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Development of an Electrodeposition Process for Producing Bulk Nanocrystalline Metals with High Strength and High Ductility

Isao Matsui

January 2014

Doctoral Thesis at Osaka Prefecture University
Acknowledgements

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Isao Matsui, January 2014
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1 Introduction

1.1 Nanocrystalline metals

It is now over 25 years since Herbert Gleiter [1] presented the first concepts for developing nanocrystalline materials (i.e., materials with a grain size of less than 100 nm) and the potential for producing special properties. These early observations or predications were:

- lower elastic moduli than for conventional grain size materials – by as much as 30%–50%;
- very high hardness and strength – hardness values for nanocrystalline pure metals (~10 nm grain size) that are 2–10 or more times higher than those of larger grained (>1 µm) metals;
- increased ductility – perhaps even superplastic behavior – at low homologous temperatures in even normally brittle ceramics or intermetallic with nanoscale grain sizes, believed to be caused by grain boundary, diffusional deformation mechanisms.

Since that time, the field of nanocrystalline materials has flourished over the last two decades, owing to the considerable interest in this topic and the scientific and technological importance. In fact, a significant number of review articles have been published [1-13]. Table 1 shows the important review articles, along with their citation (counted by Scopus on Oct., 31, 2013). In particular, the first paper published in 1989 year by Gleiter [1] has been cited over 2000 times. Also, the review article published in 2006 by Meyers et al., [12] which addressed the mechanical properties of nanocrystalline metals, has already been cited over 1000 times.
Table 1.1 Summary of principal reviews articles on UFG and nanocrystalline metals (only first author named).

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Title</th>
<th>Citation</th>
</tr>
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<tbody>
<tr>
<td>Valiev [8]</td>
<td>2000</td>
<td>Bulk nanostructured materials from severe plastic deformation</td>
<td>3091</td>
</tr>
<tr>
<td>Kumar [10]</td>
<td>2003</td>
<td>Mechanical behavior of nanocrystalline metals and alloys</td>
<td>905</td>
</tr>
<tr>
<td>Meyers [12]</td>
<td>2006</td>
<td>Mechanical properties of nanocrystalline materials</td>
<td>1130</td>
</tr>
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Fig. 1.1 Schematic view of classification for polycrystalline materials according to their grain size. The volume fraction of grain boundary drastically increases as grain sizes decrease to nanometer range.

Research on nanoscale materials has developed widely in recent years, and the terminology needs some clarification. The two terms actively used within this field are ultrafine-grained (UFG) and nanocrystalline materials, and it is useful to provide a clearer definition of these two terms. Polycrystalline materials with nano scale (2–100 nm) are termed “nanocrystalline materials”. At the upper limit of this regime, the term “UFG materials” is often used (grain sizes of 100–1000 nm). Schematic view of these classifications is shown in Fig. 1.1. Nanocrystalline materials are structurally characterized by a large volume fraction of grain boundaries, which may significantly alter their physical, mechanical, and chemical properties.
in comparison with conventional coarse-grained polycrystalline materials, which have grain sizes usually in the range 10–300 µm. Assuming the grains have the shape of spheres or cubes, the volume fraction of grain boundaries in the nanocrystalline material may be estimated as $3\Delta/d$ (where $\Delta$ is the average interface thickness and $d$ is the average grain diameter). The volume fraction of interface can be as much as 50% for 5 nm grains, 30% for 10 nm grains, and 3% for 100 nm grains, assuming an interface thickness of 1 nm [14].

Although the mechanical and physical properties of all crystalline materials are determined by several microstructural parameters, the average grain size of the material generally plays a very significant, and often a dominant role. The strength of polycrystalline materials is related to the grain size, $d$, through the Hall–Petch equation [15, 16], which states that the yield stress, $\sigma_y$, is given by

$$\sigma_y = \sigma_0 + k \cdot d^{1/2}$$  \hspace{1cm} (1.1)

where $\sigma_0$ is termed the friction stress and $k$ is a constant of yielding. A schematic drawing of this behavior is given in Fig. 1.2. The strength drastically increases with a reduction in the grain size to nanometer range, according to Hall–Petch equation. This high level of strength has led to an increasing interest in fabricating materials with extremely small grain sizes. The mechanism for the Hall–Petch behavior in conventional grain size materials has been generally explained by a pile-up of dislocations in one grain producing a stress concentration that activates a dislocation source in the adjacent grain [17]. Alternative mechanisms have involved the activation of grain boundary dislocation sources [18] or elastic and plastic incompatibility stress between neighboring grains [19]. All these models involve dislocation motion or generation. At the smallest grain sizes (~10 nm), it is believed dislocation activity ceases. At these critical grain sizes, the dislocation image forces are sufficient to eliminate dislocations by moving them into the grain boundaries. In addition, dislocation multiplication mechanisms such as the Frank–Read source would require stresses of the order of the
theoretical strength. It is predicted therefore that dislocations are absent in the nanocrystals with the critical size (~10 nm), and deformation must involve other than conventional dislocation creation and motion. This transition is usually captured as a maximum in strength in the form of Hall–Petch plots [20].

Fig. 1.2 Schematic representation of the variation of yield stress as a function of grain size in coarse-grained, UFG, and nanocrystalline metals and alloys.

1.2 Mechanical behavior of nanocrystalline metals

The most measured mechanical property of nanocrystalline metals as function of grain size is hardness (because of the difficulties in preparing nanocrystalline materials of sufficient size for the standard mechanical tests). The large number of experimental studies of the hardness of nanocrystalline metals have been reported [21]. It is clear from the data that the hardness of nanocrystalline metals can be much higher than conventional grain sized counterpart.
While hardness was the main mechanical properties measured in many of the earlier studies of nanocrystalline metals, tensile tests have also been made. Fig. 1.3 shows the tensile properties for a variety of nanocrystalline metals [22-39]. Although high yield strength is apparently achieved by decreasing the grain size to nanometer regime, the data resulted in severe underestimates of strength [23, 40], compared to the value predicted by Tabor relation [41]. On the other hand, it was found that good agreement was observed between yield stresses in compression and hardness divided by 3 following the Tabor relation [42]. The asymmetry in tension and compression may be explained by the presence of defects such as voids or incomplete particulate bonding. Since compression tests are less sensitive to such defects as pores and cracks. Fig. 1.3a shows relationship between yield strength and the elongation of nanocrystalline metals, and no relation between those two values is observed.
Fig. 1.3b shows the Hall–Petch plot of yield strength in nanocrystalline metals. Although, in nanocrystalline Cu and Ni, their strength values roughly increase with decrease in the grain size, following the Hall–Petch relationship, the values are scattered against the grain sizes. Elongation in tension is plotted vs. grain size in Fig 1.3c for a variety of metals. It is clear that for most metals with grain sizes below ~30 nm the elongation values are scatter and very low (typically less than 10%). There are only small reports that achieved the desire combination of high tensile strength and high tensile ductility.

There are two important proposals that addressed the cause of scatter in tensile properties. First, Ma [43] pointed out that nanocrystalline samples in early studies was very small and thin (<50 µm). Thus, a minor surface flaw or even roughness becomes a threat for the initiation of sufficiently large cracks to induce catastrophic failure, with or without flaws and porosity inside the bulk. In fact, the study that investigated the effect of thickness on the ductility indicated that bulk specimens are needed to evaluate the tensile properties [44]. The analysis of relationship between elongation and thickness based on reported data also indicated the importance of bulk specimens to evaluate intrinsic characteristics [45]. Second, Koch et al. [46] pointed to that perfect artifact-free bulk samples are difficult to obtain in the case of “two-step” processing, which requires a subsequent consolidation step. Compacted metals often contain an artifact. Moreover, it is difficult to obtain theoretical density without coarsening, through consolidation step [47, 48]. Even if theoretical densities are reached, particulate bonding may be weak and a favored location for fracture under applied stress. “One-step” processing methods which do not require a consolidation step are more likely to provide nanocrystalline metals with plasticity.

In summary, the strength and hardness values of nanocrystalline metals can be much larger than those of conventional grain sized metals. Asymmetries in yield strength measured by compression vs. tensile tests can sometimes be attributed to processing artifacts. In addition,
most metals with grain sizes below ~30 nm shows the limited elongation to failure less than 2%–3%. These behavior would be influenced by defects from processing [43, 46] and this area requires further improvements.

1.3 Fabrication process of nanocrystalline metals

Nanocrystalline metals and alloys can be prepared either by consolidating small clusters or breaking down the polycrystalline bulk material into crystalline units with dimensions of nanometers. These approaches have been classified into bottom-up and top-down. Also, the fabrication processes have been classified into “two-step” and “one-step” process, according to with or without a consolidation step [49]. In this section, the five most common fabrication methods, which have been developed to reduce the grain size to nanometer range, are introduced. Subsequently, the appropriate fabrication process to produce bulk nanocrystalline metals with plasticity will be discussed.

1.3.1. Inert-gas-condensation

The inert gas condensation method for the processing of nanocrystalline materials has its precursor the studies in Japan on the formation of ultrafine particles. Much of this work has been summarized by Uyeda [50]. It was pointed out that the interest in this area was stimulated by a paper published by Kubo [51] in which he predicted that ultrafine metal particles should exhibit physical properties that would be very different from those of their bulk counterpart. These methods were used by Gleiter and co-workers [1] whose studies of the structure and properties of the consolidated nanocrystalline materials stimulated the interest in the filed as it now exists. Fig. 1.4 shows schematic of inert gas-condensation method. The system consists of evaporation a metal (by resistive heating, radio-frequency,
heating, sputtering, electron beam heating, laser/plasma heating, or ion sputtering) inside a chamber that is evacuated to a very high vacuum and then backfilled with a low pressure inert gas like helium. The evaporated atoms collide with the gas atoms inside the chamber, lose their kinetic energy, and condense in the form of small particles. More details of the techniques are given in Refs. [12] and [49].

![Schematic drawing of the inert gas condensation technique for production of nanoscale powder](image)

Fig. 1.4 Schematic drawing of the inert gas condensation technique for production of nanoscale powder [49].

A great deal of the early work on mechanical properties of nanocrystalline materials used the inert gas condensation technique. In particular, Weertman, Siegel, and co-workers [40, 52-55] have used materials produced by this method. They were the first systematic studies on the mechanical properties of nanocrystalline Cu and Pd. Although this method allows the synthesis of a variety of nanocrystalline materials, the peak densities of the as-compacted metal samples have been measured with values of ~98.5% of bulk density. Thus, it has been
not overcome the challenge that porosity has a profound effect on the mechanical strength, especially in tension.

1.3.2. Mechanical attrition

The ball milling of powders (mechanical attrition) produces nanostructured materials by the structural disintegration of coarse-grained structure as a result of severe plastic deformation (Fig. 1.5). The ball milling of powders can be divided into two categories: first, the milling of elemental or compound powders is mechanical milling; second, the milling of dissimilar powders is mechanical alloying, in which material transfer occurs. The details of the mechanical attrition processes, equipment used, etc., have been covered in a number of reviews [56-59], and will not be repeated here.

As a “two-step” processing method, in general the powders formed to mechanical attribution with a nanocrystalline internal microstructure require a compaction step to obtain bulk specimens for mechanical testing and for structural applications. The consolidation problem, which good atomic bonding between the particulates along with the complete inter-particle bonding should be done without significant coarsening, is remained.

Fig. 1.5 Mechanical milling as a means of synthesis of nanostructured material.
1.3.3. Electrodeposition

The electrodeposition technique has significant advantages over other methods for synthesizing nanocrystalline materials: (1) potential of synthesizing large variety of nano-grain materials such as pure metals, alloys, and composite systems with grain sizes as small as 20 nm; (2) low cost; (3) high production rates; (4) few size and shape limitations; and (5) high probability of transferring this technology to existing electroplating and electroforming industries [12]. The fundamental knowledge of electroplating, which help us in conducting an electrodeposition, have been summarized in Ref. [60], and the mechanical properties of electroplated thin film have also been reviewed in Ref. [61].

Over the past few years, Erb et al. [62] have studied the processes, structure, and properties of electrodeposited nanocrystalline Ni. Furthermore, corporation of Erb and Integran Technologies Inc. have developed the electrodeposition system as a fabrication process of bulk nanocrystalline metals [44], and they have provided good quality nanocrystalline samples, which showed a plastic deformation, with researcher in the world. In some cases, electrodeposition technique can yield porosity-free finished products that do not require subsequent consolidation processing. However, it is a complex process: electrodeposition parameters include bath composition, pH, temperature, overpotential, bath additives, etc., while important microstructural features of the substrate are grain size, crystallographic texture dislocation density, and internal stress. While electrodeposition is a “one-step” process for producing nanocrystalline microstructures, artifacts are possible. Trapped impurities at the grain boundaries from bath additives can be a source of embrittlement. In some systems high internal stresses can be generated during electrodeposition which can cause cracking [34]. Therefore, while electrodeposition is a powerful method for producing nanocrystalline metals, the processing must be optimized to produce bulk nanocrystalline metals with high strength and high ductility.
1.3.4. **Vapor deposition**

Vapor deposition processes such as sputtering, electron beam evaporation, and pulse laser ablation can provide essentially artifact free nanocrystalline materials to finest grains sizes (<10 nm) [63]. However, the samples prepared by vapor deposition are typically limited to thin films. Therefore, they are not of interest for production of bulk samples for mechanical testing or applications.

1.3.5. **Severe plastic deformation**

Severe plastic deformation breaks down the microstructure into finer and finer grains [8, 64]. These methods include high pressure torsional straining (HPT), equal channel angular pressing (ECAP), multiple forging, accumulate roll bonding (ARB), friction stir welding, and etc. With the exception of ball milling of powders, these techniques can be classified as “one-step” processes since bulk materials are obtained and therefore do not need particulate consolidation. Among these techniques, HPT can regularly produce average grain sizes below 100 nm [65]. A small sample, in the form of a disk, is held under a high pressure and then subjected to torsional straining. The samples produced by HPT are typically limited in size, with maximum disk diameters of ~20 mm and thickness of ~1mm.

1.3.6. **Crystallization from amorphous solids**

Crystallization of amorphous precursors can be used to obtain nanocrystalline materials as another “one-step” process. Potential difficulties with this method include the possible residual amorphous material that may be present and affect the inherent mechanical properties of the sample. Another major problem is that many crystallized amorphous alloys contain brittle intermetallic phases.
As said before (section 1.2), it was suggested that “one-step” processing and bulk specimens are required to prepare the nanocrystalline metals with plasticity [43, 46]. From a viewpoint of above two points, the features of the common fabrication processes of nanocrystalline metals are summarized in Table 1.2. Among these methods, it is apparent that the electrodeposition is the most reasonable “one-step” process to produce the bulk specimens with grain sizes less than 100 nm, while continued optimization of process will be required. In the next section, the details of developments in electrodeposition process, as a fabrication process of bulk nanocrystalline metals, will be described, and the issues of this method that can mask inherent behavior of bulk nanocrystalline metals will be identified.

Table 1.2 Summary of fabrication processes of nanocrystalline metals.

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Consolidation process          | • Grain sizes (~10 nm)                          | ■ Require consolidation  
■ Contain artifacts          |
| Vapor deposition               | • Artifact free                  
• Grain sizes (~10 nm) | ■ Limited to thin films                       |
| Electrodeposition              | • Bulk samples                          
• Grain sizes (~10 nm)  | ■ Require additives: introduction of S and C.      |
| Severe plastic deformation     | • Bulk samples                        | ■ Grain sizes (>100 nm)                           |
| Crystallization from amorphous | -                                              | ■ Residual amorphous phase  
■ Brittle intermetallic phase | solids |
1.4 Developments of electrodeposition process

In electrodeposition processes, there are many parameters, including bath composition, pH, temperature, current density, bath additives, and etc. Also, important parameter of electrodeposition to produce bulk samples is current efficiency:

\[ CE = \frac{w_j}{w}, \]  

(1.2)

where \( CE \) is the current efficiency, \( w_j \) is the weight of metal \( j \) actually deposited, and \( w \) is that which would have been deposited if all the current had been used for depositing metal \( j \). The theoretical weight, \( w \), is given by

\[ w = \frac{A_{\text{wt}} \cdot C}{n \cdot F}, \]  

(1.3)

where \( A_{\text{wt}} \) is the atomic weight, \( C \) is the coulomb, \( n \) is the valence, and \( F \) is the Faraday constant. Low current efficiency makes fabricating of a bulk specimens difficult, and mediates a generation of gaseous hydrogen [66].

A large number of nanocrystalline pure metals, alloys, and metal–matrix composites have been produced by electrodeposition [67-90] (Table 1.3). Early studies demonstrated the relationship between characteristics of electrodeposits and bath composition and/or condition: the grain sizes of electrodeposited nanocrystalline metals could be varied to ~10 nm by adjusting bath composition and condition [91-93]. The grain size (Hall–Petch) effect has been understood by investigation of the mechanical properties, in addition to microstructure observations [67, 72, 73]. Improvements of current efficiency have been conducted for effectively producing of bulk specimens [94-96]. Reduction of internal stress, which can produce defects in electrodeposits, has been investigated [97, 98]. It was reported that some additives can reduce internal stress of electrodeposits [98]. Moreover, detailed investigation of microstructure indicated that electrodeposits contained some light elements such as H, O, C,
and S, [99] and the typical light elements present as a solute atom in electrodeposits [100].

Table 1.3 Examples of nanocrystalline metals, alloys, and metals matrix composites prepared by electrodeposition.

<table>
<thead>
<tr>
<th>Material</th>
<th>References</th>
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<tbody>
<tr>
<td>Ni</td>
<td>[67, 68]</td>
</tr>
<tr>
<td>Co</td>
<td>[39]</td>
</tr>
<tr>
<td>Pd</td>
<td>[69]</td>
</tr>
<tr>
<td>Cu</td>
<td>[70]</td>
</tr>
<tr>
<td>Zn</td>
<td>[71]</td>
</tr>
<tr>
<td>Ni–P</td>
<td>[72]</td>
</tr>
<tr>
<td>Ni–Fe</td>
<td>[73]</td>
</tr>
<tr>
<td>Ni–Zn</td>
<td>[74, 75]</td>
</tr>
<tr>
<td>Co–W</td>
<td>[76]</td>
</tr>
<tr>
<td>Ni–W</td>
<td>[77]</td>
</tr>
<tr>
<td>Pd–Fe</td>
<td>[78]</td>
</tr>
<tr>
<td>Ni–Fe–Cr</td>
<td>[79, 80]</td>
</tr>
<tr>
<td>Fe–Co–Ni</td>
<td>[81]</td>
</tr>
<tr>
<td>Ni–Zn–Cd</td>
<td>[82]</td>
</tr>
<tr>
<td>Co–Fe–P</td>
<td>[83]</td>
</tr>
<tr>
<td>Ni–Al$_2$O$_3$</td>
<td>[84]</td>
</tr>
<tr>
<td>Ni–SiC</td>
<td>[85, 86]</td>
</tr>
<tr>
<td>Cu–Al$_2$O$_3$</td>
<td>[87]</td>
</tr>
<tr>
<td>Ni–P–BN</td>
<td>[88]</td>
</tr>
<tr>
<td>Ni–Al(particles)</td>
<td>[89]</td>
</tr>
<tr>
<td>Ni–Nanocarbon tubes</td>
<td>[90]</td>
</tr>
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</table>
1.5 Tensile behavior of electrodeposited bulk nanocrystalline metals

Developments of an electrodeposition process as fabrication techniques for bulk nanocrystalline metals allowed producing bulk nanocrystalline samples that exhibit good ductility in a tensile test [44]. Fig 1.6 compares the relationship between tensile strength and ductility of electrodeposited nanocrystalline Ni and Ni–Fe alloys obtained from the literature [30, 31, 33, 35, 37, 38, 101-105]. Bulk nanocrystalline Ni and Ni–Fe alloys exhibited better tensile ductility compared to thin nanocrystalline Ni. Fig 1.7 shows the tensile strength of bulk nanocrystalline Ni [30, 33, 35, 37, 103-105] and Ni–Fe alloys [101, 102] as a function of the inverse square root of the grain size. The reported tensile strength increased with decrease the grain sizes, roughly following the Hall–Petch behavior.

![Graph showing tensile strength and ductility comparison](image)

Fig. 1.6 Relationship between tensile strength and ductility of electrodeposited thin nanocrystalline Ni [31], bulk nanocrystalline Ni [30, 33, 35, 37, 103-105], and bulk nanocrystalline Ni–Fe alloys [101, 102].
Specifically, the reported values are scattered, although the tensile test were conducted using bulk tensile specimens. In addition, the strength values of Ni–Fe alloys were comparable with that of Ni. Moreover, in the case of electrodeposited nanocrystalline Ni–W alloys, the hardness of the electrodeposited alloys is comparable to that of electrodeposited Ni [106]. Apparently, solid solution strengthening has a small effect on their strength relative to the grain refinement effect in electrodeposited nanocrystalline metals. However, Mukai et al. prepared nanocrystalline Al–Fe binary alloys by electron-beam deposition and showed that the strength of the as-deposited alloys increased with increasing Fe content [107]. In the nanocrystalline alloys prepared by PVD, solute addition increases strength to very high levels. Primarily, maintenance of microstructure with grain size less than 100 nm requires the some alloying elements, impurities, or second particles [108]. In fact, electrodeposited nanocrystalline Ni with grain sizes around 10 nm contained a large amount of carbon and
sulfur [99]. However, there are no detailed studies that investigate the effect of typical light element on the strength. Nieh reported that the typical light elements present as a solute atom in electrodeposits [100]. Thus, contribution of solid solution strengthening due to light elements in electrodeposited bulk nanocrystalline metals has to be studied.

Fig. 1.8 A Hall–Petch plot for tensile ductility of bulk nanocrystalline Ni [30, 33, 35, 37, 103-105] and Ni–Fe alloys [101, 102].

Fig 1.8 shows the tensile strength of bulk nanocrystalline Ni [30, 33, 35, 37, 103-105] and Ni–Fe alloys [101, 102] as a function of the inverse square root of the grain size. Although the bulk nanocrystalline Ni and Ni–Fe alloys showed the better ductility compared to thin nanocrystalline Ni, the ductility did not reach to over 10%. In addition, ductility of electrodeposited nanocrystalline metals can not be explained by the grain size alone (Fig, 1.8). What is needed to exhibit high tensile ductility above 10%? There are some proposals that are conditions of electrodeposited nanocrystalline metals for high tensile ductility [20, 44, 70].
Brook et al. [44] indicated that the bulk specimens are required to exhibit the good ductility in electrodeposited bulk nanocrystalline metals. It is noted that all bulk nanocrystalline samples do not exhibit the plastic deformation. In fact, in the study reported by Brook et al. [44], there are two types of bulk nanocrystalline Ni with ductility of ~3% and ~7%, respectively. The bulk nanocrystalline Ni were produced using an early scale-up process and a later generation process, respectively. (The difference of both process are not described in the paper.) Thus, although bulk specimen is a required condition, it is not a sufficient condition to exhibit high tensile ductility.

Li and Ebrahimi [20] pointed to that electrodeposition using no organic additives allowed to produce defect free electrodeposits. They also reported that nanocrystalline Ni–Fe alloys prepared by electrodeposition using no additives exhibited the good ductility of ~6%, along with high tensile strength. In contrast, Matsui et al. reported that bulk nanocrystalline Ni–Fe alloys prepared by electrodeposition using additives also exhibited good ductility of ~6% [109]. Thus, use of additives may not determine whether electrodeposited nanocrystalline exhibit tensile ductility or not.

Lu et al. [70] pre-introduced nano-twins to electrodeposited Cu by adjusting electrodeposition conditions, and the electrodeposited Cu with nano-twin exhibited the high tensile ductility above 10%. Therefore, several researchers have addressed investigations of deformation mechanisms mediated by nano-twin boundaries [110]. By contrast, Youssef et al. [111] prepared the bulk nanocrystalline Cu by in situ consolidation and it exhibited the high tensile ductility above 10%. In in situ consolidated bulk nanocrystalline Cu, no twin boundaries were observed by TEM observations before and after tensile tests. The results indicated that high tensile ductility of bulk nanocrystalline metals would not require nano-twin boundary.

“How are bulk nanocrystalline metals with good plasticity electrodeposited?” As described
above, there are not any answers that can explain all reported data on the tensile behavior of electrodeposited bulk nanocrystalline metals. Moreover, details of the electrodeposition process are not described in the literature. Thus, it is difficult to conduct the reproductive experiment, and to obtain the relationship between electrodeposition condition and the tensile behavior. If we get the relationship between tensile ductility and the parameter “X” as shown in Fig. 1.9, the relation will enhance ductility to very high levels, bring up the design principle, and point out the deformation mechanisms. Therefore, developments of electrodeposition process, which can produce bulk nanocrystalline metals with high tensile strength and high ductility, are needed, and then the parameter “X” has to be dictated, toward a quantitative understanding of tensile behavior in electrodeposited nanocrystalline metals.

Fig. 1.9 Relationship between tensile ductility and parameter “X”.

![](image)
1.6 Aim of this thesis

In the section 1.5, big challenges for tensile properties of electrodeposited nanocrystalline metals were identified by the literature survey:

- Scatter of strength;
- Uncertainty of conditions for high plastic deformation.

Therefore, in this thesis, electrodeposition processes for bulk nanocrystalline Ni and Ni–W alloys are developed and optimized to reveal the following points:

- Effect of light elements resulting from electrodeposition on strength;
- Dominant factor (parameter “X”) of tensile ductility.

In addition, the aim of this study is also to obtain “principle of design” for bulk nanocrystalline metals with high strength and high ductility, on the basis of obtained data and discussion.

Chapter 2 discusses the effect of interstitial carbon on the hardness of electrodeposited bulk nanocrystalline Ni using misfit strain calculated by first-principles calculations.

Chapter 3 presents developments of the electrodeposition process for bulk nanocrystalline Ni with plasticity and addresses the effect of use of additives on the tensile ductility.

Chapter 4 presents developments of the electrodeposition process for bulk nanocrystalline Ni–W alloys with plasticity and addresses the connection between the tensile ductility and current efficiency or presence of twin boundary.

Chapter 5 presents investigations of the effect of orientation on tensile ductility of electrodeposited bulk nanocrystalline Ni–W alloys.

Finally, chapter 6 summarizes the results and discussion of this thesis.
References


2 Effect of interstitial carbon on mechanical properties of bulk nanocrystalline Ni

2.1 Introduction

This study has the primary motivation of studying the effect of light elements on strength of electrodeposited nanocrystalline metals. As grain sizes reach the nanometer range, the strength of metallic materials can be drastically enhanced [1-6], following Hall–Petch effect:

\[ HV = HV_0 + k \cdot D^{-1/2} \]  

where \( HV_0 \) is the intrinsic hardness, \( k \) is a material constant, and \( D \) is the grain size. Electrodeposition has been used as a fabrication process to obtain nanocrystalline metals, and their mechanical behavior has been investigated [7-14]. Some studies [15-19] have demonstrated the Hall–Petch relationship by investigating yield stress or hardness in electrodeposited nanocrystalline Ni. (The data from the literature [15, 16, 19] represent values acquired by converting yield stress, \( \sigma_y \), to hardness, \( HV \), using the modified Tabor relation: \( 3.8 \sigma_y = HV \)[20, 21]; the results are summarized in Table 2.1.) The reported intrinsic hardness and material constant values vary among different studies. Thompson [15] demonstrated the Hall–Petch relationship using Ni with a grain size of ~10 µm and a material constant value of 18.99 GPa/nm\(^{-1/2}\). Xiao et al. [16] obtained a Hall–Petch constant of 21.53 GPa/nm\(^{-1/2}\) using the yield stress of electrodeposited Ni with a grain size of ~19 nm. Zhao et al. [18] and Wang et al. [19] estimated material constant values of 26.28 and 25.42 GPa/nm\(^{-1/2}\), respectively, using nanocrystalline Ni with a grain size of ~10 nm. The value of the constant increases with grain size up to the nanometer range. When nanocrystalline Ni undergoes only grain refinement strengthening, the value of the Hall–Petch constant should remain constant.
Table 2.1 Summary of the reported Hall–Petch equation for Ni.

<table>
<thead>
<tr>
<th>Study</th>
<th>Hall–Petch constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_0$ (GPa)</td>
</tr>
<tr>
<td>Thompson [15]*</td>
<td>0.08</td>
</tr>
<tr>
<td>Xiao et al. [16]*</td>
<td>0.03</td>
</tr>
<tr>
<td>Schuh et al. [17]</td>
<td>0.80</td>
</tr>
<tr>
<td>Zhao et al. [18]</td>
<td>1.09</td>
</tr>
<tr>
<td>Wang et al. [19]*</td>
<td>0.30</td>
</tr>
</tbody>
</table>

* The data from the literature [15, 16, 19] represent values acquired by converting yield stress to hardness using the modified Tabor relation: $3.8 \sigma_y = H_V$ [20, 21].

Therefore, we considered that a strengthening mechanism different from grain refinement strengthening operates in electrodeposited Ni. Moreover, Schuh et al. [17] obtained the Hall–Petch constant by plotting the hardness values of electrodeposited nanocrystalline Ni and Ni–W alloys. It was considered that solid solute strengthening by tungsten had a small effect on the hardness of electrodeposited nanocrystalline Ni–W alloys. In addition to electrodeposited nanocrystalline Ni–W alloys, electrodeposited nanocrystalline Ni–Co [22], Ni–Fe [23], and Ni–P [24] alloys have been reported to exhibit hardness values comparable to those of electrodeposited nanocrystalline Ni [13, 25]. By contrast, Rupert et al. reported that nanocrystalline Ni–W alloys prepared by magnetron sputtering exhibit an increase in hardness of ~43% as the W content increases to ~20 at% [26]. Mukai et al. prepared nanocrystalline Al–Fe binary alloys by electron-beam deposition and showed that the strength of the as-deposited alloys increased with increasing Fe content [27]. Interestingly, electrodeposited nanocrystalline Ni contains impurities such as carbon and sulfur [28, 29]. This is attributed to the electrodeposition baths used to produce nanocrystalline Ni, which contain large amounts of organic compounds. The presence of these impurities is interesting in itself, but it also has a
profound effect on the tensile and creep behavior of nanocrystalline Ni [16, 30]. In our previous work, we reported that the grain sizes of electrodeposited bulk nanocrystalline Ni tend to decrease with an increase in the carbon and sulfur content [31]. In addition, O’Reilly et al. reported that interstitial carbon could be present in electrodeposited Ni and that the concentration of carbon may exceed 0.5 at.% [32]. Therefore, we considered the possibility that the increase in the hardness of electrodeposited nanocrystalline Ni is due to solid solution strengthening induced by carbon and sulfur, giving nanocrystalline Ni a high hardness comparable to that of electrodeposited nanocrystalline Ni alloys.

When discussing the solid solution strengthening effect in electrodeposited nanocrystalline metals, the effect must be separated from the Hall–Petch effect. Thus, deposited alloys with different solute contents but the same grain size are desired. However, the grain size of electrodeposited alloys is intimately tied to the solute content [23, 33-35]. It is difficult to isolate the effects of grain size and solute atoms by comparing experimental results. The general equation used to predict the solid solution strengthening effect has the form [36, 37]

\[
\Delta \tau_{ss} \approx \epsilon_m^p c^q
\]  

(2.2)

where \(\epsilon_m\) is the misfit strain and \(c\) is the atomic fraction of the solutes. \(p\) and \(q\) are model-dependent exponents. The misfit strain is the local lattice distortion around solute atoms [38]. The misfit strain is determined based on measurements of the interatomic distances between solute and solvent atoms. Extended X-ray absorption fine structure (EXAFS) experiments must be performed to make such measurements [39, 40]. Thus, to predict the contribution of solid solution strengthening, the volume size factor and misfit parameter have been used as proxies for the misfit strain [38, 41]. Recently, the development of first-principles calculations has allowed researchers to estimate the misfit strain without performing experimental measurements or being constrained by the limitations presented by constituent elements [42, 43]. Moreover, the increase in the strength due to solid solution
strengthening in Al binary alloys predicted by using the Labusch model and the calculated misfit strain are in good agreement with experimental data [44]. We therefore suggest that the calculation of the misfit strain in Ni–C and Ni–S binary alloys by first-principles calculations allows for the estimation of the contribution of solid solution strengthening induced by impurities in electrodeposited bulk nanocrystalline Ni.

In this study, we made a few initial steps toward understanding the effect of impurities on the strength of electrodeposits by developing a set of idealized specimens and calculating the misfit strain in Ni–X solid solutions from first principles. We first prepared samples with a thickness of approximately 1.0 mm containing a carbon content of 30–1600 ppm and a sulfur content of 140–1200 ppm using a sulfamate bath with different complexing agents and gloss agents. The mechanical properties of these samples were investigated. The enthalpy of solution and misfit strain in Ni–X binary alloys were calculated using first-principles calculations to estimate the increase in strength due to solid solution addition. A solid solution strengthening model for an interstitial solute atom was developed to estimate the contribution of an interstitial carbon. We described the role of impurities in determining the mechanical properties of electrodeposited bulk nanocrystalline Ni and developed the Hall–Petch relationship for Ni based on the grain refinement effect.

### 2.2 Experimental procedures

Bulk nanocrystalline Ni was electrodeposited from a sulfamate bath, using different complexing agents and gloss agents. The chemical compositions of the electrodeposition bath used in the present study are given in Table 2.2. Propionic acid and citric acid were introduced as complexing agents to complex with Ni ions. Saccharin sodium, sodium allylsulfonate, and 2–butyne–1,4–diol were added to the bath to modify the impurity content of the
electrodeposits [31]. Details regarding the deposition cell and other facets of the electrodeposition process were provided in previous papers [31, 45]. The applied current density and bath temperature are given in Table 2.3. During the experiments, all electrodepositions were performed at a pH of 4.0 ± 0.1. The pH values of the solutions were maintained by adding drops of 1.0 mol/L sulfamic acid and 5.0 mol/L sodium hydroxide.

The carbon and sulfur contents of the electrodeposits were quantified by an IR absorption method after combustion in a high-frequency induction furnace. X-ray diffraction (XRD; RIGAKU Ultimate IV) analyses were carried out using Cu Kα radiation to estimate the grain size. Thin foil specimens measuring 3 mm in diameter were prepared by a twin-jet polishing technique using a nitric acid–methanol solution (20 vol.% HNO₃) at −30 °C and 15V. The microstructure was observed using transmission electron microscopy (TEM; JEOL JEM-2100F) operated at 200 kV. To evaluate the hardness of the electrodeposits, micro-Vickers hardness tests were conducted using a load of 500 g for 10 s. Each reported data point represents the average of at least 12 indentations.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfamate</td>
<td>400.0</td>
<td>400.0</td>
<td>400.0</td>
<td>400.0</td>
<td>400.0</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>-</td>
<td>20.0</td>
</tr>
<tr>
<td>Citric acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20.0</td>
<td>-</td>
</tr>
<tr>
<td>Saccharin sodium</td>
<td>0.1</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
<td>5.0</td>
</tr>
<tr>
<td>Sodium allylsulfonate</td>
<td>-</td>
<td>-</td>
<td>5.0</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>2–Butyne–1,4–diol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>
2.3 Computational details

First-principles calculations were performed using the Cambridge Serial Total-Energy Package (CASTEP) [46]. CASTEP is an ab initio pseudopotential method code for solving the electronic ground state of periodic systems, with the wave functions expanded in a plane-wave basis set using a technique based on density functional theory (DFT) [47, 48]. The electronic exchange–correlation energy was obtained by the generalized gradient approximation (GGA) proposed by Perdew et al. (PW91) using DFT [49]. Spin-polarized calculations were performed using the generalized gradient spin density approximation. Ultra-soft pseudopotentials [50] were used for all elements, including Ni, in the electronic calculation. A Gaussian smearing [51] of 0.1 eV was applied to the occupation numbers. To calculate the misfit strain in the Ni–X (X = C, S, Ti, V, Cr, Mn, Fe, Co, Cu, Zr, Nb, Mo, Ru, Ta, and W) binary alloys, we developed substitutional solid solution models by referencing models reported for Al-based solid solutions [44] and interstitial solid solution models. The $\text{Ni}_{15}X_1$, $\text{Ni}_{26}X_1$, and $\text{Ni}_{31}X_1$ substitutional solid solutions were modeled using supercells, which are periodic in all three spatial directions, containing 16, 27, and 32 atoms (Fig. 2.1(a)–(c)). The $\text{Ni}_{15}X_1$ supercell is a rhombohedral cell, which is a primitive cell of a $\text{Ni}_{30}X_2$ cubic cell. The $\text{Ni}_{26}X_1$ and $\text{Ni}_{31}X_1$ supercells are a rhombohedral cell consisting of $3 \times 3 \times 3$ primitive unit cells and a cubic cell composed of $2 \times 2 \times 2$ cubic unit cells, respectively. The supercells contain one substitutional solute atom per supercell. The supercells correspond to 6.25, 3.70, and 3.13 at.% solid solutions. The $\text{Ni}_{16}X_1$, $\text{Ni}_{27}X_1$, and $\text{Ni}_{32}X_1$ tetrahedral-interstitial and octahedral-interstitial solid solutions were modeled using supercells, which are similar to the $\text{Ni}_{15}X_1$, $\text{Ni}_{26}X_1$, and $\text{Ni}_{31}X_1$ supercells of substitutional solid solutions and which contain 17, 28, and 33 atoms (Fig. 1(d)–(i)). The $\text{Ni}_{16}X_1$, $\text{Ni}_{27}X_1$, and $\text{Ni}_{32}X_1$ supercells are similar to the supercells of $\text{Ni}_{15}X_1$, $\text{Ni}_{26}X_1$, and $\text{Ni}_{31}X_1$ substitutional solid
solutions, respectively. The supercells contain one interstitial solute atom per supercell. The supercells correspond to 5.88, 3.57, and 3.03 at.% interstitial solid solutions. Energy integration over a Brillouin zone was performed using $k$-point grids according to the Monkhorst–Pack [52] with sets of $7 \times 7 \times 7$ $k$-points for $\text{Ni}_{15}X$, and $\text{Ni}_{16}X$ and $5 \times 5 \times 5$ $k$-points for $\text{Ni}_{26}X$, $\text{Ni}_{27}X$, $\text{Ni}_{31}X$, and $\text{Ni}_{32}X$. A cut-off energy of 350 eV was used for the plane-wave basis in all calculations. The introduction of a substitutional or interstitial solute atom leads to a local lattice distortion and cell volume change. Stable atomic configurations were obtained through relaxation based on the Hellmann–Feynman forces calculated from first principles. The lattice constants at zero pressure were also optimized using a Broyden–Fletcher–Goldfarb–Shanno (BFGS) [53] minimization algorithm and the first-principles stress calculations. The convergence parameters were as follows: total energy tolerance: $1 \times 10^{-5}$ eV/atom, maximum force tolerance: 0.3 eV/nm, maximal stress component: 0.05 GPa, and maximal displacement: $1 \times 10^{-4}$ nm.

Table 2.3 Summary of electrodeposition conditions (current density, CD; bath temperature, Temp.) and impurity content (carbon, C; sulfur, S) of bulk nanocrystalline Ni.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Bath</th>
<th>CD (mA/cm$^2$)</th>
<th>Temp. (°C)</th>
<th>C (at.%)</th>
<th>S (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 [45]</td>
<td>A</td>
<td>30</td>
<td>50</td>
<td>0.015</td>
<td>0.026</td>
</tr>
<tr>
<td>Sample 2 [45]</td>
<td>B</td>
<td>25</td>
<td>50</td>
<td>0.024</td>
<td>0.038</td>
</tr>
<tr>
<td>Sample 3</td>
<td>C</td>
<td>15</td>
<td>50</td>
<td>0.151</td>
<td>0.046</td>
</tr>
<tr>
<td>Sample 4 [31]</td>
<td>C</td>
<td>15</td>
<td>40</td>
<td>0.068</td>
<td>0.031</td>
</tr>
<tr>
<td>Sample 5</td>
<td>D</td>
<td>30</td>
<td>50</td>
<td>0.219</td>
<td>0.080</td>
</tr>
<tr>
<td>Sample 6</td>
<td>D</td>
<td>30</td>
<td>40</td>
<td>0.263</td>
<td>0.075</td>
</tr>
<tr>
<td>Sample 7 [31]</td>
<td>E</td>
<td>50</td>
<td>50</td>
<td>0.776</td>
<td>0.218</td>
</tr>
<tr>
<td>Sample 8</td>
<td>E</td>
<td>100</td>
<td>50</td>
<td>0.399</td>
<td>0.219</td>
</tr>
</tbody>
</table>
2.4 Characterization of electrodeposited bulk nanocrystalline Ni

Bulk nanocrystalline Ni with thickness of ~1.0 mm was deposited from each bath under various conditions. The carbon and sulfur content were measured by an IR absorption method. The conditions and results are listed in Table 2.3. The carbon content carried from 0.02 to 0.78 at.%, and the sulfur content varied from 0.03 to 0.22 at.%. The XRD patterns of each sample showed a single phase with a face-centered cubic (fcc) structure. The sample’s grain sizes were calculated using XRD peak width and the Scherrer equation. The estimated grain sizes were ~11–23 nm. Bright-field TEM images of samples 1, 3, 5, and 7 are shown in Fig. 2.2a–d, respectively. Fig. 2.2a–d shows that the grain sizes are ~25, ~20, ~15, and ~10 nm, respectively. These sizes are close to those determined by XRD. Thus, the grain size
determined by the XRD peak widths was used in analyses discussed in later sections. Fig. 2.3 compares the relationship between grain size and (a) the carbon content and (b) the sulfur content reported for electrodeposited nanocrystalline Ni [7-9, 11, 54, 55] with that observed in this study. Fig. 2.3b shows a rough trend of decreasing grain size with increasing sulfur content. The sulfur tends to segregate toward grain boundaries [56, 57]. Klement et al. [56] reported that sulfur is dissolved in the grain boundaries without precipitates in nanocrystalline Ni. Yamaguchi et al. [57] showed, by first-principles calculations, that sulfur has a large grain boundary segregation energy. Thus, the segregation of sulfur toward grain boundaries leads to a decrease in the grain boundary energy and a decrease in the grain size of electrodeposited nanocrystalline Ni. In fact, Fig. 2.3 shows that the grain size of bulk nanocrystalline Ni decreases with increasing sulfur content. Meanwhile, the grain boundary segregation energy of carbon calculated by first-principles calculations is not as high as that of sulfur [57]. Nieh and Wang [58] investigated the presence of carbon in electrodeposited nanocrystalline Ni by atom probe field emission microscopy. The results revealed the presence of carbon in the electrodeposits and indicated that this was not related to grain boundaries or fine (<100 nm) particles or precipitates. In fact, the grain size of the electrodeposited nanocrystalline Ni was related to the sulfur content.

The hardness of the Ni specimens with 0.02–0.78 at.% carbon and 0.03–0.22 at.% sulfur was investigated by performing a micro-Vickers hardness test. The electrodeposited bulk nanocrystalline Ni exhibited hardness values of 4.1–6.9 GPa. Fig. 2.4a shows the hardness versus the inverse square root of the grain size for electrodeposited bulk nanocrystalline Ni. The hardness of bulk nanocrystalline Ni increased linearly with decreasing grain size and increasing carbon content. However, the hardness did not obey the Hall–Petch relationship when the linear relationship between grain size and carbon content collapsed. For example, sample 8 exhibited a lower hardness (6.6 GPa) than sample 7 despite a decrease in the grain
size. Although sample 6 and sample 7 had the same grain size of 12 nm, their hardness values were 6.0 and 6.9 GPa, respectively. The hardness values of electrodeposited nanocrystalline Ni reported in the literature and those observed in this work are presented in Fig. 2.4b. A scatter in the values is observed below a grain size of 30 nm. The Hall–Petch slope at grain sizes below 30 nm is higher than that at grain sizes above 30 nm. This is because the use of organic compounds to induce grain refinement led to the co-deposition of impurities, whose content varied depending on the bath composition and conditions, as shown in Fig. 2.3. These results indicate that the co-deposition of impurities led to a high degree of solid solution strengthening in the electrodeposited Ni. This strengthening enhanced the hardness of the electrodeposited Ni to a value comparable to that of electrodeposited nanocrystalline Ni–W [17], Ni–Fe [23], and Ni–P [24]. In the following sections, we will discuss the strengthening mechanism of the electrodeposited bulk nanocrystalline Ni in greater detail.

Fig. 2.2 Bright-field TEM images of samples (a) 1, (b) 3, (c) 5, and (d) 7.
Fig. 2.3 Comparison of the relationship between the grain size and (a) carbon content and (b) sulfur content of electrodeposited nanocrystalline Ni reported in previous studies [7-9, 11, 54, 55] with that determined in the current study.
Fig. 2.4 (a) Hardness of bulk nanocrystalline Ni as a function of the inverse square root of the grain size. (b) A Hall–Petch plot of hardness in electrodeposited nanocrystalline Ni obtained from the literature [7-13] and this work, along with the corresponding regression lines.
2.5 Contribution of solid solution strengthening

The experimental results indicate that carbon and sulfur solute atoms had an effect on the hardness of the electrodeposited nanocrystalline Ni. There is a possibility that carbon occurs as an interstitial solute atom in the Ni matrix because the atomic of carbon is small. To calculate the misfit strain and estimate the contribution of solid solution strengthening by first-principles calculations, it was necessary to determine the location of carbon atoms in the Ni–C binary alloys. This was accomplished by comparing the enthalpy of solution calculated by first-principles calculations for a substitutional, tetrahedral-interstitial and octahedral-interstitial solid solution model. In addition to those of a Ni–S solid solution, the solution enthalpies of a Ni–S solid solution were compared to confirm the structure. The enthalpy of solution $\Delta H$ is described as follows [59, 60]:

$$\Delta H = E[Ni_{n-1}X_1] - (n-1)\mu_{Ni} - \mu_X$$

(2.3)

where $E[Ni_{n-1}X_1]$ is the total energy of supercells with $n-1$ solvent Ni atoms and one solute X atom and $\mu_{Ni}$ and $\mu_X$ are the corresponding chemical potentials (total energy per atom) of pure Ni and X, respectively, in their ground state. The ground state structures of Ni, C, and S are fcc, graphite, and $\alpha$S–oF128, respectively.

The enthalpies of solution for Ni–C substitutional, tetrahedral-interstitial, and octahedral-interstitial solid solutions are listed in Table 2.4. The solution enthalpy of the Ni–C octahedral-interstitial solid solution was lower than the enthalpies of the other models. The results indicate that carbon atoms prefer octahedral-interstitial sites. The comparison of the solution enthalpies of the Ni–S solid solution indicated that sulfur atoms existed as substitutional solute atoms in the Ni matrix. Thus, we calculated the misfit strain by using the Ni–S substitutional solid solution model and the Ni–C octahedral-interstitial solid solution model. In addition to considering Ni–S and Ni–C solid solutions, to confirm the validity of the
misfit strain values, the misfit strains in Ni solid solutions that have already been reported [39, 42, 43] were calculated, and the results are discussed in the following section.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Enthalpy of solution (eV/atom)</th>
<th>( \Delta H_{\text{sub}} )</th>
<th>( \Delta H_{\text{tet}} )</th>
<th>( \Delta H_{\text{oct}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.97 ± 0.19</td>
<td>2.33 ± 0.22</td>
<td>0.73 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.33 ± 0.22</td>
<td>2.47 ± 0.55</td>
<td>1.08 ± 0.34</td>
<td></td>
</tr>
</tbody>
</table>

The introduction of a substitutional or interstitial solute atom into a crystal leads to lattice distortions. In this study, interatomic distances between the solute and solvent atoms were readily obtained using first-principles calculations by relaxing the lattice constants of both the supercells and the atomic configurations. The calculated local lattice distortions between the solute atom and the first nearest solvent Ni atom in Ni–X (X = S, Ti, V, Cr, Mn, Fe, Co, Cu, Zr, Nb, Mo, Ru, Ta, and W) substitutional solid solutions and Ni–C octahedral-interstitial solid solutions are listed in Table 2.5. They are compared with those obtained from other calculations [42, 43] and experimental measurements [39]. The local lattice distortions calculated in the present study agree well with the experimental data obtained by using the X-ray absorption fine structure (XAFS) technique [39].

The misfit strain is related to the difference in the interatomic distance as follows [38]:

\[
\varepsilon_m = \frac{d - d_0}{d_0}
\]  

(2.4)

where \( d \) is the interatomic distance between a solute X atom and a solvent Ni atom in a Ni–X solid solution and \( d_0 \) is the interatomic distance in pure Ni. The first nearest-neighbor solvent
atom distance in substitutional solid solutions $d_{\text{sub}}^0$ is related to the lattice constant $a_0$ by the relation $d_{\text{sub}}^0 = a_0/\sqrt{2}$. The values for the Ni$_{15}$X$_1$, Ni$_{26}$X$_1$, and Ni$_{31}$X$_1$ substitutional solid solution models are 0.2501, 0.2501, and 0.2502 nm, respectively. When the misfit strain of an interstitial solid solution model was estimated, the first nearest-neighbor solvent atom distance was calculated as the distance between a solvent atom and the location of entry. The interatomic distance in interstitial solid solutions $d_{\text{int}}^0$ is related to the lattice constant by the relation $d_{\text{int}}^0 = a_0/2$. The values for the Ni$_{16}$X$_1$, Ni$_{27}$X$_1$, and Ni$_{32}$X$_1$ octahedral-interstitial solid solution models are 0.1768, 0.1768, and 0.1769 nm, respectively. The misfit strains at the first nearest-neighbor solvent atom in the Ni–X solid solution are listed in Table 2.5. These misfit strains are based on the average values of the first nearest-neighbor interatomic distances in each model.

Solid solution strengthening results from an interaction between mobile dislocations and solute atoms. There are a number of theories regarding solid solution strengthening by substitutional solute atoms, including the Friedel model [36], which proposes that the yield stress varies as $c^{1/2}$ in dilute alloys; the Labush model [37], which applies to more concentrated solutions and leads to $\Delta \sigma \approx c^{1/3}$; and the Suzuki effect [61], which focuses on chemical effects. The hardening effect predicted by the Labush model relative to a pure matrix is described using the misfit strain caused by substitutional atoms, $\varepsilon_{\text{sub}}$, as follows [44]:

$$\Delta \sigma_{\text{sub}} = A [\varepsilon_{\text{sub}}]^{4/3} c^{2/3}$$

(2.5)

where $\Delta \sigma_{\text{sub}}$ is the increase in the yield stress due to solid solution strengthening by substitutional solute atoms and $A$ is a fitting parameter. To discuss the strengthening mechanism observed in electrodeposited nanocrystalline Ni, the Labush model for solid solution strengthening by interstitial solute atoms must be modified. The increase in the yield
stress due to solid solution strengthening, $\Delta \sigma$, is given by [37]

$$\Delta \sigma = \alpha F_m^{4/3} c^{2/3} \tag{2.6}$$

where $\alpha$ is a material parameter that depends on temperature and $F_m$ is the maximum interaction force between a mobile dislocation and a point defect such as a substitutional or interstitial solute atom. This point defect, which is inserted into a spherical hole of radius $d_0^{\text{sub}}$ or $d_0^{\text{int}}$ in an elastic matrix, has a radius of $(1 + \varepsilon_{\text{sub}})d_0^{\text{sub}}$ or $(1 + \varepsilon_{\text{int}})d_0^{\text{sub}}$, where $\varepsilon_{\text{int}}$ is the misfit strain due to an interstitial solute atom. The maximum interaction force is related to the volume of the point defect due to a solute atom, $V_0$, and misfit strain [41]:

$$F_m = F_0 V_0 |\varepsilon_m| \tag{2.7}$$

where $F_0$ is a material parameter. When $F_m$ in Eq. (2.7) is substituted into Eq. (2.6), the increase in the yield stress due to solid solution strengthening, $\Delta \sigma$, is obtained as follows:

$$\Delta \sigma = \alpha F_0^{4/3} V_0^{4/3} |\varepsilon|^{4/3} c^{2/3} \tag{2.8}$$

The volume of a point defect in a substitutional and interstitial solid solution, $V_0^{\text{sub}}$ and $V_0^{\text{int}}$, respectively, is given by

$$V_0^{\text{sub}} = \sqrt{2} \pi a_0^3 / 3 \tag{2.9}$$

$$V_0^{\text{int}} = \pi a_0^3 / 6 \tag{2.10}$$

Therefore, Eq. (2.8) is rewritten as

$$\Delta \sigma_{\text{sub}} = \alpha F_0^{4/3} V_0^{4/3} |\varepsilon_{\text{sub}}|^{4/3} c^{2/3} = A |\varepsilon_{\text{sub}}|^{4/3} c^{2/3} \tag{2.11}$$

$$\Delta \sigma_{\text{int}} = \alpha F_0^{4/3} V_0^{4/3} |\varepsilon_{\text{int}}|^{4/3} c^{2/3} = A |\varepsilon_{\text{int}}|^{4/3} c^{2/3} \tag{2.12}$$

There is a relationship between the hardness and yield strength of the following form [20, 21]:

$$HV = 3.8 \cdot \sigma_y \tag{2.13}$$
The increase in hardness due to solid solution addition, $\Delta HV$, is expressed as follows:

$$\Delta HV_{\text{sub}} = 3.8 \cdot A \left| \varepsilon_{\text{sub}} \right|^{4/3} c^{2/3} \quad (2.14)$$

$$\Delta HV_{\text{int}} = 3.8 \cdot \frac{A}{4} \left| \varepsilon_{\text{int}} \right|^{4/3} c^{2/3} \quad (2.15)$$

Fig. 2.5 shows the relationship between the rate of solid solution strengthening obtained from the literature [62] and the three-fourths power of the calculated misfit strain in Ni–X ($X = \text{Ti, V, Cr, Mn, Fe, Co, Cu, Zr, Nb, Mo, Ru, Ta, and W}$) solid solutions. It is observed that a linear relationship exists between the rate of solid solution strengthening and the misfit strain in Ni–X binary alloys. The fitting parameter $A$ was determined from the slope of the regression line; the calculated value was $576 \pm 25.9$ GPa.
Table 2.5 The first nearest-neighbor distance between the solute and solvent Ni atom $d$ and misfit strain $\varepsilon_m = (d - d_0) / d_0$ calculated from first-principles calculations.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Local lattice distortion (pm)</th>
<th>$\varepsilon_m$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni$_{15}X_1$</td>
<td>Ni$_{26}X_1$</td>
</tr>
<tr>
<td>S</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Ti</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td>V</td>
<td>−0.1</td>
<td>−1.1</td>
</tr>
<tr>
<td>Cr</td>
<td>−1.6</td>
<td>−2.2</td>
</tr>
<tr>
<td>Mn</td>
<td>2.4</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe</td>
<td>−0.2</td>
<td>−0.9</td>
</tr>
<tr>
<td>Co</td>
<td>−0.4</td>
<td>−0.8</td>
</tr>
<tr>
<td>Cu</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>9.6</td>
<td>7.0</td>
</tr>
<tr>
<td>Nb</td>
<td>5.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Mo</td>
<td>2.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Ru</td>
<td>1.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Ta</td>
<td>5.3</td>
<td>3.3</td>
</tr>
<tr>
<td>W</td>
<td>2.2</td>
<td>1.3</td>
</tr>
<tr>
<td>C*</td>
<td>9.7</td>
<td>9.0</td>
</tr>
</tbody>
</table>

* The first nearest-neighbor distance of C was calculated using the Ni$_{16}X_1$, Ni$_{27}X_1$, and Ni$_{32}X_1$ interstitial solid solution model.

2.6 Discussion

Sulfur tends to segregate toward grain boundaries [56, 57]. Even if sulfur is present in the matrix in the form of solute atoms, its contribution to the solid solution strengthening of bulk nanocrystalline Ni is subtle. In this study, the misfit strain of sulfur was 0.41%. The increase in hardness due to 0.03–0.22 at.% sulfur predicted by Eq. (2.14) was only 0.01–0.03 GPa. In contrast, the presence of carbon as an interstitial solute atom in the Ni matrix produced a high
misfit strain of 5.26%. The increase in hardness due to 0.02–0.78 at.% carbon predicted by Eq. (2.15) was 0.03–0.42 GPa. We separated the solid solution strengthening effect from the Hall–Petch effect by subtracting the increase in the hardness due to carbon from the hardness value of bulk nanocrystalline Ni. The experimental data and subtracted values are plotted in Fig. 2.6. Scatter in the experimental data was observed at grain sizes of ~12 nm. In contrast, no scattered data were observed among the subtracted values. The subtracted values converge to a value of ~6.4 GPa at a grain size of ~11 nm. These experimental results and analyses indicate that the strength of the electrodeposited bulk nanocrystalline Ni was strongly affected by solid solution strengthening due to interstitial carbon.

![Fig. 2.6 Experimental hardness values and subtracted values calculated from Eq. (2.15) for electrodeposited bulk nanocrystalline Ni as a function of the inverse square root of the grain size.](image)

Several Hall–Petch equations for Ni have been reported [15-19]. These equations show a scatter in the Hall–Petch constant values (Table 2.1). This scatter is attributed to the following
two factors: first, some of the electrodeposited Ni contained a large amount of carbon (Fig. 2.3a) because stress-relaxation and/or leveling agents, i.e., organic compounds, were used to reduce the grain size.

Second, some Hall–Petch equations were constructed to include the hardness values of electrodeposited Ni–W alloys [17]. The hardness of electrodeposited Ni–W alloys is comparable to that of electrodeposited Ni. Apparently, the addition of tungsten to electrodeposited Ni–W alloys has a small effect on their hardness relative to the grain refinement effect. This discrepancy occurs because carbon produces a much larger misfit strain of 5.26% in the Ni matrix compared with that of 0.71% due to tungsten. A carbon content of only 1.0 at.% is sufficient to increase the hardness by approximately 0.5 GPa. In contrast, a tungsten content of 6.9 at.% would be required for an equivalent increase.

Fig. 2.7 Hall–Petch plot of subtracted values calculated from Eq. (2.15) for bulk nanocrystalline Ni and the experimental hardness for Ni electrodeposited from a sulfamate bath [12] and high-purity annealed Ni [10], along with the linear regression line from the hardness values of nanocrystalline Ni.
A Hall-Petch equation was constructed for Ni using the hardness values that were not affected by solid solution strengthening due to an interstitial carbon. Fig. 2.7 shows a Hall–Petch plot of hardness for subtracted values of bulk nanocrystalline Ni obtained in this study and electrodeposited Ni with a grain size greater than 30 nm [12]. Ebrahimi et al. [12] electrodeposited nanocrystalline Ni from sulfamate electrolytes using no additives to avoid the incorporation of carbon and sulfur. A linear fit was computed for all data in Fig. 2.7 using the least squares method. The line shown to intersect the data represents the best fit and gives a Hall–Petch constant of $k = 17.3 \pm 0.84$ GPa/nm$^{1/2}$ and a value $H_0 = 0.9 \pm 0.16$ GPa. The Hall–Petch equation is as follows:

$$H = H_0 + k \cdot D^{-1/2} = 0.9 + 17.3 \cdot D^{-1/2}$$

(2.16)

The hardness values predicted using Eq. (2.16), which was obtained from hardness values for grain sizes ranging from 11 to 342 nm, are in good agreement with the hardness of high-purity annealed Ni with a grain size on the order of micrometers [10]. Eq. (2.16) expresses the hardness of nickel over a wide grain size range, including the micrometer size range.

To assess the validity of the solid solution strengthening mechanism induced by carbon drawn from our experiments and calculations, the experimental hardness data and subtracted values calculated from Eq. (2.15) and the reported carbon content [7-9, 19, 30, 55] are plotted in Fig. 2.8, along with the Hall–Petch equation (Eq. (2.16)). These data were chosen from a relatively large number of experimental studies on electrodeposited Ni because these studies describe the hardness, grain size, and impurity content of electrodeposits. The experimental data show higher hardness values than those predicted by Eq. (2.16). In contrast, the subtracted values were in close agreement with the values predicted by Eq. (2.16). We conclude from these results and analyses that solid solution strengthening due to interstitial
solute carbon occurs in electrodeposited nanocrystalline Ni. This strengthening mechanism has a significant effect on hardness, and the difference in carbon content creates a scatter in the hardness values of electrodeposited nanocrystalline Ni.

Fig. 2.8 Experimental hardness values and subtracted values calculated from Eq. (2.15) for electrodeposited nanocrystalline Ni from the literature [7,9, 19, 30, 55] as a function of the inverse square root of the grain size. The data from the literature [19, 30, 55] represent values acquired by converting ultimate tensile strength to hardness using the modified Tabor relation: $3UTS = HV$ [21].

\[
HV = 0.9 + 17.3 \times D^{-1/2}
\]
2.7 Conclusions

Bulk nanocrystalline Ni with 0.02–0.78 at.% carbon and 0.03–0.22 at.% sulfur was fabricated, and the misfit strain of Ni–X binary alloys was calculated by first-principles calculations to study the effect of typical impurities on electrodeposited Ni. The experiments and analysis based on first-principles calculations indicated that solid solution strengthening by carbon in the form of interstitial solute atoms occurs in electrodeposited bulk nanocrystalline Ni. Interstitial carbon has a large effect on the strength of electrodeposited Ni and increases the hardness of this material by 0.42 GPa at a carbon content of 0.78 at.%.

The scatter in the hardness values of electrodeposited Ni at grain sizes near 12 nm, which is not predicted by a model that considers only grain refinement strengthening, converges to ~6.4 GPa on subtracting the effect of interstitial carbon. The predicted increase in hardness caused by interstitial carbon isolates the effects of grain refinement strengthening and reflects the Hall–Petch equation for Ni.
References

014101.


3 Development of an electrodeposition process for bulk nanocrystalline Ni with plasticity

3.1 Introduction

This study has the primary motivation of developing the electrodeposition process for bulk nanocrystalline Ni with plasticity. As described in chapter 1, electrodeposition processes have been developed to produce bulk nanocrystalline metals [1, 2] and investigate the tensile properties [3-9]. Some studies reported the fabrication of electrodeposits with good tensile ductility, and suggested the cause of the good ductility, such as bulk specimens [8], using no organic additives [6], and pre-introduce of nano-twins [10]. At the same time, there are counterexamples to these suggestions [11]. It is therefore that the cause of the good ductility in electrodeposited nanocrystalline metals has to be reconstructed. As stated before, there are some papers that reported electrodeposits nanocrystalline metals with good plastic deformation [6-9]. However, reproduction of such electrodeposited nanocrystalline metals as reported is difficult because no details of the bath compositions and electrodeposition conditions are given in the literature. To reveal the cause of good tensile ductility, the developments of an electrodeposition process that can produce electrodeposits with plasticity is required.

The author paid attention to electrodeposited Ni–W alloys, to develop an electrodeposition process for bulk nanocrystalline Ni. The electrodeposited Ni–W alloys exhibited low plastic deformation of ~2% [12-16]. Several early studies indicated that the limited plastic deformation would be related to low current efficiency and high internal stress [17, 18]. (It is noted that the details of electrodeposition process for Ni–W alloys will be discussed in
Among Ni electroplating processes, a sulfamate bath shows high current efficiency and low internal stress [19]. Sulfamate bath is expected as a process for producing the bulk nanocrystalline Ni with good tensile ductility. In the present study, the author addressed to fabricate the bulk nanocrystalline Ni using a sulfamate bath with no additives or with additives, and investigated the tensile properties. Subsequently, the practicality of the sulfamate bath and the effect of organic additives on the tensile ductility are discussed.

3.2 Experimental procedures

Two bulk samples of nanocrystalline Ni were electrodeposited from a sulfamate bath with no additives or with saccharin sodium and Sodium lauryl sulfate. The details of the bath composition are described in Table 3.1. All samples were deposited onto copper substrate of commercial purity using counter electrodes of titanium basket with nickel plates (99.98%). The main components of electrodeposition system were power supplies, 5-L bath, a circulating water pump, a feed water pump, and filter to remove the precipitate: the schematic illustration of this system is shown in Fig. 3.1. The bath temperature was maintained at 50 ± 1.0 °C by a heater using an on–off controller. All electrodepositions were run at a current density of 30 mA/cm$^2$ and a pH of 4.0 ± 0.1. The pH values of the solutions were maintained by adding drops of 1.0 mol/L sulfamic acid and 5.0 mol/L sodium hydroxide.

The carbon and sulfur contents of the electrodeposits were quantified by an IR absorption method after combustion in a high-frequency induction furnace. X-ray diffraction (XRD, RIGAKU Ultimate IV) analysis was performed using Cu K$\alpha$ radiation to estimate the grain size and examine the crystalline texture. Thin foil specimens measuring 3 mm in diameter were prepared by a twin-jet polishing technique using a nitric acid–methanol solution (20% by volume of HNO$_3$) at −30 °C and 15 V. The microstructure was observed using a
transmission electron microscope (TEM, JEOL JEM–2100F) operated at 200 kV. Dog-bone specimens with a gauge length of 15 mm, width of 6.25 mm, and thickness of approximately 1.0 mm were machined for tensile tests by electrical discharge machining from the as-deposited plates. Tensile tests were performed at a strain rate of $1 \times 10^{-3}$ s$^{-1}$ and room temperature. The elongation of the specimen after fracture was measured by the change in the gauge length.

Table 3.1 Bath compositions (g/L) for bulk nanocrystalline Ni.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>N bath</th>
<th>S bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfamate</td>
<td>300.0</td>
<td>400.0</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Saccharin sodium</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>-</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Fig. 3.1 Schematic image of electrodeposition system for producing bulk nanocrystalline Ni.
3.3 Characterization and mechanical behavior measurements

Bulk samples of electrodeposited Ni were prepared by electrodeposition for 72 h from N and S baths, and these samples were assigned the following labels N and S, respectively. N and S baths showed the high current efficiencies of 92% and 94%, respectively. The carbon and sulfur contents of both samples were measured by IR absorption method, and the results are given in Table 3.2. Sample N and S contained same carbon content of 30 ppm, while the samples contained sulfur content of 40 and 140 ppm, respectively. This indicated that addition of saccharin sodium and sodium lauryl sulfate increased the sulfur content of electrodeposits.

Fig. 3.2 shows the XRD patterns of both samples and the patterns showed a single phase of face-centered cubic structure. The grain sizes of electrodeposits were estimated using XRD peak widths and Scherrer’s equation. The estimated grain size of samples N and S was 41 and 23 nm, respectively.

Fig. 3.2 XRD patterns of samples (s) N and (b) S.
Fig. 3.3 shows the bright-filed TEM images of samples (a) N and (b) S. Sample N have a microstructure with grain size of ~100–200 nm and twin boundaries (Fig. 3.3a). The twin boundary spacing was comparable with the value calculated using XRD peak width: the grain sizes estimated from the XRD peak width were affected by twin boundaries. In contrast, sample S (Fig. 3.3b) shows that the grain size was comparable to that calculated from the XRD peak width. The addition of saccharin sodium or sodium allylsulfonate reduced the grain size of nanocrystalline Ni–W alloys to ~20–30 nm. The decreased grain size would cause difficulty in formation of twin boundaries.

![Fig. 3.3 Bright-filed TEM images showing the planar views of samples (a) N and (b) S.](image)

The stress-strain curves of both samples are shown in Fig. 3.4. The strain was measured using a strain gage whose maximum measured value was 5.0%. The plastic deformation after fracture was determined by measuring the change in gauge length. Sample N exhibited a tensile strength of 1.0 GPa and a ductility of 8.8%, while sample S exhibited a tensile strength of 1.2 GPa and a high ductility of 12%. A sulfamate bath could produce bulk nanocrystalline Ni with high tensile ductility of ~10%. Moreover, the addition of saccharin sodium and sodium lauryl sulfate could increase the tensile strength and ductility. SEM images of the
fracture surface of both samples are shown in Fig. 3.5. Figs. 3.5a and b shows the dimple structures, which are observed in fracture surface of ductile materials. Comparison of Fig. 3.5a and b indicated that the dimple sizes decreased with increase in the tensile ductility.

Fig. 3.4 Tensile behavior of samples N and S. The strain was measured using a strain gauge whose maximum measured value was 5.0%.

Fig. 3.5 SEM images of fracture surface of bulk nanocrystalline Ni electrodeposition from a sulfamate bath (a) with no additives and (b) with saccharin sodium.
### 3.4 Discussion

Table 3.2 Summary of characterization and experimental data for electrodeposited nanocrystalline Ni in reported studies [20], and in the current study.

<table>
<thead>
<tr>
<th>Study</th>
<th>Additives</th>
<th>C  (ppm)</th>
<th>S  (ppm)</th>
<th>$d$ (nm)</th>
<th>UTS  (MPa)</th>
<th>$\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li and Ebrahimi</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>44</td>
<td>1080</td>
<td>9</td>
</tr>
<tr>
<td>[20] Sample Ni</td>
<td>-</td>
<td>30</td>
<td>40</td>
<td>41</td>
<td>1006</td>
<td>8.8</td>
</tr>
<tr>
<td>(This study)</td>
<td>0.1 g/L saccharin</td>
<td>30</td>
<td>140</td>
<td>23</td>
<td>1192</td>
<td>11.5</td>
</tr>
<tr>
<td>Sample S</td>
<td>(This study)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The N and S bath produced a bulk nanostructured Ni with nano-twin and bulk nanocrystalline Ni with grain size of ~23 nm, respectively. Both electrodeposits exhibited a good plastic deformation of ~10% in a tensile test. In this section, the effect of addition of additives on the impurities content, grain size, and tensile ductility of electrodeposited bulk nanocrystalline Ni will be discussed, and these characterization and experimental data are summarized in Table 3.2. Li and Ebrahimi [6, 20] mentioned the electrodeposition without using additives as a major factor for producing the nanocrystalline metals with plasticity. The use of additives induced defects, high internal stresses and/or high levels of impurities. In fact, their electrodeposited nanocrystalline Ni with grain size of 44 nm showed a tensile strength of 1.1 GPa and elongation to failure of 9%. The author also tested Ni electrodeposited from a sulfamate bath without using additives. Strength and ductility similar to that reported by Li and Ebrahimi [20] were observed. On the other hand, although the addition of saccharin sodium increased the impurities content as suggested by Li and
Ebrahimi [6], the bulk nanocrystalline Ni electrodeposited from a sulfamate bath with using additives exhibited higher strength and ductility that electrodeposited without using additives. This indicated that addition of additives did not always result in reduce in the ductility. Thus, a detailed test was conducted to investigate the effect of saccharin sodium on tensile strength [21]. Fig. 3.6 compares the relationship between tensile strength and the tensile ductility of bulk nanocrystalline Ni electrodeposited from a sulfamate bath, by varying the amount of saccharin sodium and current density. The bulk nanocrystalline Ni electrodeposited using 5.0 g/L saccharin sodium showed a higher tensile strength and ductility than that electrodeposited using 0.1 g/L saccharin sodium. These results indicated that the additives had a significant effect on tensile behavior of electrodeposited bulk nanocrystalline metals, and also suggested that the study which investigates the effect of additives on tensile behavior was important to improve the tensile properties.

Fig. 3.7 summarizes the relationship between tensile strength and tensile ductility, available from the literature, for coarse grained Ni [5, 22-24] and ultra-fine grained and nanocrystalline Ni prepared by electrodeposition [4, 5, 19, 22, 25-32], electrodeposition and annealing [32], HPT [5], ECAE and HPT [23], cryo-rolling [33], and cryo-milling [24], in comparison to the product of the current study. Among these reported data, this study demonstrated and developed the relationship between tensile strength and ductility to a higher level on nanocrystalline Ni. The study also pointed out the potency of a sulfamate bath to produce bulk nanocrystalline metals with plasticity.
Fig. 3.6 Relationship between ultimate tensile strength and tensile ductility of bulk nanocrystalline Ni electrodeposited from a sulfamate bath with no additives and with saccharin sodium.

Fig. 3.7 Ultimate tensile strength versus tensile ductility of coarse grained Ni [5, 22-24] and ultra-fine grained and nanocrystalline Ni prepared by electrodeposition [4, 5, 19, 22, 25-32], electrodeposition and annealing [32], HPT [5], ECAP and HPT [23], cryo-rolling[33], and cryo-milling [24], in comparison to the product of the current study.
3.5 Conclusions

Bulk nanocrystalline Ni was prepared by electrodeposition from a sulfamate bath with no additives or with saccharin sodium. The both sulfamate baths shows the high current efficiency of ~90%, and effectively produced bulk specimens with a millimeter thick. Sample N electrodeposited using no additives has a microstructure with grain size of ~100–200 nm and nano-twin boundaries, while sample S electrodeposited using saccharin sodium and sodium lauryl sulfate has a microstructure with grain size of ~20–30 nm. In tensile tests, both samples exhibited good plastic deformability with good tensile strength: Sample N exhibited a tensile strength of 1.0 GPa and a elongation of 8.8%; sample S exhibited a tensile strength of 1.2 GPa and a high elongation of 12%. These results indicated that increase in the current efficiency was important to produce bulk nanocrystalline metals with plasticity. The results of this study also indicated that use of additives does not determine whether the electrodeposited nanocrystalline metals exhibit plastic deformation.
References

4 Development of an electrodeposition process for bulk nanocrystalline Ni–W alloys with plasticity

4.1 Introduction

This study has the primary motivation of developing the electrodeposition process for bulk nanocrystalline Ni–W alloys with plasticity. Electrodeposited Ni–W alloys have excellent wear resistance [1], good corrosion resistance [2], and high thermal stability [3, 4]. They have, therefore, attracted significant attention with respect to their potential applications to engineering devices such as micro electromechanical systems [5, 6]. However, Ni–W alloys electrodeposited from a conventional process exhibited low tensile ductility of ~2% [7-11]. Moreover, in some case [12-14], the electrodeposited alloys were patterned by microcracks even in an as-deposited state. Several studies [13-18] addressed to improve the undesirable behavior of electrodeposited Ni–W alloys and suggested that the brittle behavior would be caused to the issues of the electrodeposition process.

There are three issues, which would make difficult to produce bulk nanocrystalline specimens with plasticity, in conventional electrodeposition process for Ni–W alloys. Firstly, conventional processes show a low current efficiency of ~30% [13-15]. It is therefore inefficient to produce bulk specimens with a millimeter thick. In fact, the thickness of electrodeposited Ni–W alloys was only less than 0.2 µm in the literatures [2, 19, 20]. It was reported that limited sample thickness could reduce their tensile ductility [21], as described in chapter 1. Secondly, electrodeposited nanocrystalline Ni–W alloys have a large internal stress which introduce defects and reduce tensile ductility of the electrodeposits [14]. There are several reports on the crack occurrence in electrodeposited Ni–W alloys that are associated
with high internal stress [12, 22, 23]. Finally, the amorphous phases are produced caused to high W content. The grain sizes are strongly tied to their composition in electrodeposited Ni–W alloys: the grain sizes decrease with increase in the W content [24]. Moreover, the phase transition from crystalline phase to amorphous phase is occurred as W content increases to >10–15 at.% [17]. In fact, formation of shear bands was observed in tensile tests using the electrodeposited nanocrystalline Ni–W alloys with grain size of ~5 nm. The amorphous materials generally exhibit no plastic deformation [8]. Mizushima et al. [13, 14] reported that the low current efficiency facilitates evolution of a large amount of hydrogen. The hydrogen co-deposition in the deposits and its subsequent release are related to the occurrence of internal stress. Therefore, high current efficiency is required to produce the bulk nanocrystalline specimens with low internal stress. In fact, in chapter 3, the sulfamate baths exhibited a high current efficiency of ~90% and effectively produce bulk nanocrystalline Ni with low internal stress and high tensile ductility [25, 26]. Therefore, the aim of this study was to develop a new electrodeposition process, which shows high current efficiency, for producing bulk nanocrystalline Ni–W alloys with plasticity, and investigate the connection between the current efficiency and the tensile ductility.

4.2 Experimental procedures

Bulk samples of electrodeposited nanocrystalline Ni–W alloys were prepared by electrodeposition from a sulfamate bath. In this study, four types of the sulfamate bath (SP, PG, SPG, and BPG) were prepared, and the details of the bath compositions are summarized in Table 4.1. All samples were deposited onto copper substrate of commercial purity using two counter electrodes of titanium baskets with nickel plates (99.98%) and tungsten rods (99.95%), respectively. The deposition cells consisted of a 1 L bath with a pH controller,
magnetic stirrer, water bath, and water-level gauge to maintain the desired bath conditions. Electrodeposition was performed at a current density of 30 mA/cm², temperature of 50 °C, and pH level of 4.0. The pH values of the solutions were maintained by adding drops of 1.0 mol/L sulfamic acid and 5.0 mol/L sodium hydroxide.

Table 4.1 Bath compositions (g/L) for bulk nanocrystalline Ni–W alloys.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>SP</th>
<th>PG</th>
<th>SPG</th>
<th>BPG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfamate</td>
<td>300.0</td>
<td>300.0</td>
<td>300.0</td>
<td>300.0</td>
</tr>
<tr>
<td>Sodium tungstate</td>
<td>6.4</td>
<td>6.4</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>-</td>
<td>8.6</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Saccharin sodium</td>
<td>5.0</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>2-Butyne-1,4-diol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The tungsten content of electrodeposited Ni–W alloys was measured by energy dispersive X-ray spectrometry (EDS) analyses using a scanning electron microscope (SEM, HITACHI S-4800). X-ray diffraction (XRD, RIGAKU Ultimate IV) analyses were carried out using Cu Kα radiation to evaluate the texture and estimate the grain size. Thin foil specimens measuring 3 mm in diameter were prepared by a twin-jet polishing technique using a nitric acid–methanol solution (20% by volume of HNO₃) at −30 °C and 15 V. The microstructure was observed using a transmission electron microscope (TEM, JEOL JEM–2100F) operated at 200 kV. Dog-bone specimens with a gauge length of 12 mm, width of 4.0 mm, and thickness of approximately 1.0 mm were machined for tensile tests by electrical discharge machining from the as-deposited plates. To evaluate the hardness of the electrodeposits, micro
Vickers tests were conducted with a load of 500 g for 10 s. Each reported data point represents an average of at least 12 impressions. To evaluate the tensile properties of the electrodeposits, tensile tests were performed at a strain rate of $1 \times 10^{-3}$ s$^{-1}$ at room temperature. The elongation of the specimen after fracture was measured by the change in the gauge length.

4.3 Optimizations of bath composition for Ni–W alloys

Optimizations of bath composition were conducted to increase the current efficiency of electrodeposition bath and reduce the internal stress of electrodeposits. As first step of the developments, sulfamate bath using propionic acid, which could produce bulk nanocrystalline Ni with high tensile ductility above 10%, was modified to electrodeposition process for bulk nanocrystalline Ni–W alloys. The bath composition of modified electrodeposition process is given in Table 4.1. Propionic acid was used as a complexing agent because Mizushima et al. reported [14] that the low current efficiency of conventional process for Ni–W alloys was caused to a large amount of citric acid used as a complexing agent. To reduce the internal stress of electrodeposits, the main component (Ni ion source) was changed from nickel sulfate to nickel sulfamate, and saccharin sodium was added to bath as a stress reliever. To obtain nanocrystalline phase, the W concentration in the deposition bath was maintained to be 2.0 at.%. As second step of the developments, the pH value of the solutions was strictly maintained to 4.0. As pH value increased to higher than 4.5, the deposition of nickel hydroxide was observed during electrodeposition using an SP bath. It was noted that conventional electrodeposition of Ni–W alloys was run at pH of greater than 6 [3]. Probably, addition of a large amount of citric acid, having chelate formability, allows to conduct electrodeposition at the high pH range.
Electrodeposition using an SP bath was conducted for 72 h. The current efficiency of the SP bath was 47%. This current efficiency is a slightly higher value compared to that of conventional process (~30%). The W content of electrodeposited alloys was ~0.45 at.%, this value was lower than the W concentration of 2 at.% in the deposition bath. Based on the results of the difference of W content, there is possible that propionic acid does not have a formability of complex with W ion.

Two tensile test specimens (samples A and B) were cut from the same Ni–W deposits. Fig 4.1 shows the XRD patterns of both samples, and a single phase with an fcc structure was observed. The grain size of both samples was calculated using XRD peak width and Scherrer’s equation. The estimated grain sizes of electrodeposits alloys were ~32 nm. Bright-field TEM image of bulk nanocrystalline Ni–W alloys is shown in Fig 4.2. The grain sizes observed by TEM image were ~20–40 nm, which were comparable to that estimated from XRD peak width.

Fig. 4.1 XRD patterns of bulk nanocrystalline Ni–W alloys electrodeposited from an SP bath.
Fig. 4.2 Bright-filed TEM image of bulk nanocrystalline Ni–W alloys electrodeposited from an SP bath.

Fig. 4.3 Tensile behavior of bulk nanocrystalline Ni–W alloys electrodeposited from an SP bath. The strain was measured using a strain gauge whose maximum measured value was 5.0%.
The stress–strain curves of samples A and B obtained from tensile tests are shown in Fig. 4.3. Sample A exhibited a tensile strength of 1.3 GPa and tensile ductility of 2.7%. Sample B exhibited a tensile strength of 1.4 GPa and a tensile ductility of 2.4%. The bulk nanocrystalline Ni–W alloys electrodeposited from an SP bath exhibited a slightly better plastic deformation compared to reported tensile ductility of ~2% [7-11]. Fig. 4.4 shows the SEM images of the fracture surface of bulk nanocrystalline Ni–W alloys electrodeposited from an SP bath. The images indicate the mixture surface of micro-voids and dimples, which are observed in brittle and ductile fracture surfaces, respectively.

Modifications of electrodeposition process for Ni–W alloys resulted in a slight increase in the current efficiency and tensile ductility. The results suggested that increase in the current efficiency could improve the tensile ductility of electrodeposits. Further modifications of electrodeposition process were needed to increase the current efficiency and promote the W deposition reaction. Weston et al. [27] reported the electrodeposition process for Co–W alloys that contained sodium gluconate as a complexing agent. The process using sodium gluconate could produce the electrodeposited Co–W alloys with W content of 14–26 at.%. Thus, sodium gluconate was expected as a complexing agent for W ion.

Fig. 4.4 SEM images of fracture surface of bulk nanocrystalline Ni–W alloys electrodeposited from an SP bath: (a) low magnification and (b) high magnification.
As final step of the developments, three types of sulfamate bath (PG, SPG, and BPG bath) contained sodium gluconate were prepared to investigate the effect of sodium gluconate and additives. The details of the bath composition are described in Table 4.1. The current efficiency of the PG, SPG, and BPG bath were 84%, 92%, and 80%, respectively. The W content of electrodeposits obtained from the PG, SPG, and BPG bath were 3.6, 1.3, and 4.5 at.%, respectively. Fig. 4.5 compares the relationship between current efficiency and the W content reported for electrodeposited Ni–W alloys [12, 14, 20, 28] with that observed in this study (including the results of chapter 5). Fig. 4.5 shows a trend of increasing current efficiency with decreasing W content. Addition of sodium gluconate increased the current efficiency to ~90%, maintaining the trend between current efficiency and W content: an optimized electrodeposition processes for producing bulk nanocrystalline Ni–W alloys was successfully developed.

Fig. 4.5 Comparison of the relationship between the current efficiency and W content in electrodeposited Ni–W alloys reported in previous studies [12, 14, 20, 28] with that determined in chapter 4 and 5.
4.4 Characterization and mechanical behavior measurements

Bulk samples of electrodeposited Ni–W alloys were prepared by electrodeposition for 72 h from a PG, SPG, and BPG bath, and these samples were assigned the following labels, PG, SPG, and BPG, respectively. The XRD patterns of each sample are shown in Fig. 4.6. The patterns show a single phase of face-centered cubic structure. The grain sizes of electrodeposits were estimated using XRD peak widths and Scherrer’s equation. The estimated grain size of the samples was ~30 nm.

Fig. 4.6 XRD patterns of samples PG, SPG, and BPG, along with peaks for the Ni powder standard from the International Center for Diffraction Data.

Fig. 4.7 shows the bright-field TEM images of samples (a) PG, (b) SPG, and (c) BPG. The formation of twin boundaries was observed in samples PG and BPG. The presence of tungsten as a solute reduces the stacking fault energy of nickel [29]. Thus, tungsten facilitated the
formation of twin boundaries in the electrodeposited bulk nanocrystalline Ni–W alloys. In samples PG and BPG, grains larger in size than those calculated from the XRD peak widths were observed because the grain sizes estimated from the XRD peak width were affected by twin boundaries [30]. In contrast, the grain sizes comparable to those calculated from the XRD peak widths were observed in samples SPG. The addition of saccharin sodium or sodium allylsulfonate reduced the grain size of nanocrystalline Ni–W alloys to approximately 30 nm. The decreased grain size caused difficulty in formation of twin boundaries.

Fig. 4.7 Bright-filed TEM images showing the planar views of samples (a) PG, (b) SPG, and (c) BPG, along with their W content.

The mechanical properties were evaluated by microhardness and tensile tests. The hardness values of samples PG, SPG, and BPG were 4.7, 4.4, and 5.2 GPa, respectively. The results of the tensile test for samples PG, SPG, and BPG are shown in Fig. 4.8. The sample SPG exhibited the tensile strength of 1.5 GPa and tensile ductility of approximately 5%. In contrast, samples PG and BPG exhibited failure, which occurred even in the elastic regime. SEM images of the fracture surface of each sample are shown in Fig. 4.9. Fig. 4.9a and c indicate a brittle fracture surfaces, while Fig. 4.9b indicates a typical ductile fracture surface in which evident plastic deformation can be seen.
Fig. 4.8 Tensile behavior of samples PG, SPG, and BPG. The strain was measured using a strain gauge whose maximum measured value was 5.0%.

Fig. 4.9 SEM images of fracture surface of samples (a) PG, (b) SPG, and (c) BPG.
Fig. 4.10 Comparison of the relationship between the ultimate tensile strength and plastic deformation of electrodeposited Ni–W alloys in reported studies [7-11], and in the current study.

Fig. 4.10 compares the relationship between ultimate tensile strength and the tensile ductility of electrodeposited Ni–W alloys [7-11] with that observed in this study. Sample SPG exhibited superior plastic deformation compared to the reported data for tensile properties of electrodeposited Ni–W alloys.

4.5 Discussion

Bulk nanocrystalline Ni–W alloys electrodeposited from a sulfamate bath with different additives showed the different tensile behavior. In this section, the association between tensile ductility and current efficiency of deposition bath, presence of nano-twin, or orientation will be discussed, and these experimental data for samples SP, PG, SPG, and BPG are summarized in Table 4.2.
Table 4.2 Summary of experimental data for electrodeposited bulk nanocrystalline Ni–W alloys.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>CE (%)</th>
<th>Twin</th>
<th>$I_{111}$</th>
<th>$I_{200}$</th>
<th>$I_{220}$</th>
<th>$\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample SP</td>
<td>47</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Sample PG</td>
<td>80</td>
<td>○</td>
<td>0.96</td>
<td>0.82</td>
<td>1.49</td>
<td>-</td>
</tr>
<tr>
<td>Sample SPG</td>
<td>92</td>
<td>-</td>
<td>0.99</td>
<td>1.38</td>
<td>0.38</td>
<td>5</td>
</tr>
<tr>
<td>Sample BPG</td>
<td>84</td>
<td>○</td>
<td>1.11</td>
<td>0.56</td>
<td>1.34</td>
<td>-</td>
</tr>
</tbody>
</table>

SP bath showed higher current efficiency of 47% compared to that of conventional electrodeposition process. Moreover, bulk nanocrystalline Ni–W alloys electrodeposited from an SP bath exhibited superior tensile ductility compared to reported data [7-11]. It was therefore considered that the improvement of tensile ductility in nanocrystalline Ni–W alloys would be achieved by increasing the current efficiency. However, samples PG and BPG prepared using the sulfamate bath, which showed high current efficiency of ~80%, exhibited no plastic deformation. Although the high current efficiency must be important to effectively produce bulk samples, increase in the current efficiency is not directly tied to high tensile ductility.

Samples PG and BPG consisted of grains of 50–100 nm in size with twin boundaries, while samples SP and SPG consisted of grains of ~30 nm in size. Although the grain size of sample BPG was much bigger than that of sample SPG, sample BPG exhibited the higher hardness value of 5.2 GPa compared to that of sample SPG. The hardness of electrodeposits was affected by the existence of twin boundaries. However, samples PG and BPG which contained twin boundaries exhibited no plastic deformation: improvement of tensile ductility by introduction of twin boundaries was not observed. Although the twin boundaries might improve the tensile ductility of electrodeposits with plasticity, the boundaries did not result in plastic deformability in electrodeposited bulk nanocrystalline metals.
The orientation indices were calculated from the X-ray diffraction patterns for each sample. The orientation index is a measure of the relative intensity of each of the characteristic peaks as compared to a randomly oriented nickel powder standard from International Centre for Diffraction Data database [31]. Samples SP and SPG, which exhibited good plastic deformation, exhibited a stronger (200) texture, whereas the other samples with no plasticity exhibited a stronger (220) texture. This trend indicated that control of the texture would have an effect on tensile ductility of electrodeposited bulk nanocrystalline Ni–W alloys. The effect of orientation on tensile ductility of bulk nanocrystalline Ni–W alloys has to be investigated in order to enable the production of bulk nanocrystalline metals with high tensile ductility. This additional study will be deeply conducted in the next chapter.
4.6 Conclusions

Bulk nanocrystalline Ni–W alloys were prepared by electrodeposition from a sulfamate bath with different additives. Ni–W electrodeposition baths contained sodium gluconate exhibited the high current efficiency of above 80%. Tensile tests were conducted using bulk samples deposited from a sulfamate bath with different additives. In particular, the bulk nanocrystalline Ni–W alloys deposited from a SPG bath exhibited superior plastic deformation of approximately 5% compared to the reported data for tensile properties of electrodeposited Ni–W alloys. In addition, the results of tensile tests indicated that there was no relationship between the tensile ductility and the grain sizes or existence of twin boundaries. On the other hand, the sample with plastic deformability exhibited a stronger (200) texture, whereas other samples with no plastic deformability, exhibited a stronger (111) texture. These experiments indicated that controlling the textures is important to improve the tensile ductility of electrodeposited bulk nanocrystalline Ni–W alloys.
References

5 Effect of orientation on tensile ductility of electrodeposited bulk nanocrystalline Ni–W alloys

5.1 Introduction

This study has the primary motivation of studying the effect of orientation on tensile ductility of electrodeposited bulk nanocrystalline Ni–W alloys in order to dictate the parameter “X”. Nanocrystalline metals are expected to exhibit high ductility due to their novel deformation mechanisms, such as grain boundary dislocation emission [1], grain boundary sliding [2], and grain boundary migration [3], in addition to high level of strength. These novel mechanisms have been studied using molecular dynamics simulations and TEM techniques. Also, there are a large number of reports that evaluate tensile properties nanocrystalline metals prepared by electrodeposition [4-10]. Although the yield strength and ultimate tensile strength of electrodeposited nanocrystalline metals primarily dictated by grain size, the tensile ductility cannot explained by grain size alone.

For example, electrodeposited nanocrystalline Ni–W alloys exhibited high strength and hardness [11]. In contrast, low plastic deformability of less than 2% was observed in tensile tests, using the electrodeposited nanocrystalline Ni–W alloys with grain size of 3–20 nm [12-16]. It was considered that the reduction in ductility of electrodeposits was caused by low current efficiency of the conventional process for Ni–W alloys [17]. Although the improvement of tensile ductility was achieved by increasing the current efficiency of electrodeposition process [17], some electrodeposits obtained from a bath that exhibited high current efficiency (>80%) also showed crack formation [18]. It is clear that the reduction in ductility of electrodeposits cannot be explained by current efficiency alone.
In chapter 4, a new electrodeposition bath for bulk nanocrystalline Ni–W alloys with plasticity was developed [17], and investigated the effect of additives on tensile properties of electrodeposits [19], to improve the tensile ductility. Bulk nanocrystalline Ni–W alloys that exhibited a tensile strength of 1.5 GPa and good tensile ductility of 4.6% could be produced using the sulfamate bath, which contained saccharin sodium as a stress reliever and propionic acid and sodium gluconate as a complexing agent (SPG bath). Moreover, samples that exhibited plastic deformability showed a stronger (200) texture, while samples that did not exhibit plastic deformability showed a stronger (111) texture. Microstructural studies on electrodeposited bulk nanocrystalline metals, including not only the grain size but also the crystallographic texture, are required to understand the intrinsic properties [20, 21]. However, the relationship between the tensile ductility and the crystallographic texture of electrodeposited bulk nanocrystalline Ni–W alloys has not been investigated. Therefore, the aim of this study was to demonstrate a correlation between tensile ductility and orientation index of electrodeposited bulk nanocrystalline Ni–W alloys experimentally to understand the ductility of electrodeposits. Electrodeposition was performed using an SPG bath by varying the amount of saccharin sodium and the bath temperature to produce electrodeposits with different textures. Subsequently, their tensile properties were evaluated.

### 5.2 Experimental procedures

In total, 7 bulk samples (LS\textsubscript{45}, LS\textsubscript{50}, LS\textsubscript{60}, HS\textsubscript{45}, HS\textsubscript{50-1L}, HS\textsubscript{50}, and HS\textsubscript{55}) of nanocrystalline Ni–W alloys were electrodeposited from an SPG bath, varying the amount of saccharin sodium and the bath temperature. The details of the bath compositions for the SPG bath are described in Table 5.1. The used amount of saccharin sodium and applied bath temperature are given in Table 5.2. All samples were deposited onto copper substrate of commercial purity
using two counter electrodes of titanium baskets with nickel plates (99.98%) and tungsten rods (99.95%), respectively. The main components of our electrodeposition system were power supplies, 5-L bath, a circulating water pump, a feed water pump, and a filter to remove the precipitate: the schematic image of this system is shown in Fig. 5.1. The bath temperature was maintained at 45, 50, 55, or 60 ± 0.5 °C by a titanium heater using a proportional–integral–derivative controller. All electrodepositions were run at a current density of 30 mA/cm² and a pH of 4.0 ± 0.1. The pH values of the solutions were maintained by adding drops of 1.0 mol/L sulfamic acid and 5.0 mol/L sodium hydroxide.

### Table 5.1 Bath compositions (g/L) for bulk nanocrystalline Ni–W alloys.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>LS</th>
<th>HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfamate</td>
<td>300.0</td>
<td>300.0</td>
</tr>
<tr>
<td>Sodium tungstate</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Saccharin sodium</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The carbon and sulfur contents of the electrodeposits were quantified by an IR absorption method after combustion in a high-frequency induction furnace. The tungsten content of the electrodeposited Ni–W alloys was measured by energy-dispersive X-ray spectrometry analysis using a scanning electron microscope (HITACHI S-4800). X-ray diffraction (XRD, RIGAKU Ultimate IV) analysis was performed using Cu Kα radiation to estimate the grain size and examine the crystalline texture. Thin foil specimens measuring 3 mm in diameter were prepared by a twin-jet polishing technique using a nitric acid–methanol solution (20%
by volume of HNO$_3$) at −30 °C and 15 V. The microstructure was observed using a transmission electron microscope (TEM, JEOL JEM–2100F) operated at 200 kV. Dog-bone specimens with a gauge length of 12 mm, width of 4.0 mm, and thickness of approximately 1.0 mm were machined for tensile tests by electrical discharge machining from the as-deposited plates. Tensile tests were performed at a strain rate of $1 \times 10^{-3}$ s$^{-1}$ and room temperature. The elongation of the specimen after fracture was measured by the change in the gauge length. With the exception of sample LS$_{60}$, each reported data point represented the average of three measurements.

Table 5.2 Summary of bath conditions, and W, C, S, and H content of bulk nanocrystalline Ni–W alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saccharin (g/L)</th>
<th>Temp. (ºC)</th>
<th>W (at.%</th>
<th>C (at.%</th>
<th>S (at.%</th>
<th>H (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS$_{45}$</td>
<td>0.1</td>
<td>45</td>
<td>3.4</td>
<td>0.04</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>LS$_{50}$</td>
<td>0.1</td>
<td>50</td>
<td>1.9</td>
<td>0.03</td>
<td>0.05</td>
<td>3</td>
</tr>
<tr>
<td>LS$_{60}$</td>
<td>0.1</td>
<td>60</td>
<td>5.3</td>
<td>0.13</td>
<td>0.06</td>
<td>66</td>
</tr>
<tr>
<td>HS$_{45}$</td>
<td>5.0</td>
<td>45</td>
<td>1.5</td>
<td>0.04</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>HS$_{50-1L}$*</td>
<td>5.0</td>
<td>50</td>
<td>1.3</td>
<td>0.02</td>
<td>0.04</td>
<td>3</td>
</tr>
<tr>
<td>HS$_{50}$</td>
<td>5.0</td>
<td>50</td>
<td>1.0</td>
<td>0.02</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>HS$_{55}$</td>
<td>5.0</td>
<td>55</td>
<td>1.5</td>
<td>0.03</td>
<td>0.04</td>
<td>-</td>
</tr>
</tbody>
</table>

*Sample HS$_{50-1L}$ was electrodeposited using a 1-L bath. The details of 1-L bath are described in chapter 4.
5.3 Characterization and mechanical behavior measurements

Electrodeposition from SPG baths was performed for 72 h to prepare the bulk samples with a millimeter thick. High current efficiencies of ~90% were obtained for electrodeposition of all samples. The W content of each sample was measured by SEM–EDS, and the results are summarized in Table 5.2. Comparison of the W contents of electrodeposits prepared by using 1.0 g/L and 5.0 g/L saccharin sodium indicated that increasing the amount of saccharin sodium reduced the W content of the electrodeposits. The alloys electrodeposited at 50 °C exhibited a lower W content than other electrodeposits. The carbon and sulfur content were also measured by an IR absorption method, and the results are given in Table 5.2. Although, these impurities can affect the resultant mechanical strength value, as described in chapter 2, the carbon and sulfur contents were close to the same among the electrodeposited alloys for this study. The contributions to the tensile properties of the test samples would, in practice, be few and similar.
Fig. 5.2 XRD patterns of bulk nanocrystalline Ni–W alloys electrodeposited from an SPG bath.

Fig. 5.3 Bright-field TEM images of (a) sample LS_{60}, (b) sample HS_{45}, (c) sample HS_{50-1L}, and (d) sample LS_{50}. 
Table 5.3 Summary of grain size, orientation index, and tensile properties of the bulk nanocrystalline Ni–W alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>d (nm)</th>
<th>$I_{111}$</th>
<th>$I_{200}$</th>
<th>$I_{220}$</th>
<th>UTS (GPa)</th>
<th>$\varepsilon_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS$_{60}$</td>
<td>18</td>
<td>0.77</td>
<td>0.17</td>
<td>3.78</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HS$_{45}$</td>
<td>22</td>
<td>1.29</td>
<td>0.79</td>
<td>0.07</td>
<td>1.36</td>
<td>1.7</td>
</tr>
<tr>
<td>LS$_{45}$</td>
<td>20</td>
<td>1.29</td>
<td>0.83</td>
<td>0.04</td>
<td>1.63</td>
<td>1.8</td>
</tr>
<tr>
<td>HS$_{50-1L}$</td>
<td>30</td>
<td>0.99</td>
<td>1.38</td>
<td>0.29</td>
<td>1.47</td>
<td>4.6</td>
</tr>
<tr>
<td>HS$_{55}$</td>
<td>26</td>
<td>0.64</td>
<td>2.34</td>
<td>0.02</td>
<td>1.32</td>
<td>7.6</td>
</tr>
<tr>
<td>HS$_{50}$</td>
<td>27</td>
<td>0.69</td>
<td>2.24</td>
<td>0.03</td>
<td>1.50</td>
<td>10.3</td>
</tr>
<tr>
<td>LS$_{50}$</td>
<td>22</td>
<td>0.54</td>
<td>2.59</td>
<td>0.04</td>
<td>1.45</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Fig. 5.2 shows the XRD patterns of each sample. The grain size of each sample was calculated using XRD peak width and the Scherrer equation. The estimated grain sizes were varied from 18 to 30 nm. Bright-field TEM images of samples LS$_{60}$, HS$_{45}$, HS$_{50-1L}$, and LS$_{50}$ are shown in Fig. 5.3. Each sample exhibited a nanocrystalline structure with a grain size of approximately 20–30 nm, which were comparable with the sizes estimated by XRD peak widths.

All samples showed a single phase with fcc structure, as shown in Fig 5.2. The orientation index is a measure of the relative intensity of each of the characteristic XRD peaks as compared to a randomly oriented nickel powder standard from International Centre for Diffraction Data database. This relative intensity is used to determine the preferred orientation of the nanocrystalline Ni–W alloys. Orientation indices were calculated using the XRD patterns for each sample and the indices $I_{111}$, $I_{200}$, and $I_{220}$ are given in Table 5.3. Sample LS$_{60}$ exhibited dominant (111) and (220) peaks and had a strong (220) texture; sample LS$_{45}$ and HS$_{45}$ exhibited dominant (111) and (200) peaks and had a strong (111) texture; samples LS$_{50}$, HS$_{50-1L}$, HS$_{50}$, and HS$_{55}$ exhibited dominant (111) and (200) peaks and had a strong (200)
texture. By varying the bath temperature, the electrodeposited alloys with different textures were successfully obtained.

The stress–strain curves of samples $L_{S45}$, $L_{S50}$, $H_{S45}$, $H_{S50-1L}$, $H_{S50}$, and $H_{S55}$ obtained from tensile tests are shown in Fig. 5.4. The ultimate tensile strength and plastic deformation determined from a measurement of the change in gauge length are given in Table 5.3. Samples $L_{S50}$, $H_{S50}$, and $H_{S55}$, which had a strong (200) texture, exhibited clear tensile ductility of 13.4%, 10.3%, and 7.6%, respectively. Fig. 5.5 shows actual specimens of sample $L_{S50}$ before and after the tensile fracture, from which plastic deformation can be seen. On the other hand, sample $L_{S60}$ which showed many cracks on the surface was too brittle for the tensile test.

![Graph showing stress-strain curves for different samples](image)

Fig. 5.4 Tensile behavior of samples $L_{S45}$, $L_{S50}$, $L_{S60}$, $H_{S45}$, $H_{S50-1L}$, $H_{S50}$, and $H_{S55}$. The strain was measured using a strain gauge whose maximum measured value was 5.0%. The sample $L_{S60}$ was too brittle to conduct tensile test.
Fig. 5.5 Photograph shows the actual specimens of sample LS$_{50}$ before and after the tensile fracture.

Fig. 5.6 Comparison of the relationship between the ultimate tensile strength and plastic deformation of electrodeposited Ni–W alloys in reported studies [16-20], and in the current study. The elongation after fracture was obtained experimentally by comparing the gauge length before and after the tensile test.
Fig. 5.6 compares the relationship between the ultimate tensile strength and the tensile ductility of electrodeposited nanocrystalline Ni–W alloys reported in previous studies [12-16], and that determined in chapter 4 and 5. The electrodeposited Ni–W alloys generally showed high strength and low plasticity. In contrast, the bulk nanocrystalline Ni–W alloys with a strong (200) texture, deposited from an SPG bath, exhibited high tensile ductility with good tensile strength, as shown in Fig. 5.6. In the following sections, the connection between orientation and tensile ductility will be discussed to understand the tensile behavior of electrodeposited bulk nanocrystalline Ni–W alloys.

### 5.4 Discussion

The plasticity of the bulk nanocrystalline Ni–W alloys could be transformed by varying the amount of saccharin sodium and the bath temperature. In the past, Erb et al. [22, 23] investigated the effect of sample thickness on the tensile ductility of electrodeposited nanocrystalline metals. From these reports, the tensile specimens with a millimeter thick used for this study are sufficient to evaluate the tensile ductility. There was no correlation between the tensile ductility and grain size or W content of the electrodeposits. In chapter 4, bulk nanocrystalline Ni–W alloys with plasticity exhibited stronger (200) texture, whereas the alloys with no plasticity exhibited stronger (111) texture. A comparison of the relationship between the tensile ductility and the orientation index of the (200) plane of bulk nanocrystalline Ni–W alloys electrodeposited from an SPG bath is shown in Fig. 5.7. (The tensile ductility of the samples, which were too brittle for the tensile test, was plotted as 0%.) In the range in which the orientation index for the (200) plane varied from 0 to 0.5, no plastic deformation was observed. As the index increases to ~0.7, low plastic deformation of ~2% was observed. The bulk nanocrystalline Ni–W alloys exhibited plastic deformation when the
orientation index exceeded 1, with the plasticity increasing from 4.6 to 13.4% as the orientation index increased from 1.4 to 2.6. In addition, the relationship between tensile ductility and the orientation index of the (200) plane of electrodeposited bulk nanocrystalline Ni–Fe alloys [22, 24] is shown in Fig. 5.7. The electrodeposited bulk nanocrystalline Ni–Fe alloys that exhibited good tensile ductility showed strong (200) texture, as well as bulk nanocrystalline Ni–W alloys. These results indicated that the plasticity of electrodeposits was dictated by their orientation index for the (200) plane, and this is just what this study has been looking for.

![Graph showing the relationship between plastic deformation and the orientation index for the (200) plane in electrodeposited nanocrystalline Ni–Fe obtained from the literature [26, 28], and Ni–W alloys electrodeposited from an SPG bath.](image)

The results of chapter 5 indicated a strong (200) texture should be a condition for exhibiting the clear tensile ductility in bulk nanocrystalline Ni alloys prepared by an electrodeposition.
This result prompted the question of how orientation index relates to the tensile ductility. Amblard et al. [25] reported that the orientation of electrodeposits reflects the mode of crystal growth during electrodeposition. They also indicated that the (111), (100), and (110) textures of electrodeposited Ni were attributed to inhibited lateral growth, free lateral growth, and out-growth, respectively. The hydrogen and nickel hydroxides behaved as an inhibitor on inhibited growth mode. Thus, the more details of effect of orientation, including the growth modes, in electrodeposited bulk nanocrystalline metals will be discussed by classifying into three states.

Firstly, in the case of an inhibited out-growth mode, hydrogen ions are discharged at the cathode surface and adsorbed as side reactions during an electrodeposition, as shown in Fig. 5.8a. This adsorption resulted in a localized Ni–W deposition reaction and a rugged surface led to inhomogeneous distribution of the electrical current. The current density was generally higher at the protrusions than at the depressions. The W atoms were localized in the area of high current density and inhibited growth, as shown in Fig. 5.8b, because W atoms are more electroactive than the Ni atoms [21]. In fact, sample LS60 with a stronger (220) texture had a higher W content compared to samples with a stronger (200) texture (Table 5.2). In addition to the increase in the W deposition, co-deposition of hydrogen would also be occurred. The hydrogen content of representative samples, which had a stronger (220), (111), and (200) textures, was 66, 7, 3 ppm, respectively (Table 5.2).
Fig. 5.8 Schematic illustration depicting how electrodeposition evolves due to an inhibited out-growth mode in the bulk nanocrystalline Ni–W alloys: (a) an initial state and (b) a final state. This schematics correspond to electrodeposits with a stronger (200) texture.

Fig. 5.9 SEM image of surface of sample LS₆₀ which had a stronger (220) texture.
Sample LS$_{60}$ which had a stronger (220) texture showed many cracks on the surface, as shown in Fig. 5.9. The cracks were mainly attributed to the co-deposition of adsorbed hydrogen.

Secondly, in the case of an inhibited lateral growth mode, gaseous hydrogen is generated at the cathode surface as side reactions during an electrodeposition, as shown in Fig. 5.10a. It was expected that the repeat of co-deposition of gaseous hydrogen and the release introduced a tensile internal stress and a nano-crack, as shown in Fig. 5.10b. In fact, the cross-sectional TEM observations showed the presence of nano-cracks in bulk nanocrystalline Ni–W alloys which had a stronger (111) texture, even at as-deposited state (Fig. 5.11). Therefore, the electrodeposits with a stronger (111) texture exhibited a low plastic deformation of ~2% due to propagation of nano-cracks. Li and Ebrahimi [26] also reported similar fracture mechanism caused as the result of the propagating crack. In addition, the inhibition of Ni–W deposition reaction and formation of nano-cracks resulted in a rugged surface led to inhomogeneous distribution of the electrical current. So, sample LS$_{45}$ and HS$_{45}$ with a stronger (111) texture had a higher W content compared to samples with a stronger (200) texture (Table 5.2).

Finally, in the case of a free lateral growth mode, the Ni–W electrodeposition reaction could occur uniformly in the absence of inhibitors, as shown in Figs. 5.12a and b. No nano- and micro-cracks were observed by cross-sectional TEM observation in the electrodeposits obtained from a free lateral growth mode, as shown in Fig. 5.13.
Fig. 5.10 Schematic illustration depicting how electrodeposition evolves due to an inhibited lateral growth mode in the bulk nanocrystalline Ni–W alloys: (a) an initial state and (b) a final state. This schematics correspond to electrodeposits with a stronger (111) texture.

Fig. 5.11 Cross-sectional TEM images of as-deposited sample HS_{45} which had a stronger (111) texture.
Fig. 5.10 Schematic illustration depicting how electrodeposition evolves due to a free lateral growth mode in the bulk nanocrystalline Ni–W alloys: (a) an initial state and (b) a final state. This schematics correspond to electrodeposits with a stronger (200) texture.

Fig. 5.11 Cross-sectional TEM images of as-deposited sample LS$_{50}$ which had a stronger (200) texture.
5.5 Development of “principle of design”

The results and discussions indicate that defect-free samples can be obtained from a free lateral growth mode, and the growth mode can be dictated by the orientation. The author would like to qualitatively summarize the connection between electrodeposition parameters and the growth mode (or orientation) and show the “principle of design” for producing bulk nanocrystalline metals with high strength and high ductility.

Fig. 5.11 shows the correlation chart that illustrates how electrodeposition parameters approximately affect to growth mode during electrodeposition (or orientation of resulted electrodeposits). The current density could be classified into three ranges, such as low, medium, and high current density range. The applied current density was reflected in current efficiency: the low and high current density resulted in lower and higher current efficiency, respectively, compared to that as applied medium current density. The lower current efficiency is caused to the inhibition of Ni–W deposition reaction by adsorption of hydrogen. The higher current efficiency is caused to the co-deposition of hydroxide because generation of gaseous hydrogen is associated with increase in the hydroxide ion concentration in the deposition bath. Thus, the medium current density is required to operate the free lateral growth mode. Obviously, the bath temperature has an effect on the current density ranges because the activity of ions and the reaction rate increased with increasing bath temperature. If bath temperature is increased, the each current density range would be relatively-translated to higher regions. Moreover, pH values determine the hydrogen ion concentration and hydroxide ion concentration. As a pH value decreases, the hydrogen ion concentration increases, and this increase promote the adsorption of hydrogen led to extension of the inhibited-out growth mode range. Also, the increase in the hydroxide ion concentration with increasing the pH value promotes the co-deposition of hydroxide led to extension of the
inhibited lateral growth mode range.

Fig. 5.11 Correlation chart, showing “principle of design” for producing bulk nanocrystalline metals with high strength and high ductility, illustrates how electrodeposition parameters approximately affect to growth mode during electrodeposition (or orientation of resulted electrodeposits).
5.6 Conclusions

Bulk nanocrystalline Ni–W alloys were electrodeposited from an SPG bath. The tensile ductility of 0–13.4% was obtained by varying the amount of saccharin sodium and the bath temperature. The results of tensile tests and XRD analysis showed that the tensile behavior could be explained by the orientation index for the (200) plane: low plastic deformability was observed when the index was below 1, while the tensile ductility increased with increasing orientation index above a value of 1. Orientation of electrodeposits is tied to the growth mode during electrodeposition. Therefore, this indicated that a growth mode determine whether the expression of tensile plastic deformation in electrodeposited bulk nanocrystalline metals. Free lateral growth mode should be required to exhibit a clear tensile ductility in electrodeposited bulk nanocrystalline Ni–W alloys.
References


6 Summary and conclusions

One sub-area that has received significant attention is the mechanical properties of materials with grain sizes less than 100 nm. The great interest in the mechanical behavior of nanocrystalline materials originates from the unique mechanical properties first observed and/or predicted by the pioneers of this field, Gleiter and co-workers, in materials prepared by the gas condensation method. Among these early observation or predictions were:

- very high hardness and strength: hardness values for nanocrystalline pure metals with grain size of ~10 nm that are 2–10 times higher than those of larger grained (>1 µm) metals;
- increased ductility: perhaps even superplastic behavior was believed to be caused by grain boundary, diffusional deformation mechanisms.

Some of these early observations and predictions have been verified by subsequent studies: there are a large number of papers that fabricated nanocrystalline metals and investigated the mechanical properties. In fact, in early studies, nanocrystalline metals exhibited the high level of hardness and strength. Although the strength could primarily be dictated by grain size according to Hall–Petch relationship, comparison of the reported data showed scatter of data points. Moreover, most of nanocrystalline metals do not exhibit the high predicted ductilities. Some researchers suggested that the undesired properties of nanocrystalline metals were caused to defects introduced by the processing procedures and limited sample size.

Electrodeposition processes have been had attention and developed as a fabrication process to produce bulk nanocrystalline metals with no artifacts. Thereby, there are recent examples of good ductility along with high strength in a limited number of cases. However, among these data, the scatter of strength was still observed. In addition, although some studies improved
the tensile ductility of electrodeposited bulk nanocrystalline metals, the details of the electrodeposition process are not given. This remains an important question in this field that is “how are bulk nanocrystalline metals with good plasticity electrodeposited?”

Two big challenges for tensile properties of electrodeposited nanocrystalline metals were identified by the literature survey: one of issues is scatter of strength in reported data; another is uncertainty of fabrication conditions for expression of plastic deformation. In this study, the aim of this study is to reveal the effect of light elements, resulting from electrodeposition process, on strength and dominant factor (parameter “X”) of tensile ductility by developments and optimization of electrodeposition processes for bulk nanocrystalline Ni and Ni–W alloys. In addition, on the basis of obtained data and discussion, principle of design for bulk nanocrystalline metals with high strength and high ductility was obtained.

In Chapter 1, concept and history of nanocrystalline metals were summarized, in particular the unique mechanical behavior. It was also showed that nanocrystalline metals have the potential of application as next generation structural materials. Reviewing of early studies on mechanical behavior of nanocrystalline metals clarified the challenges that had to be solved in order to promote the application, and then dictated the aim of this thesis.

In Chapter 2, solid solution strengthening by carbon and sulfur in bulk nanocrystalline Ni was studied by electrodeposition and first-principles calculations. Bulk nanocrystalline Ni with a carbon content of 30–1600 ppm and a sulfur content of 140–1200 ppm was prepared using a sulfamate bath with different complexing agents and gloss agents. The hardness values of the bulk nanocrystalline Ni were scattered as the grain size decreased to 12 nm with increasing carbon and sulfur content. It was found that the scatter could be explained by considering the effect of impurities such as solute atoms on the hardness of electrodeposited Ni, in addition to the Hall–Petch relationship. Thus, to determine the structure of Ni–C and Ni–S solid solutions and estimate the contribution of impurities to hardness, the enthalpy of
solution and misfit strain were calculated by first-principles calculations. The results indicate that carbon exists as an interstitial solute atom in the Ni matrix, producing large misfit strains, and sulfur exists as a substitutional solute atom, inducing no significant changes. A model of solid solution strengthening due to interstitial solute atoms was developed by considering the interaction between mobile dislocations and solute atoms. The results and discussion have effectively divided the observed solid solution effect from the grain refinement effect in electrodeposited nanocrystalline Ni. This chapter point to the origin of high-strength electrodeposited bulk nanocrystalline Ni, and reflects the Hall–Petch equation for Ni.

In Chapter 3, bulk nanocrystalline Ni was prepared by electrodeposition from a sulfamate bath with no additives or with saccharin sodium to improve the tensile ductility and investigate the effect of additives on the ductility. The both sulfamate baths show a high current efficiency of ~90%. The electrodeposits obtained from a sulfamate bath with no additives had a microstructure with grain size of ~100–200 nm and nano-twin boundaries, while that electrodeposited using saccharin sodium and sodium lauryl sulfate has a microstructure with grain size of ~20–30 nm. In tensile tests, both electrodeposits exhibited good plastic deformability with good tensile strength: Sample electrodeposited from a sulfamate bath exhibited a tensile strength of 1.0 GPa and a ductility of 8.8%; sample electrodeposited using additives exhibited a tensile strength of 1.2 GPa and a high ductility of 12%. The results of this chapter indicated that the use of additives does not determine whether the expression of plastic deformation.

In Chapter 4, development of an electrodeposition process for producing bulk nanocrystalline Ni–W alloys with high tensile ductility was addressed. Conventional electrodeposition processes for Ni–W alloys show a low current efficiency of ~30% and introduce a high internal stress to electrodeposits. To increase current efficiency and reduce internal stress, sulfamate bath for bulk nanocrystalline Ni was modified to electrodeposition
process for bulk nanocrystalline Ni–W alloys. As a result, sulfamate bath contained saccharin sodium as a stress reliever and propionic acid and sodium gluconate as a complexing agent (SPG bath) was successfully developed. The bath showed a high current efficiency of ~90% and effectively produced bulk specimens. The bulk nanocrystalline Ni–W alloys deposited from a SPG bath exhibited superior plastic deformation of approximately 5% compared to the reported data for tensile properties of electrodeposited Ni–W alloys. Among the results of tensile tests in this chapter, there was no relationship between tensile ductility of electrodeposits and current efficiency or nano-twins. In contrast, the sample with plastic deformability exhibited a stronger (200) texture, whereas other samples with no plastic deformability, exhibited a stronger (111) texture. The results of this chapter suggested that controlling the textures is important to improve the tensile ductility.

In Chapter 5, effect of orientation on tensile ductility of electrodeposited bulk nanocrystalline Ni–W alloys was studied. Electrodeposited alloys with different textures were prepared by varying the amount of saccharin sodium and the bath temperature. An elongation of 0–13.4% was obtained in a tensile test. Although there was no relationship between tensile ductility and the grain size or W content, there was the relationship between tensile ductility and the orientation index for the (200) plane in the bulk nanocrystalline Ni–W alloys. In fact, low plastic deformability was observed when the index was below 1, while the tensile ductility increased with increasing orientation index above a value of 1. The results of this chapter point out orientation index for the (200) plane as a dominate factor (parameter “X”) of tensile ductility in electrodeposited bulk nanocrystalline metals. In addition, “principle of design” for producing bulk nanocrystalline metals with high strength and high ductility was developed, based on the connection between electrodeposition parameters and the orientation along with the growth mode.

Through the studies in early chapters, the author addressed the two big challenges for tensile
properties of electrodeposited bulk nanocrystalline metals. The results and discussion in this thesis indicated that scatter in the strength values was caused to the difference in carbon content which could produce a solid solution strengthening, and tensile ductility of electrodeposited bulk nanocrystalline metals could be explained by orientation index for the (200) plane. The author developed the “principle of design” for producing bulk nanocrystalline metals with high strength and high ductility. Although this thesis focused on Ni and Ni–W alloys, in the near future, the “principle of design” will promote the fabrication of electrodeposited bulk nanocrystalline materials of practical use, such as austenite and Al alloys, with desired combination of high strength and high ductility. It must be recognized that the real benefits of structural nanocrystalline materials are likely to be many years away.