Texture and Corrosion Behavior of Thin Nickel Sheet Formed by Pulse Plating and Cold Rolling

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Thin nickel sheets were fabricated by electroforming, and cold rolled to improve their strength. The thin nickel sheets have very fine grains with a {001} (uvw) fiber texture. Cold rolling results in evolving a {001} (110) orientation and the formation of a weak {111} (uvw) fiber component. Micro-hardness of the nickel sheet on the normal direction (ND) was increased from 247.8 to 354.4 Hv by cold rolling with 87.5% reduction. The corrosion potential and corrosion rate of the nickel sheet in artificial sea water were in the ranges of −27 to −12 mV SCE and 4.2 × 10⁻² to 1.8 × 10⁻⁴ A cm⁻², respectively. The change in corrosion behavior with cold rolling on the surface normal to ND has little relation to crystallographic texture because of a stable {001} texture during rolling, unlike nickel bulk samples.

Table 1 Solution composition of a modified nickel-sulfate bath, C (mass %).

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Ni(SO₄)₂</td>
<td>79.0</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>4.0</td>
</tr>
<tr>
<td>H₂BO₃</td>
<td>8.0</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1.0</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>0.8</td>
</tr>
<tr>
<td>C₂H₇NO₃S</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Table 2 Cold rolling conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feeding number</th>
<th>Reduction in thickness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NB-2</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>NB-3</td>
<td>3</td>
<td>70</td>
</tr>
</tbody>
</table>

1. Introduction

Electroformed nickel sheet is a useful material in the electronic and information display industries for its high electro-magnetic properties.¹ There are several methods to improve its physical and chemical properties.²⁻³ Since pure metallic sheets prepared by electroforming usually have columnar grain structure, the application of high potential with ultrasonic agitation and controlling the pH tend to decrease the columnar grain size.⁴⁻⁶ Co-deposition with nano-sized ferrite particles and multi-layered deposition were developed to improve the electromagnetic properties of the material.⁷ Electroformed nickel sheets have a columnar-like orientation along the electric field during the electroforming process. Their crystallographic orientation is dependent upon the electroplating conditions, such as current wave form and bath solution.⁸⁻¹⁰ Additional plastic deformation also produces a crystallographic texture in the electroformed nickel sheet that improves the anisotropic properties. Although there have been many studies to improve the strength and electromagnetic properties of electroformed nickel sheets, little information is available to study the effect of crystallographic texture on the corrosion behavior of the electroformed sheet.¹¹,¹² Hence, the objectives of this study are to prepare nickel sheet by electroforming, to control the crystallographic texture by cold rolling and to discuss its effect on corrosion behaviors.

2. Experimental Method

2.1 Preparation of thin nickel sheet

Electroforming was carried out in a rotating aluminum drum cell set in a modified nickel-sulfate bath. The aluminum drum was rotated at a speed of 0.0167 mm·s⁻¹ by a motor in the modified nickel-sulfate bath at 45–55°C and a pH of 4.8 ± 0.1. A pulse current density of 7–10 mA·dm⁻² was supplied by a regulator (Jisan 400, Korea), with on and off times of 100 and 0.1 ms, respectively. The electroformed nickel strip was separated from a cathode using a doctor blade. The anode and the cathode used were a titanium electrode and 316 stainless steel, respectively. Table 1 shows the solution composition of the modified nickel-sulfate bath.

2.2 Characterization

Microstructural observation of the products was performed by scanning electron microscopy (SEM; JEOL JSM 6400, Japan) and transmission electron microscopy (TEM; JEOL JTM 2010-H, Japan), and chemical analysis was done using energy-dispersive spectroscopy (EDX, Oxford, UK). The TEM specimen was prepared by twin-jet polishing (Struers Tenupol-3, UK). The nickel strip was cold-rolled (M-tek, Korea) without lubricant to control microstructure and crystallographic texture. Table 2 is the cold rolling conditions. Crystallographic texture was determined by X-ray diffractometry (Bruker D8 Discover, Germany). The specimen used for texture analysis was prepared into longitudinally sectioned pieces. The pieces 15 mm in length and 10 mm in width were cold-mounted and polished using 0.3 µm diamond paste followed by electrochemical polishing.

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Micro-hardness was determined by a Vickers micro-hardness tester (Buehler micro-Vickers 5100, USA). A corrosion test was carried out by a potentiodynamic method (Gammy CMS 100, USA) in artificial seawater (ASTM D 1180) (pH = 6.3) at 25°C.

3. Results and Discussion

3.1 Electroplating and microstructure

Figure 1 shows a transmission electron microscope (TEM) image and selected area diffraction (SAD) pattern of the electroformed nickel foil. As shown in the TEM image in Fig. 1, it is difficult to find any particles or precipitates. The SAD pattern shows that the matrix has very fine crystalline grains. Although the electroformed nickel sheet has very fine grain structure, it is hard to find inner cracks by TEM. In order to confirm the inner micro-structure before cold rolling for texture analysis, small angle neutron scattering was applied to analyze the structure. Figure 2 shows small angle neutron scattering spectra of electroformed nickel layer. The SANS spectra confirmed that the materials are homogeneous and that there are no nano-sized defects. Accordingly, the electroformed nickel is a very fine-crystalline solid.

3.2 Crystallographic texture

In order to increase the anisotropic qualities and the hardness of the material, the electroformed nickel sheet was cold rolled. Figure 3 shows the microstructure of the cross-sectional surface of the rolled nickel sheets observed by scanning electron microscopy, in which it is difficult to find inner cracks, which may sometimes be introduced by cold rolling.

Figure 4 shows the crystallographic texture of the cold rolled nickel sheet. In this study, three different pole figures of {100}, {110} and {111} were determined, in which RD, TD and ND stand for rolling, transverse, and sample normal directions, respectively. Figure 4(a) shows the reconstructed pole figures from the orientation distribution function (ODF) of the as-received nickel sheet. As shown in Fig. 4(a), the {100} pole clearly concentrates to ND and the {110} and {111} poles exhibit a ring-shaped fiber texture at angles of approximately 45 and 55°, respectively, from the center of pole figure i.e., the {100} (or ⟨100⟩//ND) fiber texture. This kind of preferred orientation of the crystals is related to the electroforming conditions.\(^{10}\) It is known that the electro-crystallization of nickel tends to be a highly inhibited process, because chemical species with hydrogen, like nickel hydroxide, that are observed on the deposition surface inhibit crystal growth and determine the crystallographic texture. Nickel electroformed by pulse-plating has {100} texture of the nickel deposit due to the on-off time of the pulse current. Accordingly, electroforming by pulse current in this study results in producing the {100} fiber texture with {100} planes perpendicular to ND in the nickel sheet. Figures 4(b) and 4(c) are the reconstructed pole figures from the ODF of cold rolled nickel sheets. The sheets with 40 and 70% rolling reduction tend to form a strong ND-rotated cube texture of {100}⟨011⟩, because the {100} pole shows four peaks at an angle of about 45° between RD and TD on the outer circle.
of the pole figure, and this texture is clearly recognized in the \{110\} and \{111\} pole figures as well. This may be related to the friction generated during rolling and the microstructure with \{100\} fiber texture. If the strain state during cold rolling is plane strain compression, the \{100\} \{011\} orientation will be unstable, because crystal rotation toward stable orientations such as Copper orientation \{112\} \{111\}, S orientation \{123\} \{634\} and Brass orientation \{011\} \{211\} by cold rolling takes place easily by slip deformation. The friction from rolls probably leads to additional shear deformation, which can stabilize the \{100\} \{011\} orientation. In addition, the initial strong \{100\} fiber texture of nano-sized columnar grains may inhibit the evolution of a conventional rolling texture consisting mainly of Copper, S and Brass orientations due to the restriction of glides at many of the grain boundaries, i.e., the very short glides in the grain interior.

Since the pole figures are only qualitative representations of the texture, the ODF of the nickel sheet should be used to quantitatively analyze the change in crystallographic texture with rolling. Figure 5 shows the ODFs of the sheets in the form of Euler plots at 5° intervals of $\Phi_2$. The intensity peaks are referred to in the Euler plots, where the intensity of random orientation is unity. From the existence of an orientation tube along the $\Phi = 0^\circ$ line in each $\Phi_2$ section, a well-developed \{001\}(uv0) fiber texture can be confirmed in the ODFs of all samples. However, these ODFs clearly show that the position of the maximum orientation density varies from \{001\} \{210\} to \{001\} \{110\} with an increase of rolling reduction. As a preferred orientation other than the \{001\}(uv0) fiber component, a weak \{111\}(uvw) fiber component along the $\Phi = 55^\circ$ line in the $\Phi_2 = 45^\circ$ section is observed in the ODF of a 70% cold-rolled sample. Gradual evolution of the \{111\}(uvw) fiber component as well as significant evolution of the \{001\} \{110\} texture during cold rolling of the electroformed nickel sheet may result from the additional shear deformation by friction from rolls and the restricted glides in the grain interior due to nano-sized columnar grains.\(^{13}\) There is a possibility that the \{111\}(uvw) fiber texture component develops, especially the \{111\} \{110\} shear texture component, by heavier cold-rolling together with \{001\} \{110\} shear texture component, if the friction from rolls, which produces shear deformation in the nickel sheet, is relatively high.

### 3.3 Corrosion behavior

Since the corrosion behavior significantly depends on the surface conditions, anisotropic corrosion behavior can be expected after cold rolling.\(^{14}\) Artificial sea water tends to make pits on nickel surfaces. The relationships between pitting corrosion and crystallographic texture can be divided

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**Fig. 4** (100), (110), (111) pole figures of electroformed nickel sheets with cold rolling: (a) as-received, (b) 40% and (c) 70% reduction.

**Fig. 5** ODFs of electroformed nickel sheets with cold rolling: (a) as-received, (b) 40% and (c) 70% reduction.
into pitting nucleation and pit propagation. In case of nickel, susceptibility to pit nucleation in chloride is related to misorientation of the oxide with substrates, so that oxide breakdown rate on the [111] surface is slower than any other low index planes. Besides, pitting potentials of FCC single crystals like aluminum decrease in the order of [001] > [011] > [111]. Although a common explanation for preferentially oriented pit propagation is surface energy described by dangling bonds at a free surface, the concept of the surface energy needs to be modified to sufficiently describe the pit propagation. In this study, the micro-hardness of the electroformed nickel was determined on the surface normal to ND. The hardness was changed from 247.8 Hv for the as-received sample to 303.4 Hv by 40% cold rolling. As the second factor, it could be possible that the change of preferred orientation due to cold rolling more or less influences the corrosion behaviors. Considering the number of atoms in a unit area for the [100], [110] and [111] planes parallel to the rolling plane, the atomic densities of the [100], [110] and [111] planes in the face-centered cubic lattice are 0.785, 0.555 and 0.907, respectively. The initial texture before cold rolling consisted of the [001]uvw fiber component, while the cold rolling texture exhibited a strong [001] fiber texture with the maximum peak at [001]110 and a weak [111] fiber texture. The formation of [111] fiber texture is expected to lead to improvement in the corrosion rate in terms of the atomic density, but the experimental result does not correspond to the expectation. It may be necessary to evaluate corrosion behavior on surfaces other than the surface normal to ND, because the surfaces normal to RD or TD of the cold-rolled sample have somewhat different orientations from that of the as-received sample. This will be examined in future.

4. Conclusions

(1) Electroformed nickel sheet was prepared in a modified nickel-sulfate solution by pulse plating, and consisted of very fine crystalline grains without nano-sized defects.

(2) Electroformed nickel sheet has a [001]uvw fiber texture of the nickel deposit due to the on-off time of the pulse current. Subsequent cold rolling tends to form a strong [001]110 texture and a weak [111]uvw fiber component.

(3) The corrosion behavior of the electroformed nickel sheet in artificial sea water at 25°C does not show passivity. The corrosion potential and corrosion rate of the surface normal to ND were in the ranges of −27 to −12 mV_{SCE} and 4.2 × 10^{-7} to 1.8 × 10^{-6} A cm^{-2}, respectively. The cold rolling tends to decrease the corrosion potential, but increase the corrosion rate of the electroformed nickel sheet.

(4) Unlike nickel bulk samples, the stable [001] orientation of pulse-electroformed nickel sheet was hardly changed during cold rolling, so that the [001] texture as well as the grain shape on the surface normal to ND has less effect on the corrosion behavior than lattice defects and residual stress, which increase the corrosion rate.

REFERENCES