Fabrication of Bulk Ni–Mo Alloys by Electrodeposition with Intermittent Addition of Sodium Molybdate

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The electrocatalytic properties of Ni–Mo alloys are desirable for a wide range of electrochemical applications. However, electrodeposited Ni–Mo alloys suffer from high internal stress and low ductility. In this study, we electrodeposited Ni–Mo alloys by intermittently adding different concentrations of sodium molybdate. The microstructure and mechanical properties of the resulting alloys were examined. We identified a critical point for the Mo concentration in the deposition bath at which the properties of the electrodeposited alloys changed sharply. When the Mo concentration was below a certain threshold, the alloys consisted of relatively large grains (approximately 30–50 nm) and exhibited a tensile of approximately 10%. Conversely, when the concentration exceeded the threshold, the grain size decreased to approximately 15 nm and the ductility was limited. X-ray photoelectron spectroscopy indicated that the change of the properties corresponded to inclusion of oxides of molybdenum. On the basis of these results we suggest that producing ductile Ni–Mo alloys requires the Mo concentration in the deposition bath to be maintained at low levels.

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1. Introduction

Ni–Mo alloys have excellent hardness,1) thermal resistance,2) and show catalytic activity in the hydrogen evolution reaction in water electrolysis.3)–9) Modern electrochemistry-related industries require high electrochemical activities and relatively low cost Ni–Mo alloys.10) Metallurgical methods are inconvenient for preparing Ni–Mo alloys because of the ease of oxidation at the crystallization step and high melting temperature of Mo compared with that of Ni. Alternative processing methods have also been widely applied.11–13) Among these, electrodeposition is a convenient approach to producing Ni–Mo alloys: the alloys can be obtained from electrodeposition operated at low temperatures of approximately 40–50°C.3,14–17) Adjusting the bath composition and deposition conditions allows control over the chemical composition and microstructure of electrodeposits.1,16,18,19) In addition, Mo alloying has a strong grain refinement effect on the electrodeposited alloys in the nanometer range, resulting in an increase in the alloy strength.1,15–18,20)

Unfortunately, electrodeposited Ni–Mo alloys suffer from high internal stress:21) the formation of micro-crack networks because of internal stress, even in the as-deposited state, has been widely reported.22,23) Owing to these processing-defects, the alloys have poor ductility.14,21) When used as a catalyst in the hydrogen evolution reaction, Ni–Mo alloys are heated to approximately 80°C.22) This means that Ni–Mo alloys are subjected to repeated thermal expansion and contraction. Electrodeposited Ni–Mo alloys that have poor ductility cannot withstand the thermal volume change and will become damaged. The introduction of ductility into electrodeposited Ni–Mo alloys is important for prolonging the lifetime of components and expanding their application environments.

Low ductility is the main concern for electrodeposited Ni–Mo alloys. There are three main effects in Ni–Mo alloy electrodeposition processes that lead to high internal stress and low ductility. The first is the formation of heteropolymolybdate clusters. In the case of solutions containing only Ni and Mo ions, large heteropolymolybdate clusters are formed,24,25) which inhibit growth of electrodeposits.23,26) Electrodeposited alloys obtained from inhibited-growth modes have processing-defects and show poor ductility.27) The second effect is a decrease in the current efficiency which occurs through the addition of carboxylates. Decomposition of the heteropolymolybdate cluster can be achieved with the addition of carboxylates such as citric acid.24,25) Furthermore, citric acid forms a complex with Ni and Mo ions, which stabilizes the pH of the electrolyte solution.1,18,28) However, at high concentrations citric acid changes the Ni(II)–citrate complexes from Ni(C6H5O7)2– to Ni(C6H5O7)H2+,25) This transition results in a decrease of the current efficiency.25) Low current efficiency promotes generation of hydrogen gas and gaseous hydrogen also inhibits the growth of electrodeposits.29) The third effect is the inclusion of molybdenum oxide. To prevent the formation of heteropolymolybdate clusters or Ni(C6H5O7)H2+, complexes, the concentrations of sodium molybdate (as a Mo source) and citric acid should be maintained at relatively low levels. In Ni–Mo electrodeposition from a Ni-rich citrate bath meeting the above conditions, the formation of molybdenum oxide can occur owing to incomplete reduction reactions. Molybdenum oxide also inhibits the deposition reaction of Ni–Mo alloys.

To produce ductile Ni–Mo alloys, our studies have pointed out the need to identify electrodeposition conditions that do not lead to Mo oxide formation, in electrodeposition from a Ni-rich carboxylate bath. Moreover, under the desired condition, Mo concentration in the deposition bath was expected to be at relatively low level. In previous our study,30) we have developed an intermittent addition method that uniformly dopes solutes to the electrodeposits while keeping the solute concentration in the deposition bath at low. In this study, we have therefore applied intermittent addition techniques30) as a Mo addition method, to the electro-
deposition process for Ni–Mo alloys. In our preliminary studies we investigated the effects of the Mo source concentration on the current efficiency of the deposition process, and the Mo content and chemical state of Mo in the electrodeposited alloys. We then examined the correlation between these parameters and the microstructures and mechanical properties of the electrodeposited Ni–Mo alloys. On the basis of these experiments, we extracted the electrodeposition conditions for obtaining ductile Ni–Mo alloys.

2. Experimental Methods

Ni and Ni–Mo alloys were deposited by electrodeposition from the aqueous solution whose composition is given in Table 1. For this study, sodium gluconate was used as a carboxylic acid to decompose heteropolymolybdate clusters. The Mo source, was an aqueous solution containing 2.0–20.0 g/L sodium molybdate, as shown in Table 1. This solution was intermittently added to the deposition bath during electrodeposition of the Ni–Mo alloys. This intermittent addition of the Mo source was performed automatically with the use of a tubing pump operating with an on-time of 6 s and an off-time of 194 s. The average addition rate of the solution was approximately 2.2 mL/h and the total added amount was approximately 160 mL for each electrodeposition. The total added concentration of sodium molybdate in the deposition bath corresponded to approximately 0–4.3 g/L (Table 2). Details of the intermittent addition method and electrodeposition system used have been described in our previous reports.30,31) All electrodepositions were performed for 72 h, at a current density of 30 mA/cm², bath temperature of 55°C, and pH of 4.0. Bulk plates of Ni–Mo alloys (length of 50 mm, width of 30 mm, and thickness of 1.4 mm) were deposited onto Cu cathodes, which were subsequently cut into specimens for the following analyses.

The Mo content was determined from the surface of samples by energy-dispersive X-ray spectroscopy (EDX, Shimadzu EDX-8000). In addition, the homogeneity of the Mo content in the growth direction was confirmed with spot analysis by EDX on a scanning electron microscope (SEM–EDX, JEOL JSM-IT300HR). The chemical states of Mo present in the electrodeposited alloys were examined by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe) with Al Kα radiation operated at 15 kV. Before XPS analysis, the surfaces of samples were etched with Ar ions for 40 s to remove the oxide film and contamination. Structural characterization was conducted on an X-ray diffractometer (XRD, Rigaku MiniFlex 600) operated at 15 mA and 40 kV with Cu Kα radiation. Grain sizes and distributions were estimated by the fundamental parameter method, with the Rigaku software package PDXL2. To evaluate the hardness of the electrodeposits, micro-Vickers hardness tests were conducted on the surfaces and cross-sections of the bulk samples with a load of 500 g for 10 s. The reported hardness points obtained from the surface are the mean of 10 indentations, while those obtained from the cross-section correspond to the results of one indentation. Dog-bone specimens with a gauge length of 12 mm, width of 3.0 mm, and thickness of approximately 1.0 mm were machined by electrical discharge machining (EDM) for tensile tests. Note that the surface grinder removed the copper substrate and the layer affected by EDM.

Table 1 Compositions of deposition bath and Mo source for electrodeposition.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Amount (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deposition bath</strong></td>
<td></td>
</tr>
<tr>
<td>Nickel sulfamate tetrahydrate</td>
<td>300.0</td>
</tr>
<tr>
<td>Nickel chloride hexahydrate</td>
<td>5.0</td>
</tr>
<tr>
<td>Sodium propionate</td>
<td>20.0</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>4.2</td>
</tr>
<tr>
<td>Saccharin sodium dihydrate</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Mo source</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium molybdate dihydrate</td>
<td>2.0–20.0</td>
</tr>
</tbody>
</table>

Table 2 Summary of experimental data for electrodeposited Ni–Mo alloys.

<table>
<thead>
<tr>
<th>Mo source (g/L)</th>
<th>Corresponding conc. in bath (g/L)</th>
<th>Mo content (at%)</th>
<th>Grain size (nm)</th>
<th>Tensile strength (GPa)</th>
<th>Total elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
<td>67 ± 46</td>
<td>0.95 ± 0.01</td>
<td>11.6 ± 0.2</td>
</tr>
<tr>
<td>2.0</td>
<td>0.4</td>
<td>0.31 ± 0.04</td>
<td>46 ± 31</td>
<td>1.08 ± 0.01</td>
<td>12.1 ± 0.4</td>
</tr>
<tr>
<td>4.0</td>
<td>0.9</td>
<td>0.34 ± 0.06</td>
<td>46 ± 38</td>
<td>1.07 ± 0.02</td>
<td>10.9 ± 1.3</td>
</tr>
<tr>
<td>5.0</td>
<td>1.1</td>
<td>0.21 ± 0.04</td>
<td>34 ± 22</td>
<td>1.08 ± 0.02</td>
<td>10.2 ± 0.2</td>
</tr>
<tr>
<td>6.0</td>
<td>1.3</td>
<td>0.20 ± 0.10</td>
<td>34 ± 23</td>
<td>1.00 ± 0.07</td>
<td>11.7 ± 2.8</td>
</tr>
<tr>
<td>7.0</td>
<td>1.5</td>
<td>0.70 ± 0.29</td>
<td>17 ± 11</td>
<td>1.10 ± 0.02</td>
<td>8.7 ± 1.1</td>
</tr>
<tr>
<td>10.0</td>
<td>2.1</td>
<td>1.17 ± 0.25</td>
<td>15 ± 10</td>
<td>0.88 ± 0.00</td>
<td>4.6 ± 0.6</td>
</tr>
<tr>
<td>20.0</td>
<td>4.3</td>
<td>2.64 ± 0.06</td>
<td>14 ± 8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
tests were performed at room temperature and a strain rate of $1 \times 10^{-3}\text{ s}^{-1}$ with a universal testing machine (Shimadzu AUTOGRAPH AG-X plus). Each reported data point represents the mean of two measurements.

3. Results and Discussion

3.1 Electrodeposition of Ni–Mo alloys

We prepared bulk samples by varying the concentration of sodium molybdate in the Mo source solution. In this paper, these samples were identified by the concentration (0–4.3 g/L) in the deposition bath after completed addition. Furthermore, the formation of micro-crack networks on the surface of electrodeposits was observed at a concentration of 4.3 g/L. Thus, no further increases in the concentration were attempted. The current efficiencies of the deposition bath with intermittent addition of sodium molybdate are shown in Fig. 1. The deposition bath without addition of sodium molybdate showed the highest current efficiency of 96%. The current efficiencies decreased linearly as the final concentration of sodium molybdate was increased to 4.3 g/L: the deposition bath with added sodium molybdate of 4.3 g/L showed the lowest efficiency of 86%.

The Mo content for bulk samples is plotted against the total added concentration of sodium molybdate in Fig. 2(a). Figure 2(a) shows that there were two effects across the concentration regions. In the sodium molybdate concentration range of 0.4–1.3 g/L, an almost constant Mo content of 0.2–0.3 at% was observed, which was independent of the concentration of added sodium molybdate. When the final concentration exceeded 1.5 g/L, the Mo content increased in proportion to the concentration from 0.7 to 2.6 at%. We also addressed the homogeneity of Mo content in the growth direction for these samples. Figure 2(b) shows the Mo content as a function of length from the interface for some samples, measured by SEM–EDX. The alloys electrodeposited with a final sodium molybdate concentration of 1.3 g/L had a relatively uniform Mo content of 0.14 ± 0.04 at%. This result also agrees with the Mo content measured from the surface. Conversely, the alloys electrodeposited with higher concentrations of sodium molybdate (2.1 and 4.2 g/L) showed a gradient of the Mo content. The Mo content of the first layer was 0.16 ± 0.08 at%, while the Mo content increased up to 0.81 and 2.65 at%, respectively, approaching the surface layer.

The chemical state of Mo present in electrodeposited alloys was investigated by XPS to identify the deposition mechanism of Mo for each electrodeposition. Figure 3 shows the Mo 3d spectrum for alloys electrodeposited with sodium molybdate of 2.1 g/L. In Fig. 3, broadened peaks are observed. We separated these broadened peaks into two curves with a pseudo-Voigt function, and the results are also shown in Fig. 3. The locations of the main peaks (led dot line) were 227.17 and 230.33 eV and those of the sub peaks (green dash line) were 228.31 and 231.58 eV. The main peaks correspond to the 3d binding energies of metallic Mo (227.70 and 230.85 eV), and the sub peaks are consistent with the 3d binding energies of MoO$_2$ (229.3 and 231.0 eV). A comparison of these features suggested that the forming...
reaction and inclusion of \( \text{MoO}_2 \) occurred together with the deposition of Mo. Conversely, only peaks from Mo were observed for alloys electrodeposited in the concentration range of 0.4–1.3 g/L. These results indicated that the forming reaction of the molybdenum oxides did not occur for low concentration of sodium molybdate.

In this study, there were two types of Mo deposition, namely, only metallic Mo deposition and a mixture of the metal and oxide Mo deposition. The results of SEM–EDX on the cross section of samples (Fig. 2(b)) show that the Mo content of the alloys electrodeposited with sodium molybdate concentrations of 2.1 and 4.3 g/L increased sharply at a certain point. This would mean that the reaction of MoO\(_2\) began when the Mo concentration in the bath reached a critical concentration. The distances from the interface to the critical point for alloys electrodeposited with sodium molybdate concentrations of 2.1 and 4.3 g/L were approximately 0.8 and 0.3 mm, respectively. These lengths represented 62% and 29% of the total sample thickness. Assuming that the growth speed of the electrodeposits was constant, up to these points, the concentrations of sodium molybdate added to the bath were 1.26 and 1.18 g/L, respectively. Because the average Mo content for both samples from the interface to critical point was 0.3 mass%, the concentrations of Mo taken into the electrodeposits were estimated to be 0.09 and 0.03 g/L. The concentrations of Mo remaining in the bath at the critical point were 1.17 and 1.15 g/L, respectively: these values were consistent between both samples. Therefore, 1.2 g/L was taken to be the critical concentration required for initiating both deposition of metal and oxide Mo.

Belotowska and Indyka\(^{23}\) reported that oxide Mo was deposited from Mo(VI)-citrate complexes as follows:

\[
\text{H}_2\text{MoO}_4 (\text{C}_6\text{H}_5\text{O}_7)^{3-} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MoO}_2 + (\text{C}_6\text{H}_5\text{O}_7)^2^- + 3\text{OH}^- \tag{1}
\]

In this study, at Mo concentrations higher than the critical concentration, oxide Mo was deposited from the Mo(VI)-gluconate complex via a similar reaction as follows:

\[
\text{HMoO}_4 (\text{C}_6\text{H}_11\text{O}_7)^{3-} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MoO}_2 + (\text{C}_6\text{H}_11\text{O}_7)^{-} + 3\text{OH}^- \tag{2}
\]

For Mo concentrations higher than the critical concentration the reaction in eq. (2) was promoted. As a result, the Mo content of the alloys increased in proportion to the Mo concentration in the deposition bath, with a total added concentration range of 1.5–4.3 g/L. Conversely, at concentrations lower than the critical concentration, oxides were not detected and the Mo content of the alloys was independent of the Mo concentration in the bath (Fig. 2(a)). These results suggested the possibility that the deposition reaction of Mo via Mo(VI)-gluconate complex did not occur to a great extent in the low concentration bath. Here, the Mo(VI)-species present were isopolymolybdates \( \text{H}_2\text{Mo}_7\text{O}_{18}\text{O}_4 \) or \( \text{H}_2\text{Mo}_7\text{O}_{18}\text{O}_4 \), as reported by Murase et al.\(^{23}\) The reduction reaction from these isopolymolybdates to metal Mo did not occur. Thus, we considered that the Mo content of the alloys remained constant at 0.2–0.3 at% regardless of the Mo concentration in the deposition bath, in the final concentration range of 0.4–1.3 g/L.

In summary, electrodeposition with intermittent addition of sodium molybdate produced two types of Ni–Mo alloys: one type with a lower constant Mo content of 0.2–0.3 at%, and another type with a higher Mo content of 0.7–2.7 at%, some of which existed as a dioxide. In the following section, we will examine the microstructure and mechanical properties of these alloys and discuss the effects of Mo on these properties.

### 3.2 Microstructure and mechanical properties

Figure 4(a) shows XRD patterns for the electrodeposited samples obtained from the surface layers. All these XRD patterns showed a single face-centered cubic (fcc) structure. The microstructure of the samples changed from a dominant (200) texture to a dominant (111) texture as the concentration of sodium molybdate was increased. Several studies\(^{29,33,34}\) have reported that the orientation of electrodeposits reflects the growth mode: uninhibited growth modes produce a dominant (200) texture. Conversely, inhibited growth modes produce a dominant (111) or (220) texture. As mentioned above, at high sodium molybdate concentrations, the forming reaction for MoO\(_2\) occurred. These dioxides could inhibit the growth of electrodeposits, resulting in a dominant (111) texture. A similar transition of the texture has been reported in a study of electrodeposited Ni–Mo by Bigos et al.\(^{23}\)

The grain size distributions estimated from the XRD patterns are shown in Fig. 4(b). These results suggested that samples electrodeposited with a sodium molybdate below 1.3 g/L consisted of relatively large grains with a broad size distribution. In contrast, at final concentrations greater than 1.5 g/L, the grain size decreased to approximately 15 nm, resulting in a narrow distribution. The calculated average grain size is plotted against the final concentration of sodium.

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**Fig. 4** (a) Representative XRD patterns of Ni–Mo alloys electrodeposited with different concentrations of sodium molybdate. (b) Corresponding grain size distribution estimated by fundamental parameter analysis with concentration of sodium molybdate. (c) Calculated average grain size as a function of sodium molybdate concentration.
These alloys contained MoO$_2$ in addition to metal Mo. The Mo content of the alloys was high at 0.7 higher concentrations of sodium molybdate of 1.5 with the formation of dioxides (Fig. 2(a) and Fig. 3). For molybdate changed at concentrations between 1.3 and 4.3 g/L, the Mo content of the alloys was high at 0.7–2.6 at% and these alloys contained MoO$_2$ in addition to metal Mo. The included MoO$_2$ could pin grain boundaries, stabilizing a finer nanocrystalline grain structure.$^{35}$ The increase of both the Mo content and inclusion of MoO$_2$ notably affected the grain refinement effect, as observed in Fig. 4(c) for final sodium molybdate concentrations of 1.3 and 1.5 g/L.

Figure 5(a) shows the hardness values obtained from the surface layers of the Ni–Mo alloys as a function of sodium molybdate concentration. The pure Ni showed a hardness value of 2.6 GPa. The addition of 0.2–1.3 g/L sodium molybdate increased the hardness to 3.0–3.5 GPa. Further increases of the sodium molybdate resulted in an even higher hardness of 4.6–5.2 GPa. We also examined the cross-sectional hardness, because the sample electrodeposited with sodium molybdate concentrations of 1.5–4.3 g/L had an inhomogeneous Mo distribution (Fig. 2(a)). Figure 5(b) shows the cross-sectional hardness as a function of length from the interface for Ni–Mo alloys electrodeposited with sodium molybdate concentrations of 1.3, 2.1, and 4.2 g/L. The alloys electrodeposited with a sodium molybdate concentration of 1.3 g/L had a relatively uniform hardness of 3.2 ± 0.2 GPa, which was also in agreement with their surface hardness values. Conversely, the alloys electrodeposited with higher concentrations of sodium molybdate (2.1 and 4.2 g/L) showed a hardness gradient. The hardness of the first layer was 3.4 ± 0.2 GPa, while the hardness increased to 5.0–5.3 GPa approaching the surface layer. The changes of the surface and cross-sectional hardness values agreed with the trend in the Mo content, as shown in Figs. 2(a) and (b). This agreement was attributed to the grain size of the electrodeposited alloys depending on their Mo content (Figs. 2(a) and 4(c)). Furthermore, the hardness of the Ni–Mo alloys is strongly linked with their grain size according to Hall–Petch relation.$^{36,37}$ as shown in Fig. 5(c). Figure 5(c) shows that the hardness increased in proportion to the inverse square root of the grain size. The slope for the Ni–Mo alloys was 18.09 GPa/nm$^{-1/2}$, and this value was slightly higher than the value of the Ni (17.33 GPa/nm$^{-1/2}$). The strength of the Ni–Mo alloys derived mainly from grain refinement effects, and solid solute strengthening by Mo or precipitation strengthening by MoO$_2$ also played a role.

Figure 6 shows the representative stress-strain curves of Ni–Mo alloys electrodeposited with sodium molybdate concentrations of 0.4, 1.5, and 2.1 g/L, and the details of tensile tests are given in Table 2. Note that the sample electrodeposited with a sodium molybdate concentration of 4.3 g/L was not subjected to a tensile test because micro-crack networks were formed on the surface, as mentioned above. The pure Ni exhibited a tensile strength of 0.95 GPa and an elongation of 11.6%. The addition of 0.2–1.3 g/L sodium molybdate slightly increased the tensile strength by 0.1 GPa and the tensile elongation remained unchanged. Conversely, for higher final concentrations of sodium molybdate in the range of 1.5–2.1 g/L, the elongation decreased to 4.6% as the concentration was increased. The samples electrodeposited with higher final concentrations of sodium molybdate ruptured without work hardening. This behavior was attributed to the stress concentration, which derived from crack formation in the hard layer containing the MoO$_2$ deposited from an inhibited growth mode, as shown in Figs. 4(a) and 5(b). Electrodeposited alloys obtained from inhibited-growth modes have processing-defects.$^{27}$ A similar behavior has been reported for electrodeposited multi-layers.$^{30}$

For these tensile tests, the electrodeposited Ni–Mo alloys exhibited clear plastic deformation, although there was only a
trace amount of Mo content (0.2–0.3 at%). This result indicates that the addition of Mo did not affect the plastic deformability of the electrodeposited Ni alloys. We conclude indicates that the addition of Mo did not a
levation. Moreover, the forming reaction of the dioxides could start at very low Mo concentrations (1.2 g/L) in the deposition bath. It has been incorrectly inferred that oxides are not formed in electrodeposition processes to a higher degree than those of conventional casting process.10)

The inclusion of MoO₂ is inevitable as the Mo content can be attributed to oxide contamination. In fact, as shown in Fig. 6, the inclusion of MoO₂ effectively decreased the tensile elongation. Among the alloys containing MoO₂, increasing the Mo content decreased the tensile elongation. Although the inclusion of dioxides resulted in a constant Mo content of 0.2–4.4 at%, the electrodeposited Ni alloys. One type with metal Mo and another containing both metal and molybdenum oxides. Varying the sodium molybdate concentration revealed that 1.2 g/L in the deposition bath was the critical concentration required for initiating both deposition of metal and oxide Mo.

(2) In the final sodium molybdate concentration range of 0.4–1.3 g/L, which was lower than the critical concentration, the electrodeposited Ni–Mo alloys had a constant Mo content of 0.2–0.3 at% and a relatively large grain size of 34–46 nm. These alloys exhibited clear plastic deformation in tensile tests. These results indicate that addition of Mo did not limit the plastic deformability of the electrodeposited Ni.

(3) In the total added sodium molybdate concentration range of 1.5–4.3 g/L, which was higher than the critical concentration, the electrodeposited Ni–Mo alloys had a higher Mo content of 0.7–2.6 at% and a fine grain size of approximately 15 nm. Among the alloys containing MoO₂, increasing the Mo content decreased the tensile elongation. Although the inclusion of dioxides resulted in an effective grain refinement effect, the inclusion is the main cause of reduced ductility in the electrodeposited Ni–Mo alloys.

4. Conclusions

(1) Electrodeposition with intermittent addition of sodium molybdate produced two types of Ni–Mo alloys. One type with metal Mo and another containing both metal and molybdenum oxides. Varying the sodium molybdate concentration revealed that 1.2 g/L in the deposition bath was the critical concentration required for initiating both deposition of metal and oxide Mo.

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