Novel Electroforming Process for Bulk Nanocrystalline Ni-W Alloys with Minimizing W-Concentration Gradient and Fluctuation

Yoshihisa Kimoto, Shin Wakayama, Akari Fujii, Yorinobu Takigawa and Kenji Higashi

Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai 599-8531, Japan

An electroforming process for fabricating bulk nanocrystalline Ni-W alloys with minimizing W-concentration gradient and fluctuation is presented. The homogeneities of W-concentration in both micrometer scale and millimeter scale are guaranteed from the W-concentration profiles obtained by the linear analyses of the energy dispersive x-ray spectroscopy (EDS). Mass balance analyses of the metallic ions in the electrolyte are performed by the combination of the experimental results of the inductively coupled plasma mass spectrometry (ICP-MS) and the exact solutions of the simultaneous differential equation. The homogeneous bulk nanocrystalline Ni-W alloy with the thickness above 2 mm is featured for the first time.

(Received December 11, 2006; Accepted March 19, 2007; Published May 25, 2007)

Keywords: electroforming, bulk, nanocrystalline, nickel-tungsten alloy, homogeneity, concentration fluctuation, mass balance

1. Introduction

Grain size refinement had been believed until recently to be the promising way to strengthen materials while maintaining the ductility and toughness. In contrast with many researchers’ expectations, many studies on nanocrystalline materials have reported that the hardness peaks out at around the dozen nanometer before reaching amorphous limit and that the ductility of nanocrystalline metals are quite low. In response to these results, optimizing the microstructures for better ductility has been emerged as an important agenda on the nanocrystalline studies. At present, most of the studies have failed in escaping from the trade-off balancing between the strength and ductility. However, it is rarely recognized that such disappointing conclusions have been derived in the experimental studies using thin-film specimens.

The mechanisms of the embrittlement of the nanocrystalline metals are supposed as follows: 1) A plenty of the grain boundaries with high interfacial energy mediates the plastic deformation through the localization of the plastic deformation and the formation of shear bands, and 3) The insufficient thickness of the specimens makes the materials sensitive to the surface notch and roughness. T. Mukai, et al. have indicated from the tensile testing of metallic glasses that under dynamic strain rate condition the fracture stress is more sensitive in ribbon specimens than in bulk specimen, because of the notch brittleness. Various attempts have been made against these embrittlement factors. For instance, Y. Wang, et al. have successfully balanced both the strength and ductility by a thermomechanical treatment yielding the microstructure in which micrometer-sized grains embedded in the nanocrystalline matrix serve the strain hardening. However, drastic strategies have never been developed for the insufficient thickness, which may hide an inherent potential of the single-phase nanocrystalline materials.

Toward the industrial application of the nanocrystalline materials to a structural material, the reliability of the mechanical properties is of great necessity, as well as the enhanced ductility. Figure 1 shows the results of tensile tests of electrodeposited Ni-W alloys. The statistical trend clarifies the Hall-Petch breakdown, but the data of tensile strength scatters largely. As mentioned above, the first reason of the scattering is the high notch sensitivity brought about the insufficient thickness of the specimens (typically 20 μm). Furthermore, the inhomogeneity of the nanostructure should be taken into consideration as the second reason. Although the electrodeposited Ni-W alloy had been regarded as the single phase nanocrystalline and the single phase amorphous in the W-concentration range below and above 20 at%, respectively, it has been clarified from three dimensional atom probe (3DAP) analyses and the nano-beam diffraction (NBD) patterns that the electrodeposited Ni-W alloys including 16.7 at% and 17.7 at% W have been identified as amorphous/nanocrystalline duplex composites with the volume fraction of amorphous phases 49.0% and 53.4%, respectively. These quantitative data indicates that the small W-concentration fluctuation of ±0.5 at% can cause the considerable change of around 14% in the volume fraction of the amorphous phase, which can significantly affect the scattering of the strength. For the reliable characterization of the properties of nanocrystalline materials, minimizing the concentration gradient and fluctuation are indispensable.

In this study, the bulk nanocrystalline Ni-W alloys with minimized W-concentration gradient and fluctuation are
demonstrated. The homogeneities of W-concentration in both micrometer scale and millimeter scale are guaranteed from the W-concentration profiles obtained by the linear analyses of the energy dispersive x-ray spectroscopy (EDS). The bulk nanocrystalline Ni-W alloy with the thickness above 2 mm and minimizing W-concentration gradient and fluctuation is featured for the first time.

2. Theoretical Background

To realize the homogeneous bulk electroforming, there were two major problems in the conventional thin-film electrodeposition processes. The first problem is the side reactions that pollute the electrolyte and keep us from stoichiometry analyses. The second problem is the upset of a chemical mass balance due to the reduction of the metallic ions and the residues of by-products during electrodeposition, which triggers the gradient and fluctuation of the W-concentration in the deposits. To solve these two problems, we employed a Ni-W continuous electroplating system.\(^{13}\) This system was developed as an environmental-friendly plating system, alternative for hexavalent chromium plating. The system has a good track record in the remanufacturing of amorphous thin-films plating over one month with no waste solutions, and the amorphous bulk electroforming with 1 mm thickness.\(^{13}\) As shown in Fig. 2(a), the system had three anode, an insoluble anode of Pt (or Ir-Ta alloy) and two soluble anodes of Ni and W. The three anodes were connected parallel to the Cu cathode. The distribution of the total anode current to the three anodes was determined corresponding to the deposition efficiency and W-concentration in the Ni-W electrodeposits, so as to maintain the metallic-ion concentrations and pH in the electrolyte.

2.1 Suppression of the side reaction

On an insoluble anode (typically made of Pt or Ir-Ta) in the Ni-W electrodeposition, the oxidative decomposition of the organic acid such as a citric acid yields a contaminant of the Ni-W electrodeposition, the oxidative decomposition of the 2.1 Suppression of the side reaction

To realize the homogeneous bulk electroforming, there were two major problems in the conventional thin-film electrodeposition processes. The first problem is the side reactions that pollute the electrolyte and keep us from stoichiometry analyses. The second problem is the upset of a chemical mass balance due to the reduction of the metallic ions and the residues of by-products during electrodeposition, which triggers the gradient and fluctuation of the W-concentration in the deposits. To solve these two problems, we employed a Ni-W continuous electroplating system.\(^{13}\) This system was developed as an environmental-friendly plating system, alternative for hexavalent chromium plating. The system has a good track record in the remanufacturing of amorphous thin-films plating over one month with no waste solutions, and the amorphous bulk electroforming with 1 mm thickness.\(^{13}\) As shown in Fig. 2(a), the system had three anode, an insoluble anode of Pt (or Ir-Ta alloy) and two soluble anodes of Ni and W. The three anodes were connected parallel to the Cu cathode. The distribution of the total anode current to the three anodes was determined corresponding to the deposition efficiency and W-concentration in the Ni-W electrodeposits, so as to maintain the metallic-ion concentrations and pH in the electrolyte.

2.1 Suppression of the side reaction

On an insoluble anode (typically made of Pt or Ir-Ta) in the Ni-W electrodeposition, the oxidative decomposition of the organic acid such as a citric acid yields a contaminant of the polymer molecule with a complex structure, and seriously pollutes the electrolyte.\(^{13}\) A formic ion is decomposed to the carbon dioxide in priority to the citric acid, and slows the decomposition of the citric acid. However, the citric acid begins to decompose immediately after the formic ions are exhausted. The most appropriate way to prevent the citric acid from the decomposition is the use of a diaphragm cell with a cation-exchange membrane. In the pH range from 5 to 8, the citric acid forms anions H\(_2\)Cit\(^{-}\), HCit\(^{-}\) and/or Cit\(^{3-}\) in the electrolyte.\(^{14}\) As shown in Fig. 2(b), the citric anions cannot pass through the cation-exchange membrane, and the oxidative decomposition of the citric acid can be avoided. Both the sacrifice anode oxidant of the formic ion and the diaphragm cell with the cation-exchange membrane effectively suppress the side reactions at the insoluble anode and enable us to analyze quantitatively the chemical mass balance in the electrolyte.

2.2 Principle for preserving the mass balance in the electrolyte

Theoretical quantitative considerations on the chemical mass balances between consumed ions by electrodeposition and supplemented ions by the solution of Ni and W anodes are given in this section. On the Cu cathode, the alloy-deposition reaction occurs in competition with the production of hydrogen:

\[
\begin{align*}
(1 - \alpha) \text{Ni}^{2+} + \alpha \text{WO}_4^{2-} + 8\alpha \text{H}^+ + 2(1 + 2\alpha) \text{e}^- &\rightarrow \text{Ni}_{1-\alpha} \text{W}_\alpha + 4\alpha \text{H}_2\text{O}, \quad (c1) \\
2\text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{H}_2 + 2\text{OH}^-, \quad (c2)
\end{align*}
\]

where, \(\alpha\) is the W atomic ratio in the deposit (0 < \(\alpha\) < 1). Inside the diaphragm cell with the cation-exchange membrane, oxygen is produced from the water oxidation on the insoluble (Pt) anode:

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-.
\]

The nickel ions and tungstate ions consumed by the alloy-deposition reaction of (c1) are supplemented through the solutions of the soluble Ni and W anodes:

\[
\begin{align*}
\text{Ni} &\rightarrow \text{Ni}^{2+} + 2\text{e}^-, \quad (a2) \\
\text{W} + 4\text{H}_2\text{O} &\rightarrow \text{WO}_4^{2-} + 8\text{H}^+ + 6\text{e}^-.
\end{align*}
\]

To maintain the mass balance in the electrolyte, the currents for three anodes of Ni, W and Pt (denoted as \(I_{\text{Ni}}, I_{\text{W}}\), and \(I_{\text{Pt}}\), respectively) should be controlled corresponding to the W-concentration of the deposit \(\alpha\) and the cathode current efficiency. Providing the cathode current efficiency on the alloy-deposition reaction of (c1) is \(e\) (0 < \(e\) < 1), the mass balances of the ion species \(\text{Ni}^{2+}, \text{WO}_4^{2-}, \text{H}^+, \text{and OH}^-\) during the time \(\Delta t\) are given in the following equations:

\[
\begin{align*}
L\Delta[\text{Ni}^{2+}] &= - \frac{1 - \alpha}{2(1 + 2\alpha)} \cdot \frac{e \Delta t}{F} + \frac{1}{2} \cdot I_{\text{Ni}} \Delta t, \quad (1) \\
L\Delta[\text{WO}_4^{2-}] &= - \frac{\alpha}{2(1 + 2\alpha)} \cdot \frac{e \Delta t}{F} + \frac{1}{6} \cdot I_{\text{W}} \Delta t, \quad (2) \\
L\Delta[\text{H}^+] &= - \frac{4\alpha}{1 + 2\alpha} \cdot \frac{e \Delta t}{F} + \frac{1}{3} \cdot I_{\text{Pt}} \Delta t, \quad (3) \\
L[\text{OH}^-] &= \frac{(1 - e)I_{\text{Pt}} \Delta t}{F},
\end{align*}
\]

where, \(L[A]\) is the change of the molar concentration of an ion \(A\) during the time \(\Delta t\), and \(F\) is the Faraday constant (9.65 \times 10^4 \text{C/mol}), and \(L\) is the volume of the electrolyte, and \(I\) is the total current (= \(I_{\text{Ni}} + I_{\text{W}} + I_{\text{Pt}}\), which is equal to the product of the current density and the deposition area on the Cu cathode. Taking the neutralization reaction \(\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}\) into account, the latter two equations are put into one equation:

\[
L\Delta[\text{H}^+] = - \frac{4\alpha}{(1 + 2\alpha)} \cdot \frac{e \Delta t}{F} + \frac{1}{3} \cdot I_{\text{Pt}} \Delta t + \frac{4}{3} \cdot \frac{I_{\text{W}} \Delta t}{F} - \frac{(1 - e)I_{\text{Pt}} \Delta t}{F}
\]

The conditions required to maintain the mass balance in the electrolyte is \(\Delta[\text{Ni}^{2+}]/\Delta t = \Delta[\text{WO}_4^{2-}]/\Delta t = \Delta[\text{H}^+)/\Delta t = 0\). The optimized currents for preserving the mass balance are derived by imposing the condition on the equations (1), (2) and (3):

\[
I_{\text{Ni}} = \frac{1 - \alpha}{1 + 2\alpha} e I, \quad I_{\text{W}} = \frac{3\alpha}{1 + 2\alpha} e I, \quad I_{\text{Pt}} = (1 - e)I. \quad (4)
\]

Under an ideal condition satisfying the constant current efficiency and no side reactions, the molar concentrations of...
the ion species in the electrolyte can be kept constant by applying these constant currents to each anode.

3. Experimental Procedure

The electrolyte presented in the Ref. 13) was mainly optimized for the nearly amorphous electroplating with good gross and corrosion resistance suitable to the plating industry, not for the nanocrystalline bulk electroforming. The process parameters in the bulk electroforming and the thin-film electrodeposition are listed in Table 1. The electrolyte for the bulk electroforming has been constructed in this work by changing Ni-source chemical and W molar ratio from those of the electrolyte in Ref. 13). The parameter optimizations will be discussed in another report. The electrolyte for the thin-film electrodepositions is one of the conventional electrolytes for the Ni-W electroplating, developed by T. Yamasaki, et al.15)

W-concentration profiles along the thickness direction were obtained by EDS linear analyses on the scanning electron microscopy (SEM) at the accelerating voltage of 25 kV. The EDS specimens were cut from the electro-deposited Cu substrates using a wire-electrical discharge machine, and the cross sections were mechanically polished for the removal of the work-affected layer and the SEM observations. A ZAF correction was applied to the EDS spectrum for the quantitative analyses. The dwell time in the measurement of each spot was set to be 5 second. The repeat accuracy of W concentration for the same spot was approximately $\pm 0.5$ at%, and the repeat measurements of W-concentration profiles along the same line showed similar fluctuation, increasing and/or decreasing. The variations of the molar concentration of nickel ions were evaluated by applying the inductively coupled plasma mass spectrometry (ICP-MS) to the 6 electrolyte samples. The grain sizes of the samples were determined by applying the Scherrer equation for the peak broadening to the $(1 1 1)$ reflections in the XRD spectrum.

4. Results

The micrometer-scale W-concentration profiles of the samples fabricated by the bulk electroforming process and the thin-film electroforming processes are compared in
Fig. 3(a) and (b). The W-concentration profiles show the fluctuation of the W-concentration in the range up to 20 micrometer from the Cu substrate. The samples with average W concentration of 16.4 at% and 12.4 at% in Fig. 3(a) were electrodeposited by the thin-film electrodeposition processes at the bath temperature of 343 K and 328 K, respectively. The grain sizes of the thin-film samples were estimated to be 8 nm and 23 nm, respectively, by the Scherrer equation. These W-concentration profiles show a great fluctuation. The bulk sample with average W concentration of 16.5 at% in Fig. 3(b) was electroformed at the current density of 0.08 A/cm$^2$, with the W ratio in the bath 0.20. The grain size of the bulk sample was estimated to be 10 nm. The bulk sample with average W concentration of 11.3 at% in Fig. 3(b) was electroformed at the current density of 0.05 A/cm$^2$, with the W ratio in the bath 0.17. The grain size of the bulk sample was 11.4 nm. The standard deviations in the samples produced by the thin-film processes were 1.01 at% and 1.58 at% for the samples with average W concentrations of 16.4 at% and 12.4 at%, respectively. On the other hand, those in the samples produced by the bulk electroforming process were 0.71 at% and 0.88 at% for the samples with average W concentrations of 16.5 at% and 11.3 at%, respectively. The standard deviations are decreased by 30% and 44% for both the higher (16.4 at% and 16.5 at%) and lower (12.4 at% and 11.3 at%) average W concentrations. The gradients of the W concentration in the samples obtained by the thin-film processes were 0.011 at%/m and 0.23 at%/m for the samples with average W concentrations of 16.4 at% and 12.4 at%, respectively. On the contrary, those in the samples fabricated by the bulk electroforming process were 0.0017 at%/μm and 0.015 at%/μm for the samples with average W concentrations of 16.4 at% and 12.4 at%, respectively. On the other hand, those in the samples produced by the bulk electroforming process were 0.71 at% and 0.88 at% for the samples with average W concentrations of 16.5 at% and 11.3 at%, respectively. The standard deviations are decreased by 30% and 44% for both the higher (16.4 at% and 16.5 at%) and lower (12.4 at% and 11.3 at%) average W concentrations. The gradients of the W concentration in the samples obtained by the thin-film processes were 0.011 at%/μm and 0.23 at%/μm for the samples with average W concentrations of 16.4 at% and 12.4 at%, respectively. On the contrary, those in the samples fabricated by the bulk electroforming process were 0.0017 at%/μm and 0.015 at%/μm for the samples with average W concentrations of 16.5 at% and 11.3 at%, respectively. The W-concentration gradients are reduced to one-sixth and one-fifteenth for the higher and lower average W concentrations, respectively, by employing the bulk electroforming process.

Table 1 Process parameters and conditions in the bulk electroforming and thin-film electrodepositions.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Bulk electroforming</th>
<th>Thin-film electrodepositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni source, W source</td>
<td>Nickel formate, Sodium tungstate</td>
<td>Nickel Sulfate, Sodium tungstate</td>
</tr>
<tr>
<td>[Ni$^{2+}$]+[WO$_4^{2-}$] (mol/L)</td>
<td>0.32</td>
<td>0.20</td>
</tr>
<tr>
<td>Complexer</td>
<td>Citric acid 0.35 mol/L</td>
<td>Trisodium citrate 0.50 mol/L</td>
</tr>
<tr>
<td>Enhanced current efficiency; pH adjuster</td>
<td>Aqueous ammonia (to pH=6.3)</td>
<td>Ammonium chloride 0.50 mol/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>—</td>
<td>Sodium bromide 0.15 mol/L</td>
</tr>
<tr>
<td>Current density (A/cm$^2$)</td>
<td>0.08, 0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>Bath temperature (K)</td>
<td>343</td>
<td>328, 343</td>
</tr>
<tr>
<td>W molar ratio in the bath</td>
<td>0.20, 0.17, 0.075</td>
<td>0.70</td>
</tr>
<tr>
<td>[WO$_4^{2-}$] / ([Ni$^{2+}$]+[WO$_4^{2-}$])</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Supplement of metallic ion by anodic dissolutions</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Use of diaphragm cell with cation-exchange membrane</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Deposition time (hours)</td>
<td>50-120</td>
<td>0.5-2.0</td>
</tr>
<tr>
<td>Deposition thickness (μm)</td>
<td>900-2200</td>
<td>20-50</td>
</tr>
</tbody>
</table>

Fig. 3 Micrometer-scale W-concentration profiles for the samples fabricated by (a) thin-film electrodeposition processes and (b) bulk electroforming process.
Fig. 4 Millimeter-scale W-concentration profiles for the samples fabricated by the bulk electroforming process.

With the conventional thin-film electrodeposition processes, the achievable thickness was at most 100 μm due to the transition from the smooth deposition to the powder deposition. After the transition, the further electrodeposition resulted in the increase of the thickness of the powder layer. It would be impossible for the conventional processes to form the bulk sample. Figure 4 shows the mm-scale W-concentration profiles for the sample obtained by the bulk electroforming process. The sample with average W concentration of 12.9 at% in Fig. 4 was electroformed at the current density of 0.05 A/cm$^2$, with the W ratio in the bath 0.17. The grain size of the bulk sample was 12.0 nm. The sample with average W concentration of 6.9 at% in Fig. 3(b) was electroformed at the current density of 0.05 A/cm$^2$, with the W ratio in the bath 0.075. The grain size was 14.5 nm. The standard deviations of the W concentration are suppressed to approximately 1 at%. The W-concentration gradients are vanishingly small. The bulk electroforming process has successfully overcome the obstacles against the scale-up from micrometer to millimeter thickness.

5. Discussions

The experimental results of the bulk electroforming seem to be fairly good and certainly remind reading audience that the electroforming proceeded under the ideal condition. However, unlike the reproduction of the thin-films plating, the bulk nanocrystalline electroforming was difficult to progress under the equilibrium steady state. The ideal condition of the constant current efficiency and no side reactions were insufficiently satisfied in the real experiments. The current efficiency was monotonically decreased during electroforming. To make matters worse, the ICP-MS of the electrolyte samples revealed that Ni ions in the electrolyte reduced roughly by half. In contrast with these facts, the electroformed bulk nanocrystalline alloy was unreasonably homogeneous. In this discussion, it is described how we cope with the decrease of the current efficiency and why the reduction of the Ni ions did not damage the W-concentration homogeneity of the bulk specimen.

Figure 5 shows the typical progress of the surface morphology during nanocrystalline bulk electroforming. The surface transited from the lower-gross and smooth one to the higher-gross and rough one. Compared to the bulk amorphous electroforming, it was difficult to reduce the surface roughness. It can be speculated that the surface roughness retarded the desorptions of the hydrogen bubbles from the surface. The bubbles inhibited the alloy-deposition reaction and will cause the decrease the current efficiency. The variation of the current efficiency with the thickness is shown in Fig. 6. We measured the weight of the deposited alloy at arbitrary interval $\Delta t$ and stoichiometrically estimated the average current efficiency $\bar{\varepsilon}$ by the following equation:

$$\Delta w_w = \frac{I(1 - \alpha)M_{Ni} + \alpha M_W}{2(1 + 2\alpha)F} \bar{\varepsilon},$$

where, $\Delta w_w$ is the increment of the weight from the previous measurement, and $M_{Ni}$ and $M_W$ is the atomic weight of Ni and W, respectively. Using the estimated $\bar{\varepsilon}$ and eq. (4), the currents for each anode were updated. The histories of the staircase controls of the anode currents are also shown in Fig. 6.

Figure 7(a) shows the experimental and calculated values of the W concentration in the deposit and molar concentrations of nickel and tungstate ions in the electrolyte. The ICP-MS of the electrolyte sample revealed that Ni ions in the electrolyte decreased roughly by half during the 2-mm bulk electroforming. On the contrary, the W concentration in the electroformed bulk specimen does not have a notable gradient. To figure out this discrepancy, the analytical consideration is advanced in the following.
The mass balance equations (1) and (2) are based on the assumption that the Ni and W anodes dissolve at the efficiency of 100%. Now that the ICP-MS has found that Ni ions decreased by half, the current efficiencies of the dissolution reactions on the Ni and W anodes, denoted as $\epsilon_{\text{Ni}}$ and $\epsilon_{\text{W}}$, respectively, should be taken into account. The reconstructed mass balance equations are as follows:

$$L \Delta \left[ \text{Ni}^{2+} \right] = -\frac{1 - \alpha}{2(1 + 2\alpha)} \frac{e_l \Delta t}{F} + \frac{1}{2} \frac{\epsilon_{\text{Ni}} e_{\text{Ni}} \Delta t}{F},$$

(6)

$$L \Delta \left[ \text{WO}_4^{2-} \right] = -\frac{\alpha}{2(1 + 2\alpha)} \frac{e_l \Delta t}{F} + \frac{1}{6} \frac{\epsilon_{\text{W}} e_{\text{W}} \Delta t}{F}.$$  

(7)

The W atomic ratio in the deposit $\alpha$ are roughly proportional to the W molar ratio in the bath $[\text{WO}_4^{2-}]/([\text{Ni}^{2+}]+[\text{WO}_4^{2-}])$ and weakly depend on the sum of the concentrations of the nickel and tungstate ions $[\text{Ni}^{2+}]+[\text{WO}_4^{2-}]$ in the same electrodeposition bath (See appendix A). Therefore, as a first approximation, the W atomic ratio in the deposit $\alpha$ is expressed as:

$$\alpha = k[\text{WO}_4^{2-}]/([\text{Ni}^{2+}]+[\text{WO}_4^{2-}]),$$

(8)

where $k$ is the proportionality constant inherent in the electrodeposition bath.

Assigning eq. (8) to eqs. (6) and (7), and limiting $\Delta t$ to 0 lead to:

$$\frac{d[\text{Ni}^{2+}]}{dt} = -\frac{[\text{Ni}^{2+}] + (1 - k)[\text{WO}_4^{2-}]}{2e_l} \frac{1}{F} \frac{e_{\text{Ni}} e_{\text{Ni}}}{2k}[\text{WO}_4^{2-}]),$$

(9)

$$\frac{d[\text{WO}_4^{2-}]}{dt} = -\frac{k[\text{WO}_4^{2-}]}{2} \frac{[\text{Ni}^{2+}] + (1 + 2k)[\text{WO}_4^{2-}]}{e_l} \frac{1}{F} \frac{e_{\text{W}} e_{\text{W}}}{6}[\text{WO}_4^{2-}]),$$

(10)

This simultaneous differential equation can be solved analytically. The mathematical procedures and the solutions are given in the appendix B. With these differential equations and eq. (8), the variations of the molar concentrations of nickel and tungstate ions in the electrolyte and the W concentration profiles in the deposit can be simulated and utilized for the interpretation of the experimental data.

In Fig. 7(a), the experimental data in the electroforming of the bulk nanocrystalline sample with the average concentration of 6.9 at% are compared to the simulation results. The calculated variation of the molar concentration of nickel ion at the Ni anode current efficiency $\epsilon_{\text{Ni}}$ of 50% shows good fit to the experimental data from ICP-MS. In case of the same Ni anode current efficiency, if the W anode current efficiency $\epsilon_{\text{W}}$ is 100%, the electrolyte is predicted to trend toward the W-rich, and the W concentration in the deposit $\alpha$ is supposed to increase largely as shown by the dotted line in Fig. 7(a). To rationalize the homogeneity of the bulk nanocrystalline sample, it is a good guess that the tungstate ions were supplemented under the moderately low current efficiency. A broken line in Fig. 7(a) is the simulation result at the Ni and W anode current efficiencies $\epsilon_{\text{Ni}}$ and $\epsilon_{\text{W}}$ of 50% and 40%, respectively. The good fit to the experimental data shows that, even if the anode currents are not correct to maintain the mass balance, the W-concentration in the deposit can be stabilized only if the W molar ratio in the bath $[\text{WO}_4^{2-}]/([\text{Ni}^{2+}]+[\text{WO}_4^{2-}])$ happens to be maintained constant. If the Ni and W anode current efficiencies are nearly equivalent, and the initial W molar ratio in the bath is close to the initial W atomic ratio in the deposit $\alpha$, the mass balance in the bath is supposed not to be upset seriously during electroforming.

In other words, an electrolyte with the amount $\alpha([\text{Ni}^{2+}]+\text{WO}_4^{2-})$
Novel Electroforming Process for Bulk Nanocrystalline Ni-W Alloys with Minimizing W-Concentration Gradient and Fluctuation

6. Conclusions

The electroforming system equipped with a diaphragm cell with cation-exchange membrane and three anodes has removed a bottleneck in the scale-up of the electrodeposited Ni-W alloys. The system successfully produced the bulk nanostructured Ni-W alloys with minimizing W-concentration and fluctuation. Mass balance analyses of the metallic ions were carried out by the combination of the experimental results of ICP-MS and the exact solutions of the simultaneous differential equation. The following conclusions can be drawn:

(1) By employing the bulk electroforming process, the standard deviation of W-concentration has been decreased by 30–44%, and the gradient is reduced to roughly one-10th, compared to the conventional thin-film processes.

(2) Homogeneous nanocrystalline Ni-W alloys with the W-concentration fluctuation of approximately ±1 at%, the vanishingly small W-concentration gradients and the thickness above 2 mm have been firstly developed.

(3) The implementation of the nickel and tungstate ions is inevitable to form the bulk Ni-W alloys through electrodeposition. The mass balance analyses suggested that an electrolyte, having the initial W molar ratio in the bath close to the initial W atomic ratio in the deposit, is recommended for the homogeneous bulk electroforming.

Acknowledgement

We would like to thank M. Yokoi in Technology Research Institute of Osaka Prefecture and T. Ikeda in Nomura Plating Co., Ltd. for their helpful advice on the continuous electroplating system and sample fabrication. The samples for EDS analyses were fabricated in the Production Technology Center of Osaka Prefecture University. The authors would like to thank Mr. K. Kitaura and Mr. M. Shoumura for their technical supports.
Appendix A: The relationship between the W atomic ratio in the deposit and the W molar ratio in the bath

In this appendix, we verify the validity of eq. (8). The relationships between the W atomic ratio in the deposit $\alpha$ and the W molar ratio in the bath $[\text{WO}_4^{2-}] / ([\text{Ni}^{2+}] + [\text{WO}_4^{2-}])$ are summarized in Fig. 8(a). It can be seen from Fig. 8(a) that $\alpha$ increases almost linearly at least among the baths constructed by the same researchers. In the bulk electro-forming in this study and electrodepositions by K. Itoh, the W atomic ratios in the deposit were controlled by changing the W molar ratio in the bath with the total concentrations of nickel and tungstate ions $[\text{Ni}^{2+}] + [\text{WO}_4^{2-}]$ kept constant. O. Younes and Gileadi changed the molar concentration of the tungstate ion $[\text{WO}_4^{2-})$ with that of the nickel ion $[\text{Ni}^{2+}]$ kept constant. In the thin-film electrodepositions in this study, the bath temperature was changed to control the W atomic ratio in the deposit, with the molar concentrations of $[\text{Ni}^{2+}]$ and $[\text{WO}_4^{2-}]$ kept constant. Although T. Omi et al. changed both the total concentrations $[\text{Ni}^{2+}] + [\text{WO}_4^{2-}]$ and the W molar ratio $[\text{WO}_4^{2-}] / ([\text{Ni}^{2+}] + [\text{WO}_4^{2-}])$, but the W atomic ratios in the deposit increased almost linearly.

To check how much the W atomic ratio in the deposit $\alpha$ depend on the total concentrations $[\text{Ni}^{2+}] + [\text{WO}_4^{2-}]$, the amount $\alpha([\text{Ni}^{2+}] + [\text{WO}_4^{2-}]) / [\text{WO}_4^{2-}]$ is plotted along the vertical scale. The deviations of $k$ are within ±15%. A simulation assuming of the constant $k$ in eq. (8) can include the local errors in certain range of the W molar ratio in the bath, but the errors cannot affect the global trend of the simulation results. Consequently, it is reasonable to assume eq. (8) to examine the trends of the mass balances.

Appendix B: The solution of the simultaneous differential equation on the mass balance

On the assumption of the linearity between the W atomic ratio in the deposit and the W molar ratio in the bath, the simultaneous differential equation on the mass balance (eq. (6) and (7)) can be analytically solved. Multiplying eq. (10) by 3 plus eq. (9) equals

$$\frac{d}{dt} ([\text{Ni}^{2+}] + 3[\text{WO}_4^{2-}]) = \frac{1}{2} \frac{e_{\text{Ni}} J_{\text{Ni}} + e_{\text{W}} J_{\text{W}} - e t}{F L}. \quad (B\cdot1)$$

Integrating eq. (B\cdot1) and imposing the initial conditions $[\text{Ni}^{2+}] = P_0$, $[\text{WO}_4^{2-}] = Q_0$ at $t = 0$ on the eq. give $[\text{Ni}^{2+}] = \frac{1}{2} \frac{e_{\text{Ni}} J_{\text{Ni}} + e_{\text{W}} J_{\text{W}} - e t}{F L} + P_0 + 3Q_0 - 3[\text{WO}_4^{2-}]. \quad (B\cdot2)$

Assigning eq. (B\cdot2) to eq. (10) and denoting $[\text{WO}_4^{2-}] = y$ gives

$$\frac{dy}{dt} = -cy + b + d. \quad (B\cdot3)$$

The constants $a$, $b$, $c$ and $d$ are the functions of the process parameters:

$$a = \frac{e_{\text{Ni}} J_{\text{Ni}} + e_{\text{W}} J_{\text{W}} - e t}{4(k-1)F L}, \quad b = \frac{P_0 + 3Q_0}{2(k-1)}, \quad c = \frac{ke}{4(k-1)F L}, \quad d = \frac{e_{\text{W}} J_{\text{W}}}{6FL}. \quad (B\cdot4)$$

Solving eq. (B\cdot3) for $y$ leads

$$y = \varphi \left( \frac{dy}{dt} \cdot t + \psi \left( \frac{dy}{dt} \right) \right). \quad (B\cdot5)$$

where,

$$\varphi(p) = -a \left( 1 - \frac{c}{p - (d - c)} \right), \quad \psi(p) = -b \left( 1 - \frac{c}{p - (d - c)} \right), \quad p = \frac{dy}{dt} = \frac{d[\text{WO}_4^{2-}]}{dt}. \quad (B\cdot6)$$

Eq. (B\cdot5) is called d’Alembert’s differential equation. Differentiating eq. (B\cdot5) with respect to $t$ leads

$$p = \varphi(p) + t\varphi'(p) \frac{dp}{dt} + \psi(p) \frac{dp}{dt}. \quad (B\cdot7)$$

Looking upon $t$ as the function of $p$ and solving eq. (B\cdot7) for $dt/dp$ give

$$\frac{dt(p)}{dp} + \varphi(p) - p \varphi(p) = 0. \quad (B\cdot8)$$

This is the first order normal differential equation that can be solved using the variation of parameters. The exact solutions are given in an implicit form using the parameter $p = d[\text{WO}_4^{2-}] / dt$:

$$t(p) = \left\{ \begin{array}{ll}
\frac{b}{a} \left[ p - (d - c) \right] / p - \beta \left[ p_0 - \beta \right]^{1-r} / p - \gamma \left[ p_0 - \gamma \right]^{1+s} - b / a & \text{if } t + b / a > 0 \\
\frac{b}{a} \left[ p - (d - c) \right] / p - \beta \left[ p_0 - \beta \right]^{1-r} / p - \gamma \left[ p_0 - \gamma \right]^{1+s} - b / a & \text{if } t + b / a < 0
\end{array} \right. \quad (B\cdot9)$$

where, $|A|$ is the absolute value of $A$, and the parameters $\beta$, $\gamma$, $r$ and $s$ are expressed as

$$\beta = -(a - d + c) + \sqrt{(a - d + c)^2 + 4ad}/2, \quad \gamma = -(a - d + c) - \sqrt{(a - d + c)^2 + 4ad}/2, \quad r = \frac{\beta}{\gamma - \beta}, \quad s = \frac{\gamma - (d - c)}{\gamma - \beta}. \quad (B\cdot10)$$
When a certain value of $p$ is assigned to eq. (B·9), the time $t$ is determined, and then $[\text{WO}_4^{2-}]$ is known by eq. (B·5) $([\text{WO}_4^{2-}] = \psi(p)t + \psi(p))$, and subsequently $[\text{Ni}^{2+}]$ is derived from eq. (B·2). By assigning a series of values of $p$ to eq. (B·9) and utilizing eq. (B·2) and (B·5), the variation of $[\text{WO}_4^{2-}]$ and $[\text{Ni}^{2+}]$ with the time $t$ can be traced. At the same time, the variation of the W atomic ratio in the deposit with the time $t$ can be traced using eq. (8). The increment of deposited thickness $\Delta D$ during the time $\Delta t$ is evaluated by

$$\Delta D = \frac{\Delta w_a}{\sigma_a S} = \frac{eI}{2(1+2\alpha)FS} \cdot \frac{(1-\alpha)M_{\text{Ni}} + \alpha M_{\text{W}}}{\sigma_0 + \kappa \alpha} \Delta t,$$

(B·11)

where, $S$ is the deposited area and $\sigma_a$ is the density of the alloy $\text{Ni}_{1-x}\text{W}_x$, which is roughly estimated by $\sigma_a = \sigma_0 + \kappa \alpha = 15.6\alpha + 8.87$ (g/cm$^3$). The deposited thickness $D$ (i.e. the distance from substrate) at the time $t$ is numerically derived by the integration of eq. (B·11),

$$D(t) = \int_0^t \frac{eI}{2(1+2\alpha)FS} \cdot \frac{(1-\alpha)M_{\text{Ni}} + \alpha M_{\text{W}}}{\sigma_0 + \kappa \alpha} \, dt.$$  

(B·12)

The $[\text{WO}_4^{2-}]$, $[\text{Ni}^{2+}]$, $\alpha$ as a function of $D$ are calculated through above procedures using the experimental process parameters for both the thin-film electrodeposition processes and the bulk electroforming process, and drawn in Fig. 7(a) and (b).

REFERENCES

13) JP2001158998.