Local Atomic Structure and Catalytic Activities in Electrodeposited Mo–Ni Alloys

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The atomic structures of Mo–Ni alloys electrodeposited from aqueous solutions containing various molybdenum and nickel concentrations were studied by X-ray diffraction. The films are arranged with respect to molybdenum concentrations in the films. That is, the Group I (Mo < 10%), the Group II (20% < Mo < 30%) and the Group III (Mo ≈ 40%). In the Group I, the structures of the films are fcc crystals of nickel solid solutions. The films in the Groups II and III are amorphous. The hydrogen evolution as an electrode in alkaline water electric cell was also compared. At about 20% molybdenum, the nickel film shows the maximum hydrogen evolution.

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1. Introduction

Electrodeposited molybdenum alloy films provide us some attractive physical and chemical properties, such as hardness, corrosion-resistance and catalytic activities of hydrogen evolution from alkaline-water electric cells. Pure metallic molybdenum is not electrodeposited from aqueous solution. Only molybdenum alloys are electrodeposited from a solution containing iron-group metallic ions. This phenomenon is called as “induced codeposition”. Its mechanism was studied by some workers. Recently, Shinoda et al. studied the atomic structure of molybdenum ions in solutions by the anomalous X-ray scattering (AXS) method. This indicates that atomic structures of polymolybdate ions in electroplating bath change as a function of concentrations of complex forming reagents and the molybdenum alloy is electrodeposited only in a solution containing polymolybdate ions with a certain atomic structure. Furthermore, they suggested that electrodeposition of nickel is essential to electrodeposition of molybdenum. Therefore, we electrodeposited molybdenum–nickel alloys by varying the ratios of molar fractions of molybdenum ions to nickel ions in solutions from 0.005 to 50. The concentrations of these films and their atomic structures were compared. Furthermore, their catalytic activities for hydrogen evolution from alkaline-water electric cells were compared when they are used as an electrode.

2. Experimental

Molybdenum and nickel aqueous solutions in Table 1 were prepared from the prime class reagents of Nickel sulfate (NiSO₄·6H₂O), sodium molybdate (Na₂MoO₄·2H₂O), citric acid monohydrate (C₆H₈O₇·H₂O, expressed as H₃Cit) and sodium sulfate (Na₂SO₄) (Wako Chemical Co. Ltd, Japan). Every solution contains 0.5 mol/dm³ Na₂SO₄ as an electrolyte and pH buffer, and the pH-value of 5 is maintained by using diluted HCl or NaOH aqueous solution. A concentration of citric acid in every solution that forms a certain nickel citrate complex (NiCit⁻; Cit⁻ = C₆H₇O₇⁻) was calculated from the experimentally determined complex forming constants. The sample solutions were settled down for one day at room temperature in tightly sealed glass vessels. Nickel-citrate and molybdenum-citrate complexes in the solutions were checked by the UV-Visible absorption spectra.

Molybdenum and nickel alloys were electrodeposited on a well-polished OFHC (oxygen-free high-conductivity) Cu electrode of 15 by 18 mm² under the potential-static condition at −1.10 V vs. SHE for 120 s. The atomic structures were determined by X-ray diffraction with Mo Kα radiation and the atomic concentrations were analyzed by X-ray fluorescence (XRF) analyses. The chemical states of Mo and Ni in the films were also analyzed by X-ray photon spectroscopy (XPS). The surface morphology was observed by scanning electron microscopy (SEM).

<table>
<thead>
<tr>
<th>Sample solutions</th>
<th>Na₂MoO₄·2H₂O [mol/dm³]</th>
<th>NiSO₄·6H₂O [mol/dm³]</th>
<th>Citric acid [mol/dm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0005</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.001</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>0.002</td>
<td>0.1</td>
<td>0.102</td>
</tr>
<tr>
<td>4</td>
<td>0.005</td>
<td>0.1</td>
<td>0.105</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>0.1</td>
<td>0.11</td>
</tr>
<tr>
<td>6</td>
<td>0.02</td>
<td>0.1</td>
<td>0.12</td>
</tr>
<tr>
<td>7</td>
<td>0.05</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>8</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
<td>0.02</td>
<td>0.12</td>
</tr>
<tr>
<td>11</td>
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<td>0.01</td>
<td>0.11</td>
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<tr>
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<td>0.1</td>
<td>0.005</td>
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<tr>
<td>13</td>
<td>0.1</td>
<td>0.002</td>
<td>0.102</td>
</tr>
</tbody>
</table>
3. Results and Discussion

In the previous studies, the molybdenum and nickel alloys are electrodeposited from the solution containing 0.1 mol/dm$^3$ nickel and 0.2 mol/dm$^3$ citric acid. As mentioned above, the deposition of molybdenum is depended on that of nickel. Then, the concentration of each metal ion changed drastically in this experiment. In the series of the solutions 8 to 13, the nickel concentration decreases in the solution containing 0.1 mol/dm$^3$ molybdenum ions. In order to compare the solutions 8 to 13, the series of the solutions 1 to 8 were prepared. In these solutions, the concentration of molybdenum ions varies from 0.0005 to 0.1 mol/dm$^3$ while the concentration of nickel ions of 0.1 mol/dm$^3$ is maintained. The solution condition is summarized in Table 1. When preparing the electroplating bath for molybdenum and nickel alloys, decrease in the concentration of molybdenum ions and increase in that of nickel ions are unreasonable in the conventional sense, because nickel metal is easily electrodeposited in the aqueous solution and the molybdenum metal is not.

The good quality electrodeposited alloy films were obtained in the solutions 1 through 10. The SEM micrographs of the electrodeposited films in the solutions 8 and 2 are shown in Fig. 1. For the further discussion, they are simply called the films-A and -B, respectively. The film-A consists of very fine particles and forms a relatively flat surface. On the other hand, the film-B has a rough surface consisting of submicron-meter particles. Due to the difference of the surface morphology, the glossy silver-colored films were obtained from the solutions 4 to 10 and none glossy silver colored film was deposited in the solutions 1 to 3. With decrease in nickel concentrations of the solutions 11 and 12, electrodeposition of the alloy worsened and no electroplating was observed in the solution 13. This result strongly indicates that the molybdenum and nickel alloy is only electrodeposited under the condition that the nickel is electrodeposited. The current efficiency drastically decreases with Mo ion in the solution as shown in Fig. 2. Namely, the electrodeposition of nickel is extremely controlled in the solution containing a little amount of molybdenum ions. In the present study, the presence of 0.5% molybdenum ions relative to nickel ions is good enough to retain the decomposition of nickel on the Cu plate. This result brings us up a new problem of the induced decomposition of molybdenum and nickel alloys.

The XPS analysis of the film-A is shown in Fig. 3. It reveals that there are oxygen and carbon as well as molybdenum and nickel at the very most surface of the film. The peaks of molybdenum and nickel are small and broad at the surface. Especially the peak of nickel is much smaller than those of molybdenum. After sputtering some surface layers of the film, the sharp peaks of metallic molybdenum and nickel clearly appear and at the same time, the peaks of oxygen and carbon disappear. Except for the surface layer, the peak shapes and positions of molybdenum and nickel are not changed across the film. Thus, the electrodeposited film consists of metallic molybdenum and nickel. The similar results are obtained in the other films.

The compositions of the films determined by the XRF are summarized in Fig. 4. The molybdenum concentration increases with the ratios of Mo to Ni in the solutions and the...
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Fig. 3 XPS spectra of the Film-A. Vertical line shows the number of the sputtering times (10 sec, 12 times).

Fig. 4 Composition of Mo in the electrodeposited Mo–Ni alloy films.

Films deposited in the solutions 1 to 3, 4 to 10, and 11 to 12 are categorized to three groups with their compositions. The concentrations of molybdenum in the groups I, II and III correspond to less than 10%, 20 to 30%, and about 40%, respectively. In the molybdenum–nickel phase diagram, there are four different phases in the nickel-rich region, i.e. the nickel solid solution, Ni₂Mo, Ni₃Mo and NiMo. The solubility limit of molybdenum in the nickel solid solution is about 15% at room temperature and the Ni₂Mo and Ni₃Mo are the equilibrium phases in the system containing about 15 to 25% molybdenum. In the system containing more than 25% molybdenum, the Ni₃Mo and NiMo phases become thermally favorable. Since electrodeposition is not always satisfied with the thermal equilibrium, we only discuss in a qualitative manner. In the present study, the structural analysis of the films of group III has not been achieved because its thickness is extremely thin. Now we are carrying out the structural analysis of the films of group III by the grazing incident X-ray scattering method.

Atomic structures of the films A and B were determined by XRD. Intensity contribution from the Cu substrate in the film A is much larger than that in the film B because the thickness of the film is much thinner in the solutions containing the larger ratio of Mo to Ni. Intensity profiles corrected for scattering of the Cu substrate are shown in Fig. 5(a). The profile of the film A is a typical intensity profile of an amor-

Fig. 5 (a) XRD and (b) Radial distribution function (RDF) of (a) Film-A and (b) Film-B.
phous alloy and that of the film B consists of some diffraction peaks of fine crystalline particles. The radial distribution functions (RDFs) of the films A and B are also shown in Fig. 5(b). As it is expected from the intensity profiles in Fig. 5(a), the RDF of the film B is composed of some distinct peaks that are ascribed to Ni crystalline particles. On the other hand, that of the film A is a broad profile except for the first relatively sharp peak. The positions of Ni–Ni and Ni–Mo pairs that are calculated from the atomic radii of Mo (0.278 nm) and Ni (0.248 nm) are indicated in Fig. 5(b). From this figure we easily see that contribution from Ni–Mo pairs is larger in the film A than in the film B. This supports the result that the atomic structure of the film B is the nickel solid solution containing a few percents molybdenum.

Figure 6 shows the effect of the molybdenum composition on the hydrogen evolution from the alkaline-water electric cell. The amount of hydrogen gas increases with the molybdenum concentration within the group I (Mo < 10%), and it decreases for any further increase in the molybdenum concentration as seen in the group II range (20% < Mo < 30%). In the case of the molybdenum and nickel alloy electrodeposited in the solution 3, hydrogen gas is evolved about 10 times larger (c.a. \(6.0 \times 10^{-5}\) mol/hour/cm²) than in the case of the pure Ni film. In the present study, hydrogen gas evolution on the Ni–Mo electrode in alkaline water was investigated. It is well known that a hydroxide film is formed on the pure nickel surface. This prevents the formation of hydrogen gas. The present result, however, clearly shows that the alloying Ni with Mo changes the hydroxide film. The details of the modification of the surface structure of the alloy electrode have not been known. Thorough structural and electro chemical analysis are carrying out in the region of alloy concentrations from the sample No. 2 to No. 5. This will give us the further discussion on the role of Mo in their alloy electrodes.

Figure 7 shows the change of the potential with and without molybdenum in the film at galvanostatic condition of 100 mA. As seen in the figure, the potential in the case of the pure Ni is changed from \(-0.9\) V to \(-1.1\) V vs. SHE within 4 s and become almost constant of about \(-1.1\) V vs. SHE with some fluctuation. On the other hand, in the case of Mo–Ni alloy film electrodeposited from the solution 2, the potential is quickly changed from \(-0.45\) V to \(-0.5\) V vs. SHE within about 0.3 s and becomes stable at about \(-0.51\) V vs. SHE. Namely, because the hydrogen overvoltage is less in the alloy film than in the pure nickel film, the hydrogen evolution from the alkaline-water electric cell is larger in the alloy film.

4. Conclusion

The present electrodeposition experiments indicate that the electrodeposition of nickel is always required in the electrodeposition of molybdenum and the presence of molybdenum ions in solution suppresses the electrodeposition of nickel on a cupper electrode. The deposited films are arranged in the three groups, i.e. the Group I (Mo < 10%), the Group II (20% < Mo < 30%) and the Group III (Mo ≈ 40%) with the molybdenum concentration. Amorphous molybdenum and nickel alloys are formed in the solution containing molybdenum ions more than 5% of nickel ions. The crystalline films of the nickel solid solutions are electrodeposited in the solution containing molybdenum ions less than 2% of nickel ions. The hydrogen overvoltage significantly changes by the existence of a certain amount of molybdenum in the film. This causes the high catalytic activity of the molybdenum and nickel films for the evolution of hydrogen gas.

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