Comparison of Tensile Properties of Bulk Nanocrystalline Ni–W Alloys Electrodeposited by Direct, Pulsed, and Pulsed-Reverse Currents

Isao Matsui* and Naoki Omura

Structural Materials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463–8560, Japan

The effects of current types on the microstructure and tensile properties of electrodeposited bulk nanocrystalline Ni–W alloys were studied. We electrodeposited bulk Ni–W alloys using direct current, pulsed current, and pulsed-reverse current. We measured the W content of the resulting samples to be in the range of 0.8–2.2 at%. An increase in the peak current density or the use of a reverse current reduced the W content. The reduction of W content increased the grain size from 26 to 40 nm. The hardness and yield strength increased as the grain size decreased. However, tensile elongation showed no dependence on grain size or W content. Most alloys exhibited a similar uniform elongation of approximately 5%, while the local elongation varied from 0.1% to 6.9%. The application of a pulsed current increased the peak current density and reduced the tensile elongation. The use of a reverse current stripped the surface of deposits formed during electrodeposition, resulting in higher tensile elongation at the same peak current densities. The results of this study indicate the effectiveness of a reverse current in electrodeposition for adjusting solute content and reducing processing defects.


(Received August 15, 2017; Accepted October 27, 2017; Published November 27, 2017)

Keywords: electrodeposition, nanocrystalline alloys, nickel–tungsten, pulsed current, tensile properties

1. Introduction

Nanocrystalline materials include polycrystalline materials that have fine structures with grain sizes less than 100 nm. Grain refinement into the nanocrystalline regime considerably increases flow stress according to the Hall–Petch relationship. Over the past 25 years, the unusual mechanical properties of nanocrystalline structures have generated great interest in terms of fundamental scientific research and for their technological applications. Electrodeposition has been developed as a preferred technique for producing bulk quantities of these materials. Over the course of research into electrodeposition, many efforts have demonstrated the relationships between grain size and strength and/or hardness. Although electrodeposited bulk nanocrystalline metals and alloys are inherently strong, they do suffer from a major drawback in terms of their limited ductility. This limitation is typically related to either a lack of resistance to plastic localization or to processing defects.

Several recent studies have overcome the difficulty of producing artifact-free electrodeposits and improved the ductility of bulk nanocrystalline Ni alloys. For example, Matsui et al. reported bulk nanocrystalline Ni–W alloys, which exhibited a high elongation of 13%. Brooks et al. produced many bulk nanocrystalline Ni and Ni–Fe alloys with an elongation of approximately 8%. However, the ductility achieved in these cases remains inadequate. In the above reports, different types of applied current were used. For example, Matsui et al. used a direct current, while Brooks et al. applied a pulsed current (Fig. 1(a)). Pulse electrodeposition yields finer grains than direct electrodeposition. One reason for this is that a higher instantaneous current density is possible during pulse electrodeposition, which results in an increased nucleation rate leading to the formation of finer grains. A pulsed-reverse current (Fig. 1(b)), features a stripping time in the pulse deposition cycle, which can selectively dissolve protrusions on the metal surface, resulting in a more uniform surface. Although different current characteristics in electrodeposition can affect the tensile properties of the resulting electrodeposited bulk nanocrystalline Ni alloys, there have not yet been any reports of this relationship. Therefore, the main goal of this study was to electrodeposit bulk nanocrystalline Ni alloys with the use of these currents types and to investigate the effects on the resulting microstructure and tensile properties. We electrodeposited bulk nanocrystalline Ni–W alloys by direct current, pulsed current, and pulsed-reverse currents. The microstructure and tensile properties of the resulting alloys were examined.

* Corresponding author, E-mail: i-matsui@aist.go.jp

Fig. 1  Waveforms of (a) pulsed and (b) pulsed-reverse current.
2. Experimental Procedure

One type of deposition bath was prepared and the composition is given in Table 1. All samples were deposited onto copper substrates of commercial purity with the use of two counter electrodes based on nickel plate (99.98%) and tungsten rods (99.95%) in a 1-L system. Full details of the deposition system have been described in a previous paper. All the electrodeposition experiments were performed at a bath temperature of 55°C and a pH of 4.0. The pH values of the solutions during electrodeposition were maintained by the addition of drops of 1.0 mol/L sulfamic acid and 5.0 mol/L sodium hydroxide.

The electrodepositions were performed with the use of a direct current, pulsed current, and pulsed-reverse current. The direct current was defined by a current density and the density was set to be 20 mA/cm². The waveforms of (a) pulsed and (b) pulsed-reverse current were defined by a positive peak current density \(I_p\), negative peak current density \(-I_p\), current on-time \(T_{on}\), and current off-time \(T_{off}\), as illustrated in Fig. 1. Also, the frequency \(F\) and duty ratio \(D\) were calculated based on the current on-time and off-time as follows:

\[
F = 1/(T_{on} + T_{off}) \tag{1}
\]

\[
D = T_{on}/(T_{on} + T_{off}) \tag{2}
\]

The average current densities of the pulsed current and pulsed-reverse current \(I_{Ave}\) were calculated in accordance with the following relationship:

\[
I_{Ave} = (I_p \cdot T_{on} - I_n \cdot T_{off})/(T_{on} + T_{off}) \tag{3}
\]

Details of the conditions are as shown in Table 2. In setting these conditions, the average current densities were in the range of 17–20 mA/cm². The target thickness of the electrodeposits was typically 1 mm for mechanical testing.

The W content of the electrodeposited Ni–W alloys was determined by energy-dispersive X-ray spectrometry (EDX, Shimadzu EDX-8000). The C and S contents were quantified by infrared absorption after combustion in a high-frequency induction furnace (LECO CS–LS600). X-ray diffraction (XRD, Rigaku MiniFlex600) analysis was performed with Cu Ka radiation to confirm the orientation and estimate the grain sizes. Transmission electron microscope (TEM) specimens were prepared by ion milling and examined with a JEOL JEM-2010, operated at 200 kV for observation of the microstructure. To evaluate the hardness of the electrodeposits, micro-Vickers hardness tests were conducted on bulk samples with a load of 500 g for 10 s. Each reported data point represents the average value of at least 12 indentations. 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 for the tensile tests. The copper substrate and affected layer were removed by a surface grinding machine. The tensile 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 average of three measurements.

3. Results and Discussion

3.1 Electrodepositions

One important effect in pulsed electrodeposition techniques is the modification of the diffusion layer. Under pulse-deposition conditions, the Nernst diffusion layer is split into two layers, namely a pulsating diffusion layer and a stationary diffusion layer, as described in Ref. 23). Maintaining the ion concentration at the cathode surface is important. The rapid method for selection of discharge time \(t_d\) of the double layer in relation to the applied peak current density is given below.

\[
t_d = 120/I_p \tag{4}
\]

The conditions for pulse electrodeposition, based on eq. (4), were determined and the resulting correlation diagram is shown in Fig. 2. In this diagram (Fig. 2), the solid line...
shows the discharge time calculated from eq. (4). By setting the average current density, the duty ratio and on-time were determined. In Fig. 2, the current on-times (dashed line) were determined such that the average current density was set to be 20 mA/cm². The frequency (dotted line) was also determined by setting the on- and off-times.

We electrodeposited six types of specimens under the conditions given Table 2. These samples were labeled by the used current, duty ratio, and frequency: DC, PC0.5_1.7, PC0.2_20, PC0.5_20, PRC0.2_20, and PRC0.5_20. The sample PC0.5_1.7 satisfies the conditions shown in Fig. 2, while the other samples are not satisfied. For all electrodeposits, a high current efficiency, in the range 92%–95%, was confirmed. Current types have no effect on the current efficiency of deposition bath.

### 3.2 Effects on microstructure

The W content of each sample is summarized in Table 3. The W content of the alloys decreased as the peak current density was increased from 20 to 100 mA/cm². Furthermore, the application of a reverse current decreased the W content, similarly to that of previous reports26): the reverse current preferentially removed W atoms, rather than Ni atoms, from the electrodeposits. Thus, reverse-pulsing is an effective method for fine-tuning the W content.

We electrodeposited six types of specimens under the conditions given Table 2. These samples were labeled by the used current, duty ratio, and frequency: DC, PC0.5_1.7, PC0.2_20, PC0.5_20, PRC0.2_20, and PRC0.5_20. The sample PC0.5_1.7 satisfies the conditions shown in Fig. 2, while the other samples are not satisfied. For all electrodeposits, a high current efficiency, in the range 92%–95%, was confirmed. Current types have no effect on the current efficiency of deposition bath.

![Comparison of Tensile Properties of Bulk Nanocrystalline Ni–W Alloys Electrodeposited by Direct, Pulsed, and Pulsed-Reverse Currents](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>W (at%)</th>
<th>d (nm)</th>
<th>HV (GPa)</th>
<th>σ₀.2% (GPa)</th>
<th>σ₀.2% (GPa)</th>
<th>σ₀.2% (GPa)</th>
<th>εUniform (%)</th>
<th>εLocal (%)</th>
<th>εTotal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>2.2</td>
<td>28</td>
<td>4.91 ± 0.01</td>
<td>1.09 ± 0.03</td>
<td>1.57 ± 0.01</td>
<td>4.9 ± 0.1</td>
<td>6.9 ± 3.5</td>
<td>11.7 ± 3.6</td>
<td></td>
</tr>
<tr>
<td>PC0.5_1.7</td>
<td>1.6</td>
<td>26</td>
<td>5.05 ± 0.03</td>
<td>1.08 ± 0.03</td>
<td>1.65 ± 0.01</td>
<td>4.9 ± 0.4</td>
<td>0.9 ± 0.7</td>
<td>5.9 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>PC0.2_20</td>
<td>1.3</td>
<td>30</td>
<td>4.80 ± 0.01</td>
<td>1.06 ± 0.04</td>
<td>1.63 ± 0.01</td>
<td>5.2 ± 0.3</td>
<td>3.3 ± 3.8</td>
<td>8.5 ± 3.9</td>
<td></td>
</tr>
<tr>
<td>PC0.5_20</td>
<td>1.5</td>
<td>29</td>
<td>4.91 ± 0.03</td>
<td>1.01 ± 0.02</td>
<td>1.50 ± 0.02</td>
<td>2.2 ± 0.2</td>
<td>0.1 ± 0.0</td>
<td>2.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>PRC0.2_20</td>
<td>0.8</td>
<td>40</td>
<td>3.95 ± 0.02</td>
<td>0.77 ± 0.04</td>
<td>1.10 ± 0.03</td>
<td>4.7 ± 0.1</td>
<td>4.4 ± 1.8</td>
<td>9.1 ± 1.7</td>
<td></td>
</tr>
<tr>
<td>PRC0.5_20</td>
<td>1.3</td>
<td>33</td>
<td>4.44 ± 0.03</td>
<td>0.85 ± 0.03</td>
<td>1.28 ± 0.02</td>
<td>5.2 ± 0.1</td>
<td>6.9 ± 0.7</td>
<td>12.0 ± 0.8</td>
<td></td>
</tr>
</tbody>
</table>

![Comparison of Tensile Properties of Bulk Nanocrystalline Ni–W Alloys Electrodeposited by Direct, Pulsed, and Pulsed-Reverse Currents](image)

Fig. 3 Typical bright-field TEM images of (a) sample PC0.2_20 and (b) sample PRC0.2_20.
size of approximately 30 nm. The introduction of a reverse current increased the grain sizes up to approximately 50 nm. According to electrorystallization theory, a high cathodic overpotential, usually induced by a high current density, promotes the nucleation process and results in fine-grained deposits. However, the grain sizes of the Ni–W alloys did not decrease as the peak current density was increased from 20 to 100 mA/cm² (Table 3). In fact, contrary to theory, the Ni–W alloy had finer grains as the W content increased from 0.8 to 2.2 at%, irrespective of the current density. This behavior is consistent with a reported relationship between grain size and W content in electrodeposited Ni–W alloys. Nanostructured metals are generally unstable; their grains grow rapidly even at low temperatures. Alloying is an effective way to improve stability and maintain the nanocrystalline structure. We speculated that high current densities increase the nucleation rate but do not necessarily result in fine-grained deposits.

3.3 Effects on mechanical properties

The hardness of the samples was examined with a micro-Vickers hardness test and the results are described in Table 3. A homogeneous hardness was observed in each sample: the standard deviation of the hardness values was less than 0.03 GPa. The hardness values were in the range of 3.95–5.05 GPa. This increase in the hardness was attributed to grain refinement and increased according to the Hall–Petch relationship.

Typical stress-strain curves of bulk nanocrystalline Ni–W alloys are shown in Fig. 5, and the obtained results are listed in Table 3. The yield and tensile strength increased as the grain size decreases. However, the elongation was not related to grain size but instead depended on the applied current type. The samples electrodeposited with use of pulse current exhibited lower total elongation compared with that of the sample DC (Fig. 5(a)). The sample PC₀.5₂₀ showed a particularly poor uniform elongation of 2.2%, although the other samples showed uniform elongation of 4.7%–5.2%. In contrast, the samples PRC₀.2₂₀ and PRC₀.5₂₀ exhibited higher total elongation than that of samples PC₀.2₂₀ and PC₀.5₂₀, respectively. Furthermore, the standard deviation in the local elongation of the samples PRC₀.2 and PRC₀.5 at 1.8% and 0.7%, respectively, was lower than that of that samples DC and PC₀.2₂₀.

Unlike the above constant values of 5.0%, the sample PC₀.5₂₀ showed a lower uniform elongation of 2.2%. In nanocrystalline metals, the lack of elongation is most often related to processing defects. As mentioned in section 3.1, to obtain electrodeposits free from processing defects, maintaining the ion concentration at the cathode surface is important. The discharge time of the double layer can be estimated using the eq. (4). The estimated times for adequate replenishment of ions at the cathode surface was 300 ms as applying the peak current density of 40 mA/cm². On the contrary, the sample PC₀.5₂₀ was electrodeposited at a peak current density of 40 mA/cm² and current off-time of 25 ms. The imposed off-times were too short, which resulted in a considerable decrease in the concentration of cations in the pulsating diffusion layer. This low concentration contributed to side reactions, such as hydrogen evolution and defect formation. On the other hand, although the PC₀.2₂₀ was also electrodeposited with short off-time of 40 ms against estimated value of 120 ms, the sample showed a good total elongation of 8.5%. This indicates the modification in the eq. (4) for producing the defect free nanocrystalline metals by a pulse electrodeposition.

Pulse-reverse electrodeposition features a reverse current
that can dissolve the surface. The samples PRC\textsubscript{0.2,20} and PRC\textsubscript{0.5,20} were prepared by the application of a reverse current of 4 mA/cm\textsuperscript{2} to the pulsed current in the conditions used to fabricate the samples PC\textsubscript{0.2,20} and PC\textsubscript{0.5,20}. Comparison between PC\textsubscript{0.5,20} and PRC\textsubscript{0.5,20} show that the introduction of a stripping time improved the uniform elongation from 2.2\% to 5.2\%. The improvement indicate that the intermittent dissolution induced by the reverse current removed processing defects, which formed through side reactions. Although the electrodeposition-time required to obtain bulk specimens increased owing to the dissolution, the reverse current enabled defect-free electrodeposition without restrictions on the electrodeposition conditions, as shown in Fig. 2.

Tensile tests for this study indicated that most alloys exhibited a similar uniform elongation of approximately 5.0\% independent of grain size or W content (Table 3). Brooks et al.\textsuperscript{16)} reported similar results on electrodeposited nanocrystalline Ni and Ni–Fe alloys that uniform elongation was independent of microstructure over the grain size range of 10–80 nm and the values were relatively constant at 4.3\%. They also suggested that the constant uniform elongation was due to limited dislocation storage capacity in the grain interiors of nanocrystalline metals. More deep understanding of uniform elongation require the further research on dislocation source in the grain interiors by high resolution TEM observations in the future.

Although electrodeposited samples, except sample PC\textsubscript{0.5,20}, showed constant uniform elongation, the local elongation varied from 0.9\% to 6.9\%. One of the most convincing study of the fracture mechanisms in nanocrystalline metals is the one by Kumar el al.\textsuperscript{44)} on electrodeposited Ni with grain size around 30 nm. For instance, in the first stage of loading, the as-formed flat interfacial nanovoids gradually transform into pore. Plastic strain is localized and gives rise to neck formation. Then, ductile fracture occurs through coalescence of pores. According to this model, a decrease in local elongation causes early coalescence of pores. We can suggest a possibility that condition of current cause a change to promote pore propagation. To make this discussion clearer, it is required that future microstructural studies on the fracture processes of nanocrystalline metals including investigation of effect of current condition on not only grain size but also grain shapes.

4. Conclusions

In this study, we have demonstrated the effects of different current types on the microstructures and tensile properties of electrodeposited bulk nanocrystalline Ni–W alloys, with the use of direct, pulse, and pulse-reverse electrodeposition techniques. A pulsed current resulted in no obvious change in grain size and texture compared with the effects of direct current. However, a pulsed-reverse current increased the grain size and orientation of the (200) plane owing to a decrease of W content induced by the reverse current. The Ni–W alloys prepared with a pulsed current at 20 Hz exhibited poor tensile elongation of 2.3\%, while the alloys prepared at 1.67 Hz showed a better tensile elongation of 5.9\%. This behavior can be explained by the discharge time of the double layer as estimated from eq. (4). These results and our discussion highlight the importance of determining the current off-time to obtaining high-tensile elongation. By incorporating a stripping time into the pulse cycle at 20 Hz, we produced bulk nanocrystalline Ni–W alloys with a high local elongation of 4.4\%–6.9\%, together with a uniform elongation of approximately 5\%. The improvement of uniform elongation was attributed to the removal of processing defects that formed in side reactions. The results of pulse-reverse electrodeposition indicate that application of intermittent dissolution during electrodeposition produces defect-free bulk nanocrystalline Ni alloys.

Acknowledgments

This study was financially supported by the NAGAI Foundation for Science & Technology. The authors are also grateful to Ms. C. Otomo (AIST) for her technical help.

REFERENCES


25) J. C. Puipe and F. Leaman: Theory and Practice of Pulse Plating,