Microstructure homogeneity and mechanical properties of electrodeposited nanocrystalline Ni

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Abstract. Microstructure and mechanical properties of an electrodeposited nanocrystalline Ni (nc-Ni) were investigated. Electrodeposition was done on two different kinds of Cu substrates. One was a Cu sheet having coarse grains, and the other was a sheet having a nanocrystalline Cu (nc-Cu) layer on the surface. The substrates were chemically removed after the electrodeposition of Ni. Then, sheets of fully dense nc-Ni with a thickness of approximately 100 µm were obtained. The surface of the sheets which had touched the substrate showed a mat surface appearance, while the other surface was mirror-like. In the nc-Ni electrodeposited on the coarse grained Cu substrate, the mirror-like surface showed homogeneous equiaxed grain structure, while the mat surface showed inhomogeneous structure. In the nc-Ni electrodeposited on the nc-Cu substrate, the microstructure of the mirror-like surface was similar to that in the nc-Ni deposited on the coarse grained Cu. However, the mat surface showed the homogenous structure, different from that in the nc-Ni deposited on the coarse grained Cu. This result indicates that the grain size and homogeneity of the microstructure of nc-Ni sheets were affected by the microstructure of the substrate. The electrodeposited nc-Ni performed strength four times higher than that of the conventionally coarse-grained pure Ni with grain size of 28 µm. In the tensile test, the total elongation of the nc-Ni electrodeposited on the coarse grained Cu was smaller than that of the nc-Ni electrodeposited on the nc-Cu. It is suggested that the homogeneity of microstructure significantly affects the mechanical properties of nc-Ni.

1. Introduction
Grain refinement is one of the ways to improve mechanical properties of metallic materials. It is well known that ultrafine-grained (UFG) materials fabricated by severe plastic deformation (SPD) processes [1-4] exhibit high strength and peculiar mechanical properties [5, 6]. However, it is difficult to fabricate nanocrystalline materials whose grain size is about several tens nanometers through the SPD process. Thus, it is still unclear whether the mechanical properties of the nanocrystalline materials are similar to that of the UFG materials or not.

Electrodeposition has been known as a technique for fabricating nanocrystalline materials having the mean grain size of several tens nanometers [6, 7]. In the present study, microstructure of an electrodeposited nanocrystalline Ni is observed in detail. In addition, mechanical properties of the nanocrystalline Ni are also evaluated by tensile test.
2. Experimental procedure

The material investigated in the present study is an electrodeposited nanocrystalline Ni (nc-Ni). The solution containing NiSO$_4$, NiCl$_2$, H$_3$BO$_4$, saccharine and sodium lauryl sulfate was used as the plating bath for the production of nc-Ni. Electrodepositions were done on two different kinds of Cu substrates at 65°C and pH 5.0 with current density of 0.05A/cm$^2$ for 3 hours. One of the substrates was a fully annealed Cu sheet having coarse grains, and the other was a sheet having a nanocrystalline Cu (nc-Cu) surface layer fabricated by plating. The substrates were chemically removed after the electrodeposition of Ni. Then, sheets of fully dense nc-Ni with a thickness of approximately 100 µm were obtained. The surface of the sheets which had touched the substrate showed a mat surface appearance, while the other surface which had touched the plating solution was mirror-like.

The structure of the nc sheets was characterized by TEM (transmission electron microscopy). In order to compare the structure of the mirror-like surface and the mat surface, the TEM specimens were prepared for both surfaces.

The mechanical properties of the nc-Ni were investigated by Vickers hardness test and tensile test. Tensile specimens 5mm in gage width and 10 mm in gage length (1/5 of JIS-5 specimen) were tested at ambient temperature at an initial strain rate of $8.3 \times 10^{-4}$ s$^{-1}$. Vickers hardness was measured on the cross-sections of the nc-Ni sheets to clarify the difference throughout thickness of the sheets.

3. Results and discussion

3.1. Microstructure of the nc-Ni sheets

The TEM micrographs of the nc-Ni electrodeposited on the coarse grained Cu substrate were shown in Fig.1. The microstructure of mirror-like surface (solution side) and mat surface (substrate side) were shown in Fig. 1 (a) and (b), respectively. The mirror-like surface showed homogeneous equiaxed nanocrystalline grain structure. The mean grain size of the mirror-like surface was 31 nm. On the other hand, the mat surface showed inhomogeneous structure composed of small nanocrystalline grains and large grains with diameters larger than 100 nm. The mean grain size of the small grains and large grains in the mat surface region were 54 nm and 128 nm, respectively. The nc-Ni grains involve diffraction contrasts which might be caused by defects within the grains, such as dislocations. Some dislocations were observed in the nc-Ni grains by high resolution TEM observation (Fig.1 (c)). In Fig.1 (c), white lines show the lattice plane and an extra half plane was observed. The result confirms that the dislocations were introduced even in the electrodeposition process.

Figure 2 shows the TEM micrographs of the mirror-like surface (a) and the mat surface (b) in the nc-Ni electrodeposited on the nc-Cu substrate. The microstructure of the mirror-like surface was homogeneous, which was similar to that in the nc-Ni deposited on the coarse grained Cu (Fig.1 (a)). The mean grain size of the mirror-like surface was 28 nm. The mat surface also showed the relatively homogenous structure having the mean grain size of 40 nm, which was different from that in the nc-Ni deposited on the coarse grained Cu (Fig.1 (b)). These results indicate that the grain size and

![Figure 1](image-url)

**Figure 1.** TEM micrographs of the nc-Ni electrodeposited on the coarse grained Cu substrate. (a) mirror-like surface (solution side), (b) mat surface (substrate side) and (c) high resolution TEM microstructure of mirror-like surface.
microstructural homogeneity of the electrodeposited Ni are affected by the microstructure of the substrate. Such an inhomogeneity in the electrodeposited materials has not been reported and focused. However, it is important when considering mechanical properties, as will be shown in the following sections.

3.2. Vickers hardness of the nc-Ni sheets
Vickers hardness of the nc-Ni is shown in Fig. 3 as a function of the normalized distance from the mat surface, \( t/t_0 \), where \( t \) is the distance from the mat surface and \( t_0 \) is the total thickness of the nc sheet. Therefore, \( t/t_0 = 0 \) indicates the mat surface, while \( t/t_0 = 1 \) the mirror-like surface. In Fig. 3, the circles and triangles indicate the hardness of the nc-Ni electrodeposited on the coarse grained Cu and the nc-Cu, respectively. In the nc-Ni electrodeposited on the coarse grained Cu substrate, the hardness near the mat surface was significantly smaller than that near the mirror-like surface. The hardness increased with increasing \( t/t_0 \) up to 0.2, and then the hardness showed nearly a constant value after that. On the other hand, in the nc-Ni electrodeposited on the nc-Cu substrate, the dependence of hardness on \( t/t_0 \) was not significant. The hardness distributions coincide well with the microstructural results shown in Figs. 1 and 2.

3.3. Tensile test for the nc-Ni sheets
In most of reports for nanocrystalline metallic materials, Vickers hardness tests were carried out for investigating mechanical properties. Tensile test can give more information to understand deformation behaviors of the nanocrystalline materials. Thus, tensile test was done in the present study at ambient temperature at an initial strain rate of 8.3 \( \times 10^{-4} \) s\(^{-1} \). The stress-strain curves of the nc-Ni sheets obtained by the tensile test are shown in Fig. 4. For comparison, the curve of a coarse grained Ni (99.9% purity) having the mean grain size of 28 µm, which was prepared through conventional wrought and recrystallization processes, is also shown in the figure. For the coarse grained Ni, the yield stress was 43MPa, the ultimate tensile strength (UTS) of the coarse grained Ni was 331MPa and the total elongation was 65.5%. These are typical values of conventional polycrystalline pure Ni having coarse grains. It was found that the UTS of the nc-Ni electrodeposited on the coarse grained Cu was similar to that of the nc-Ni electrodeposited on the nc-Cu substrate. The 0.2% proof stress of the nc-Ni electrodeposited on the coarse grained Cu and the nc-Cu substrate were
0.98 GPa and 1.03 GPa, respectively. The UTS of the nc-Ni electrodeposited on the coarse grained Cu and the nc-Cu substrate were 1.42 GPa and 1.44 GPa, respectively. The UTS of nc sheets was more than four times higher that that of the coarse grained Ni.

The total elongation of the nc-Ni electrodeposited on the coarse grained Cu and the nc-Cu substrate were 3.2% and 4.6%, respectively. These are much smaller than the total elongation of the coarse grained Ni. The total elongation of the nc-Ni electrodeposited on the coarse grained Cu was smaller than that of the nc-Ni electrodeposited on the nc-Cu. From the stress-strain curves, it was found that the nc-Ni electrodeposited on the coarse grained Cu fractured around the UTS point. This indicates that early fracture occurred during uniform deformation. On the other hand, in nc-Ni electrodeposited on the nc-Cu substrate, the flow stress increased up to the UTS, decreased gradually after that, and then, the specimen was fractured. That is, this nc-Ni had certain amount of post-uniform elongation. These results suggest that the homogeneity of microstructure affects the mechanical properties of the electrodeposited nc-Ni.

4. Summary

The microstructure and mechanical properties of the nc-Ni sheets electrodeposited on the Cu substrates having different microstructures were investigated. From TEM observation and Vickers hardness test, the nc-Ni electrodeposited on the nc-Cu substrate showed relatively homogeneous nanocrystalline microstructure, while that electrodeposited on the coarse Cu substrate showed inhomogeneous microstructure. It was found that the microstructure of the nc-Ni could be affected by the microstructure of the substrate. The tensile test results showed that the total elongation of the nc-Ni electrodeposited on the nc-Cu was larger than that of the nc-Ni electrodeposited on the coarse grained Cu. The difference in the total elongation corresponded with the difference in the post-uniform deformation behavior. The homogeneity of microstructure was suggested to affect the mechanical properties, especially post-uniform elongation, of the nc-Ni sheets.

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