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Vickers hardness and deformation of Ni/Cu nano-multilayers electrodeposited on copper substrates

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Ni/Cu nano-multilayers were fabricated by an electrodeposition technique. Ratio of the Ni:Cu layer thickness was kept at 1:1. By laminating nickel and copper layers at a very narrow spacing, we obtained highly-densified parallel interfaces which can give rise to high strength. Dependence of Vickers hardness and tensile deformation on individual layer thickness h was investigated on the Ni/Cu multilayers. The Vickers hardness increased with decreasing layer thickness for the multilayers of $h \geq 10$ nm. This change in the hardness was consistent with the Hall-Petch relation. At the 10 nm layer thickness, the hardness attained more than three times higher than that of the copper substrate. On the other hand, the hardness decreased rapidly with the layer thickness at $h < 10$ nm. The tensile deformation tests were also carried out at the substrates coated with the multilayer of $h = 5$, 20 and 100 nm. The SEM observations revealed that the slip lines of the deformed substrates were terminated by the multilayer at the multilayers of $h = 20$ and 100 nm. On the other hand, a lot of slip lines penetrated into the multilayer of $h = 5$ nm. These slip observations were compatible with the layer thickness dependence of the hardness.

1. Introduction

According to the Hall-Petch relation, strength of metallic materials increases with decreasing average grain size. Grain boundaries play an important role on this strengthening because dislocation movements are inhibited. Hence, configuration of high-density grain boundaries whose average spacing is reduced down to nanometer scale will enable significant strengthening of materials. Several methods have been developed to obtain the nanostructured materials which exhibit excellent strengths. In the well-known processes such as the gas-condensation method [1] and the severe plastic deformation [2], the high-density boundaries are achieved by reducing diameter of each grain (i.e., three dimensional structure). Differently from the above fine-grained structures, the authors paid attention to multilayered structures (i.e., one dimensional structure). It is expected that thinning of component layers will lead to similar enhancement in the strength.

In practical engineering uses, damage evolutions start frequently from free surface of materials because of wear, fatigue, corrosion, and so on. In this sense, durability against such phenomena is possibly improved just by local strengthening of near surface region. In the present study, we employed the coating of Ni/Cu multilayered film at the surface using the electrodepositing method.

Fabrication of the Ni/Cu multilayer by the electrodeposition is realized by applying different polarization potentials alternately to a substrate in the electrolytic solution containing nickel and copper ions. An individual layer thickness can be reduced to nanometer scale by shortening periodic time of the alternate potential applications. The electrodepositing method has some advantages in comparison with a sputter deposition method: it can form the deposits at wide variety of substrate shapes at considerably lower cost. Such characteristics are very favorable when one intends to strengthen the surfaces of engineering parts.

In the early investigations on the electrodeposition of the nano-multilayers, their high strengths have not been focused yet. Microstructures [3–8] and the giant-magnetic resistance (GMR) properties [9–12] which were examined also in the nano-multilayer produced by the sputter deposition were mainly studied. Whereas the nano-multilayer may possess promising potential to increase strength, the number of such researches has been relatively small. As far as we know, the mechanical properties of the Ni/Cu multilayers were reported for the tensile strength [13–15], the hardness [16], the wear [17] and the fatigue [18]. In order to improve such mechanical properties, it seems necessary to clarify the factors which govern the strength of the nano-multilayer. In the present study, the authors paid attention to the thickness of individual layers, which is an inverse of the density of boundaries. Dependence of the layer thickness on the Vickers hardness and tensile deformation was examined on the Ni/Cu system.

2. Experimental procedure

2.1. Electrodeposition of the Ni/Cu multilayers

We prepared two kinds of polycrystalline copper substrates of 99.99% purity as schematically shown in Fig. 1. One is for the Vickers hardness test, and the other is for the tensile test. Because we used a rotating electrode technique, the substrates had disk-like shapes. Both the substrates were annealed at 973 K for 1 h in vacuum. Average grain size of the substrates was about 45 μm. Surface of the substrates were mechanically and electrolytically polished. Target areas for the deposition were limited to a circle and a rectangle as indicated in Fig. 1. The other areas were coated with lacquer for insulation.

The aqueous solution for depositing the Ni/Cu multilayer contained $Ni(H_2NSO_3)_2$, $CuSO_4$ and H_3BO_3. The pH of the solution was maintained to be 3.6–3.9. Temperature of the electrolytic solution was kept at 303 K. Electrochemical condition was controlled by a potentiostat (Hokuto-Denko HA-303). Electric current to a substrate was supplied through a counter electrode of a nickel plate. The polarization potential was measured with an Ag/AgCl reference electrode. The potential was controlled to be constant values of -30 and -650 mV vs. SHE during the copper and nickel depositions, respectively. Potential waveform for depositing the multilayer is shown in Fig. 2. By applying the rectangle potential waveform, the nickel and copper layers can form alternately. A preliminary potential of $+199$ mV vs. SHE was inserted before the copper deposition potential in order to sufficiently reduce the diffusion layer around the substrate prior to the copper deposition for obtaining smooth deposits. The control of the diffusion layer thickness during the nickel and the copper depositions was achieved also by rotating the substrates at 100 and 500 rpm, respectively.

According to Faraday's law, amount of an electrodeposit is proportional to electron charge transferred by reduction reaction occurring at a substrate. For this reason, the electron charge during the deposition was monitored to obtain regularly-spaced multilayer. If the electric charge became a certain value which had been calculated in advance, the electric potential was switched to another one. In the present study, a ratio of the Ni:Cu layer thickness was kept at 1:1. At the substrates for the hardness test, total thickness of the multilayer coating was approximately 1 μm and the thickness of the individual layer h was altered from 3 nm to 500 nm; thus the number of layer stacks increases with the decreasing individual layer thickness. For the tensile tests, three kinds of the multilayer coating were prepared: $h = 5$, 20 nm and 100 nm. The aimed total thickness was set at 10 μm. However in the present experimental condition, dendritic growths started after a certain amount was deposited as mentioned later.

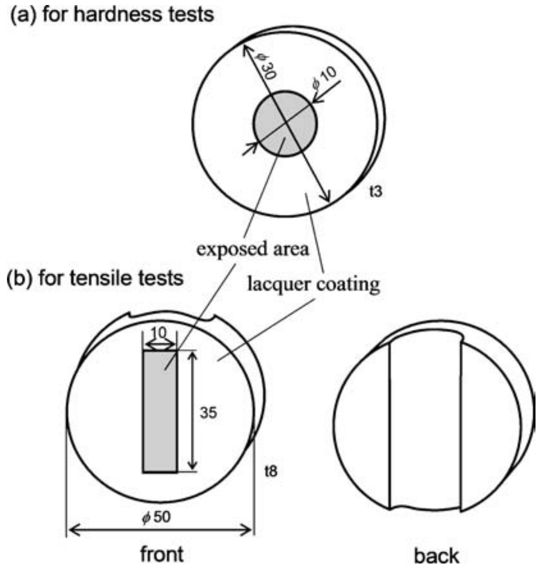

Figure 1 Schematic illustration of copper substrates for (a) Vickers hardness tests and (b) tensile tests. The substrates were coated with lacquer except the areas exposed to electrolytic solution.

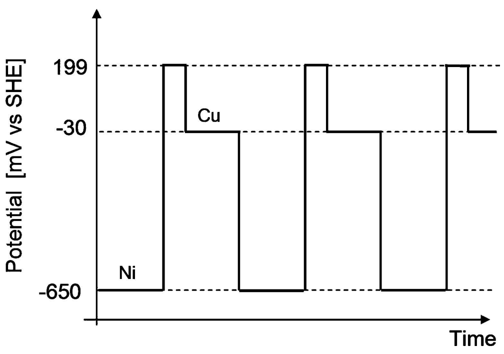

Figure 2 Potential waveform for the electrodeposition of Ni/Cu multilayer.

2.2. Mechanical tests

The Vickers hardness tests were carried out in air at room temperature in SHIMAZDU DUH W201 hardness tester. Because the fabricated Ni/Cu multilayers were very thin, it is difficult to measure the hardness of a multilayer film being removed from the substrate. Hence, the hardness was measured at the situation that the multilayers were not removed from the copper substrates. The measured hardness was averaged among different ten points for each specimen.

Strip specimens for the tensile tests were cut from the electrodeposited substrates as indicated in Fig. 3. By polishing the specimen surface, we can observe deformation trace of the Ni/Cu multilayer at the corner of gage part. The specimens were strained at an initial strain rate of 3×10^{-4} s^{-1} until 10% plastic strain. By

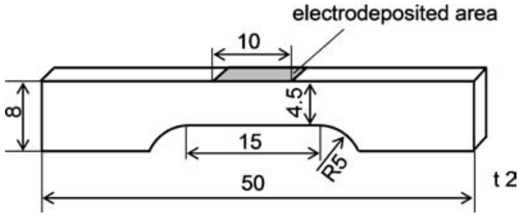

Figure 3 Shape and dimension of the strip specimen, where a side surface is coated with the Ni/Cu multi-layer.

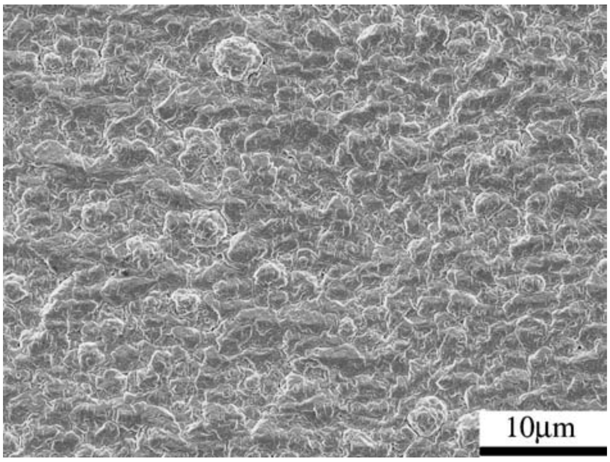

Figure 4 An SEM photograph showing a surface of electrodeposited Ni/Cu multilayer which was grown until 5 μm total thickness.

interrupting the tensile tests at appropriate strain, the development of slip lines and crack formations at the multilayer was observed with a high-resolution SEM (JEOL JSM-6500F).

3. Results and discussion

3.1. Fabrication of the Ni/Cu multilayer

Preceding to the fabrication of the Ni/Cu multilayers, chemical compositions of the electrodeposits obtained at the polarization potentials of −30 and −650 mV vs. SHE were analyzed with an EDS system. The composition of the deposit at the −30 mV vs. SHE was Cu of more than 99% purity. On the other hand, the Ni-8%Cu alloy was deposited at the −650 mV vs. SHE. Although the strict notation should be given by "Ni-8%Cu/Cu" multilayer, in this paper we denoted the multilayer briefly by "Ni/Cu".

Fig. 4 shows the surface of the electrodeposit whose total thickness was about 5 μm. The deposit seems to grow almost uniformly, but it is also recognized that small surface roughness exists certainly. At the beginning of the electrodeposition, the roughness was almost negligible. The electrodeposits showed a tendency that the roughness due to the dentritic growth became outstanding as the total thickness increased.

Cross sections of the electrodeposits are shown in Fig. 5. The substrates coated with the multilayers of $h = 10$, 50 and 100 nm were cut perpendicular to the deposited plane, and then the cross sections were etched after mechanical polishing. Bright contrast in the SEM photographs corresponds to the nickel layer. Formations of the Ni/Cu laminates are confirmed at least in $h = 50$ and 100 nm. It can be said that the electrodeposition technique is a productive method to fabricate the highly-densified boundaries. At the deposit of $h = 10$ nm, the identification of individual layers was somewhat difficult because the SEM resolution is insufficient. Thus, the cross section of the $h = 5$ nm multilayer was observed with a TEM. The TEM photograph shows modulation in the contrast whose average spacing was about 10 nm. This length corresponds to the sum of nickel and copper layer pair.

3.2. Vickers hardness test

In the present study, the hardness measurements were performed under the situation that the Ni/Cu multilayers were not removed from the substrates as described in above. Hence, the measured hardness would be affected by the deformation of the annealed copper substrates which are significantly softer than the nanostructured Ni/Cu multilayers. It is anticipated that the degree of such a substrate aftereffect depends on both total thickness of the coating and the indentation force. Since all the coatings in the hardness tests had the same total thickness of 1 μm, the effect of the total thickness was untreated here. Dependence of the indentation force on

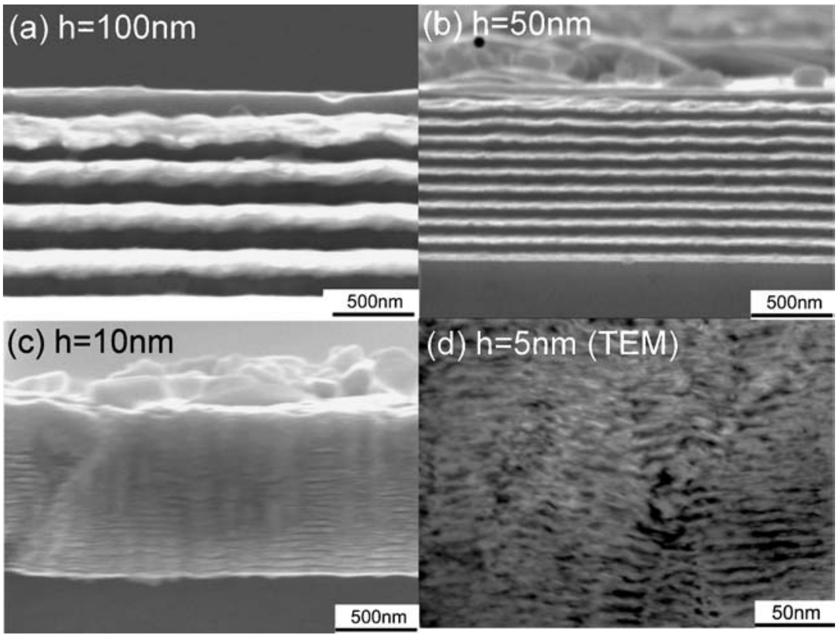

Figure 5 SEM and TEM photographs showing cross-sections of the Ni/Cu nano-multilayers.

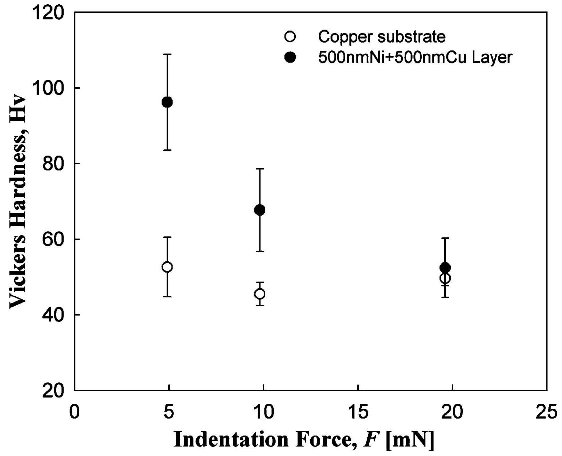

Figure 6 Dependence of the Vickers hardness on indentation force for the copper substrate and the Ni/Cu coating of which one pair of Ni and Cu layers of 500 nm thickness consists.

the hardness was examined at both the substrate and the deposited one. Fig. 6 shows the relationship between the Vickers hardness and the indentation force ranging from 5 to 20 mN. When the indentation force was reduced to less than 5 mN, the measurements became somewhat unstable and the average hardness decreased slightly with compared to that of 5 mN. This instability can be ascribed to the roughness of the deposited surface as shown in Fig. 4, if the indentation depth was small enough in comparison with the scale of the surface relief. At the indentation forces more than 5 mN, the hardness of the substrate was almost independent of the indentation force. On the other hand, the hardness of the multilayer increased with decreasing indentation force. This result indicates that the multilayers certainly contributed to the hardness increasing and at a high indentation force the substrate deformation induced the considerable reduction in the multilayer hardness. For these reasons, following measurements were carried out at the indentation force of 5 mN. At this condition, the hardnesses of the substrate and the single nickel deposit of 1 μm thickness were Hv52 and Hv66, respectively.

The Vickers hardness plotted against the individual layer thickness is shown in Fig. 7. A dashed line in the figure indicates the substrate hardness. At the regime of $h > 10$ nm, the hardness increased with the decreasing layer thickness. This result is consistent with the Hall-Petch relationship, given that the layer thickness is equivalent to an average grain size. At $h = 10$ nm, the hardness of the multilayer was more than three times higher than that of the substrate. On the other hand, the hardness was degraded rapidly at a regime of $h < 10$ nm. This kind of the hardness peak with respect to layer thickness has also been reported in the investigations on the yield stress [14] and the ultimate tensile strength [13] of the Ni/Cu multilayers. These strength peaks were attained at the copper layer thickness of 3–4 nm. Because the ratio of the Ni:Cu layer thickness was 9:1 in these literatures, equivalent mean thickness of the Cu and Ni layers can be estimated to be 15–20 nm. This value is close to the layer thickness at the peak hardness of Fig. 7. In the granular nanocrystalline nickel [19] and Ni-P [20], the peak yield stress and Vickers hardness have existed also at average grain diameter near 10 nm. It seems likely that the peak strength of the nanostructured materials appears at about 10 nm boundary spacing, regardless of whether the boundary arrangement is one or three dimensional.

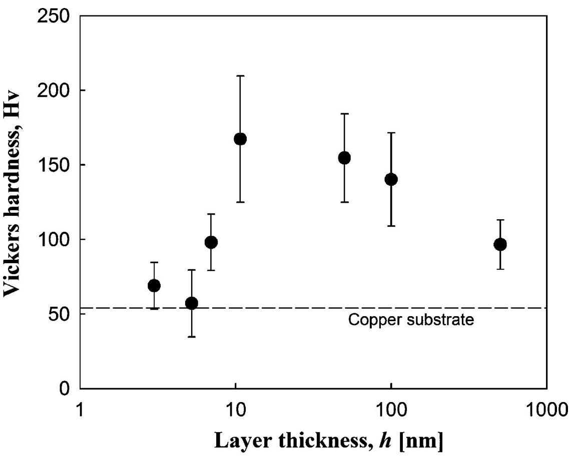

Figure 7 Dependence of the Vickers hardness on individual layer thickness of the Ni/Cu multilayer, where the ratio of Ni and Cu layer thickness was 1:1. Total thickness of the coating was kept at about 1 μm.

3.3. Tensile test

In order to investigate the role of the Ni/Cu multilayer on the deformation of the substrate, we should first detect the location of the multilayer/substrate interface at the polished cross section. Fig. 8 shows a SEM photograph and EDS mappings of the cross section of the strip specimen deformed until 6% plastic strain. Side surface of the specimen was coated with the multilayer of $h = 100$ nm. Bright contrast in the EDS mappings corresponds to high concentration of each element. From the distribution of the nickel and copper elements, it is recognized that uniform growth of the Ni/Cu multilayer occurred until the total thickness reached approximately 4 μm. The dendritic growth became dominant during the further electrodeposition, in the present condition. Inclined parallel lines visible in the substrate are slip lines formed by the plastic deformation. All the slip lines were terminated at the Ni/Cu multilayer/substrate interface, except for one slip line. Hence, it can be said that the Ni/Cu multilayer acts as a strong film which prevents the slip transmission.

Fig. 9 shows topographic SEM images of the multilayer cross sections ($h = 20$ nm and 5 nm) after the tensile straining until $\varepsilon_p = 10\%$. At the multilayer of $h = 20$ nm, the slip lines were ended at the multilayer/substrate interface, as well as those of $h = 100$ nm. Because no any slip lines were detectable in the deposited layer even after the 10% substrate deformation, the $h = 20$ nm multilayer can be concluded to possess very high resistance against the plastic deformation. Instead of the slip traces, a nucleation of a crack was recognized at the $h = 20$ nm multilayer. On the other hand, numbers of slip lines passed through the Ni/Cu multilayers of $h = 5$ nm. It is apparent that this multilayer failed to function as a barrier against dislocation passages. This result agrees well with the layer thickness dependence of the Vickers hardness

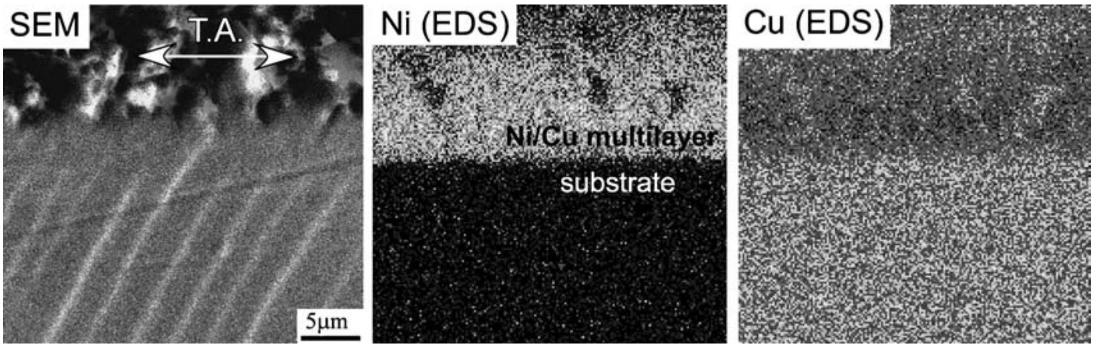

Figure 8 An SEM photograph and its EDS mapping of the deformed specimen whose side surface was coated with the Ni/Cu multilayer having the 100 nm layer thickness.

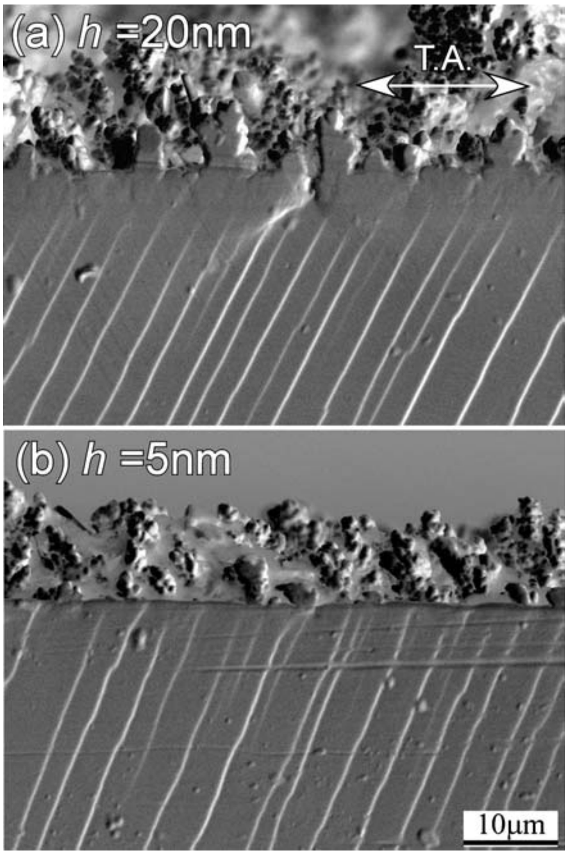

Figure 9 The slip lines of the strip specimens coated with the Ni/Cu multilayers of (a) $h = 20$ nm and (b) $h = 5$ nm. Both the specimens were strained until 10%.

which decreased rapidly at the very narrow layer thickness.

In the X-ray diffraction analysis of the electrodeposited Ni/Cu multilayers [21], it has been pointed out that epitaxial coherency was maintained for low index orientation including (111), (110) and (100) planes. The TEM observations of the Ni/Cu multilayer cross sections have also shown that the preferred crystallographic directions of the growth were <111> and <110> [7]. Hence, it is reasonable to assume that the present Ni and Cu layers were stacked coherently along the low index planes such as the (111). In this situation, the interfaces cannot act as effective barriers against dislocation passages because all slip systems are common between neighboring layers. However, even if there is no misorientation between Ni and Cu layers, dislocations would exist at the Ni/Cu interface because of the lattice parameter mismatch. For example, the misfit dislocations are estimated to exist at every 96.4 nm along the (111) Ni/Cu interface. At the multilayer of $h = 100$ nm, the misfit dislocation density can amount to about 10^{14} m^{-2}. This kind of the misfit dislocations can be the obstacles against the moving lattice dislocations which come from the deformed substrates. Being inversely proportional to spacing between the Ni/Cu interfaces, the dislocation density should increase with decreasing layer thickness. This misfit dislocation density model is consistent with the change in the Vickers hardness at $h \geq 10$ nm. However, the rapid decrease of the hardness at $h < 10$ nm is impossible to be understood by the misfit dislocation model.

At the electrodeposited Ni/Cu multilayer having very narrow layer thickness (2.5 nm Ni + 1.4 nm Cu), it has been found in the HREM observations that the lattice planes were not straight through the interfaces [8]. The lattice planes in the Ni and Cu layers were slightly tilted each other. This phenomenon presumably suggests that the lattice mismatch is accommodated by the slight tilting and thus the interface is fully coherent. Since the misfit dislocations should be annihilated at such fully coherent boundaries, the blockage effect against the lattice dislocation is unexpected at the very narrow layer stacks. The hardness reduction at $h < 10$ nm can be interpreted by the annihilation of the misfit dislocations.

4. Conclusion

From the investigation on the Vickers hardness and the tensile deformation of the Ni/Cu nano-multilayers fabricated by the electrodeposition, we could obtain following conclusions.

1. It was confirmed that the highly-densified Ni/Cu boundaries could be fabricated by laminating the nickel and copper layers using the electrodeposition technique.
2. In the multilayers having the individual layer thicknesses of $h \geq 10$ nm, the Vickers hardness increased with decreasing layer thickness. The hardness at $h = 10$ nm was more than three times higher than that of the copper substrate. On the other hand, the hardness decreased drastically when the layer thickness was less than 10 nm.

3. The SEM observation revealed that the slip lines of the deformed substrates were terminated at the multilayer/substrate interfaces when the substrates were coated with the $h = 20$ and 100 nm multilayers. On the other hand, a lot of slip lines penetrated into the multilayer of $h = 5$ nm. Accordingly, it is suggest that the formation of the very short layer thickness not always contributes to the strengthening the materials.

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