alloys, except at 500 A/m². At this current density, the deposit was harder on the unplated surface than on the Ni-plated surface. This result corresponds to the deposit mor-
phologies shown in Figs. 5 and 6. On the unplated surface, the deposits exhibit a smooth surface with a layered texture; on the Ni-plated surface, they form a columnar structure of fine platelet crystals. These morphologies seem to affect the hardness of the deposits. The hardness was increased by annealing, regardless of initial Ni plating and current density. After annealing, the deposit obtained at 500 A/m² was harder on the unplated surface than on the Ni-plated surface, whereas the reverse was observed at 1000 and 3000 A/m².

Figure 11 shows the cross-sectional hardness of the Ni–W alloys with various compositions deposited at current densities of 500, 1000, and 3000 A/m² with and

Fig. 8. Secondary and backscattered electron images of annealed Ni–W alloys deposited on Ni-plated and non-plated substrates at various current densities.

Fig. 9. SEM-AsB images of annealed Ni–W alloys deposited on Ni-plated and non-plated substrates at various current densities.
without initial Ni plating. This hardness was measured at the central area in the thickness direction of the deposits. The cross-sectional hardness of the pre-annealed samples was almost unaffected by initial Ni plating. After annealing, the cross-sectional hardness values reflected the surface hardness values.

4. Discussion

Initial Ni plating suppressed the precipitation of Ni₄W and NiW during annealing. We attribute this suppression to (1) the decreased W content in deposits on the Ni-plated surface, and (2) diffusion of Ni from the Ni-plated surface into the deposits during annealing. Regarding (1), the W content of deposits on the Ni-plated surface cannot be measured by ICP. Therefore, we performed an EDX spot analysis at the central cross-sectional area in the thickness direction of the deposits. As presented in Fig. 12, the X-ray intensity ratio of W to Ni in the deposits was smaller on the Ni-plated surface than on the unplated surface. Figure 13 shows SEM images of the surface morphologies of Ni-plated and unplated steel substrates. The surface roughness was larger on the plated Ni than on the steel substrate. The surface roughness Ra of the steel substrate and Ni-plated surface was 0.040 μm and 0.062 μm, respectively. Therefore, the true current density of deposition should be smaller on the Ni-plated surface than on the steel substrate. Below 1000 A/m², the W content in deposited Ni-W alloys reportedly increases with current density,9) suggesting that the W content in the deposits is reduced on the Ni-plated surface. Thus, the overpotential of W and Ni in alloy deposition should be substrate-dependent. Specifically, the overpotential for Ni deposition is assumed to be smaller on the plated Ni than on the steel substrate. The significant morphological differences in the cross sections of deposits on Ni-plated and unplated surfaces, obtained at 500 A/m² before annealing, can be explained by the lower W content of the deposits on the Ni-plated surface. The texture of the deposits on the
unplated surface shifted to a layered type from 500 A/m², probably because the W ion concentration in the cathode vicinity easily fluctuated under the high W content in the deposits. On the Ni-plated surface, the deposited granular crystals aggregated into 1–2-μm clusters at 1 000 and 3 000 A/m² (see Fig. 5). The cluster size corresponded to the concavities and convexities of the Ni-plated surface (see Fig. 13). This indicates that the morphology of the initially plated Ni influences the clustering phenomenon.

To confirm that Ni diffused from the Ni-plated surface into the deposited Ni–W alloy during annealing, the Ni–W alloy deposited at 3 000 A/m² was annealed at 700°C for 100 seconds. The cross section of the deposit was then analyzed by EDX. Figure 14 shows the X-ray intensity ratios of W, Ni, and Fe in deposits on the Ni-plated and unplated surfaces. According to the linear EDX analysis, Ni and W were uniformly co-deposited in the thickness direction prior to annealing. By contrast, after annealing, the Ni of Ni–W alloy deposited on unplated surfaces diffused into the steel substrate, increasing the W/Ni ratio in the vicinity of the steel substrate. Consequently, significant Ni₄W and NiW precipitation occurred near the steel substrate (see Fig. 9). Conversely, on the Ni-plated surface, Ni was concentrated in the upper region of the deposited Ni–W alloy, indicating that Ni diffused from the Ni-plated surface into the Ni–W alloys. This diffusion reduced the W content in the deposits, suppressing the Ni₄W and NiW precipitation. Therefore, the initial Ni plating shifted the precipitation to the upper parts of the deposits, removing it from the substrate vicinity.

The initial Ni plating reduced the post-annealing hardness of Ni–W alloys deposited at 500 A/m², but increased the hardness of alloys deposited at 1 000 and 3 000 A/m². To elucidate the reason for this trend, we measured the cross-sectional hardness of the post-annealed deposits at 3 000 A/m² on the Ni-plated surface along the thickness direction. The results are plotted in Fig. 15. The deposits were uniformly hard from the steel substrate vicinity to the...
center, but the hardness reduced in the upper regions of the deposits. As shown in Fig. 9, the precipitates deposited on the Ni-plated surface at 3 000 A/m² were small (<10 nm) from the steel substrate to the center, and large (> 100 nm) in the higher regions. Therefore, the hardness of the deposit depends on the size and distribution of the precipitates. The smaller precipitates increase the hardness because they are uniformly distributed. At 500 A/m², the deposited precipitates were smaller on the unplated than on the Ni-plated surfaces. Conversely, at 1 000 and 3 000 A/m², the precipitates were smaller on the Ni-plated surface throughout the whole thickness and from the steel substrate to the central thickness, respectively. These results are consistent with the negative relationship between hardness and precipitate size. As mentioned above, the morphology of the deposits obtained at 500 A/m² differed on the Ni-plated and unplated surfaces. At 500 A/m², columnar-textured deposits formed on the Ni-plated surface, whereas fine crystals were deposited on the unplated surface. The precipitates were smaller (< 10 nm) in the layered texture than in the columnar texture. We conclude that the hardness of the deposited Ni–W alloys after annealing increases when the Ni₄W and NiW precipitates are smaller than 10 nm and uniformly distributed through the deposit.

5. Conclusion

The effect of initial Ni plating on the structure and hardness of deposited Ni–W alloys was investigated before and after annealing. On both steel substrate and Ni-plated steel, Ni₄W and NiW precipitates were identified in the deposits, which were obtained at various current densities after annealing. On the unplated surface, large precipitates formed in the vicinity of the steel substrate; on the Ni-plated surface, these precipitates were smaller. Without the initial Ni plating, the W content in the deposited Ni–W alloys increased near the steel substrate after annealing, because Ni diffused from the Ni–W alloys to the steel substrate. Conversely, the W content of the deposits was reduced on the Ni-plated surface, because Ni diffused from the Ni-plated surface into the Ni–W alloys. Prior to annealing, the deposited W content was lower on the Ni-plated surface than on the unplated surface. The increased W content and Ni diffusion from the Ni-plated surface into the alloys suppressed the W precipitation. After annealing, the hardness of the deposited Ni–W alloys increased under conditions of small (<10 nm) and uniformly distributed Ni₄W and NiW precipitates.

REFERENCES