Failure of Ni/Cu Laminated Nanostructures

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Laminated nanostructures of nickel and copper were fabricated via electrodeposition and their microstructure, strength and fracture behavior were characterized using x-ray diffraction, tensile testing and electron microscopy techniques. The results of this study indicated that the formation of porous regions is responsible for the brittleness of electrodeposited Ni/Cu laminated structures. Microprobe analysis revealed that within these porous regions copper is deposited with a low efficiency. It is suggested that local depletion of copper ions and formation of hydrogen bubbles due to hydrodynamics effects are responsible for the low efficiency of copper deposition and formation of pores. The brittle fracture of nickel and copper layers is discussed in terms of cleavage and tearing mechanisms.

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1. Introduction

Laminated structures, also known as compositionally modulated or multilayered structures, consisting of periodic layers of two different metals show improved physical and mechanical properties relative to the components. Electrodeposition is a versatile and inexpensive method for fabricating metallic nanolayered structures. Electrodeposited nickel/copper nanolaminates have been the focus of many studies because of their giant magnetoresistance (GMR) property, and enhanced mechanical properties. Transmission electron microscopy (TEM) has revealed that the electrodeposited Ni/Cu layered structures may show columnar growth morphology. The columnar growth results in curved deposition fronts, and hence curved layers. The boundaries between columns may not always represent the grain boundaries in these structures. Indeed, it has been shown that at high deposition rates while the columns are in the order of hundreds of nanometers the grain size can be only a few tens of nanometers. Similar observation has been made in electrodeposited Cu/Ag layered structures. The columns grow in width as the deposit thickness increases. The width of the columns usually correlates with the size of macroscopic nodules on the surface. Another microstructural feature observed in Ni/Cu layered structures is twinning. The average width of twins is usually much larger than the layer thickness values but smaller than the columns’ width. The layers continue through the twin boundaries without any interruption, suggesting epitaxial growth of the layers.

There have been a limited number of studies on the strength of electrodeposited Ni/Cu laminated structures. There is a large scatter in tensile strength of a given deposit and the reported strength values as a function of the bi-layer thickness are contradictory. Results reported by Menezes and Anderson for a nickel to copper layer ratio of nine show that the tensile strength increases with a decrease in the bi-layer thickness and that tensile strengths as high as 1.8 GPa can be achieved in this system. However, Tench and White, using similar experimental set-up and layer ratio, have reported a much weaker dependency of the strength on the bi-layer thickness. The maximum tensile strength reported by them is about 1.1 GPa. Both hardness and tensile testing data indicate that the strength of electrodeposited Ni/Cu layered structure drops at very small bi-layer thickness values (approximately less than 20 nm). This decrease may be associated with the coherency of interfaces and/or the discontinuity of the layers at small layer thickness values. Menezes and Anderson have shown that the strength of the electrodeposited Ni/Cu laminated structures is very sensitive to the copper content in the electrolyte and for their experimental set-up, maximum strength was achieved at approximately 7 mM (10⁻⁵ mole/liter = mole/m³) of copper. It has been reported that a decrease in the ratio of nickel to copper layer thickness in electrodeposited layered structures, contrary to the vacuum deposited structures, causes a decrease in tensile strength accompanied with a very brittle behavior.

We have studied the fracture behavior of electrodeposited Ni/Cu laminated structures as functions of deposition parameters such as bath temperature, purity of the electrolyte, and copper content of the electrolyte, as well as the sample thickness and layer thickness values. We have found a variety of fracture behaviors, from completely ductile fracture with the so-called knife-edge behavior to very brittle behavior. The purpose of this study has been to investigate the reasons for brittleness of Ni/Cu laminated structures, with specific emphasis on the effects of copper concentration in the electrolyte and copper layer thickness.

2. Experimental Procedures

The Ni/Cu multilayer were deposited potentiostatically on an annealed polycrystalline copper substrate at 40ºC using a sulfate-based commercial electrolyte. A conventional rotating disc electrode with a diameter of 35 mm was used. Both copper and nickel were deposited potentiostatically at -0.12 and -1.05 V versus saturated calomel electrode (SCE), respectively. In order to avoid the possible passivation of the nickel layer surface, we dropped the voltage first from -1.05 to -0.7 V for a short period (2 s) and then lowered it to -0.12 V for the copper layer deposition. The details of electrodeposition procedure and the cell set-up have been reported elsewhere. Table 1 presents the deposition conditions for the samples reported in this study. To evaluate the effect of
electrolyte copper content, its level was varied from 4 mM to 7 mM for a given copper and nickel deposition time (discs 1 through 4). Discs 5, 6 and 7 were deposited with 7 mM copper in the electrolyte, however, the deposition times for the two layers were increased in comparison to disc 4. During the deposition of all the discs, except for disc 7, a copper sulfate solution was added gradually to the electrolyte using an automatic syringe system in order to keep the concentration of the copper in the electrolyte constant. It should be noted that the injected amounts of copper are very small in comparison to the concentrations of copper in the electrolyte. Except for disc 1, the number of the bi-layers (or the number of cycles) was kept at 1500. The current versus time was measured during the last deposition cycle for each disc. The layer thickness for nickel, \( \lambda_{Ni} \), and copper, \( \lambda_{Cu} \), were calculated based on the measured current and the substrate cross-section area using the Faraday's law (see Table 1). The calculated values are usually larger than the actual measured values because of the side reactions that reduce the efficiency and the roughening of the interface, which result in a lower actual current density.

Dog-bone tensile specimens with a gage length of 10 mm were prepared from the free-standing deposits and tested at a nominal strain rate of 2 \times 10^{-3} \text{s}^{-1}. Cross-sectional metallographic specimens were prepared from selected deposits. X-ray diffraction, scanning electron microscopy (SEM) and microprobe analysis were used to characterize the microstructure and fracture behavior of the deposits. The thickness of deposits was measured edge-on in SEM.

3. Results

3.1 Microstructural characterization of deposits

Table 2 presents the out-of-plane crystallographic texture as measured by x-ray diffraction analysis on the substrate and the solution sides of the deposits. The texture was evaluated as the intensity ratio \( I_{111}/I_{200} \) for both nickel and copper peaks, because the (220) peaks were absent in most x-ray profiles. Considering that this ratio is around 2 for random crystallographic orientation of these metals, in general, the substrate sides showed a strong (100) texture, and the solution sides exhibited a strong (111) texture. The strong (100) texture of the deposits on the substrate side reflects the (100) rolling-plane of the annealed copper substrate used in this study. In order to evaluate the change in texture through the thickness of the deposits, a strip of disc 5 was mechanically polished a few micrometers at a time from the substrate side and x-ray analysis was performed at each step. Figure 1 presents the variation in the \( I_{111}/I_{200} \) ratio as a function of distance for both nickel and copper peaks. The ratio changed exponentially within the first 10 \( \mu \text{m} \), where it reached a value close to the ratio obtained from the solution side of the deposit and remained constant after that. Note that for a better resolution, the curves are truncated at a point before the constant level is reached. The change appears to be slightly faster for copper than it is for nickel. In the case of the CuKα radiation used in this study, 90% of the diffracted x-rays come from a depth of approximately 10 \( \mu \text{m} \) at a nominal diffraction angle of 22.5° in copper and nickel. Therefore, the curves presented in Fig. 1 suggest that the texture changed from (200) to (111) within the first few micrometers. The close correspondence between the variations in texture for copper and nickel layers implies that they formed epitaxially.

The roughness of the surface on the solution side was evaluated by the size of nodules observed using SEM. Figure 2(a) shows an example of the nodules found on the solution surface and the average size of them varied between 7 to 15 \( \mu \text{m} \) as shown in Table 2. These nodules covered the whole surface uniformly and they tended to be elongated in a particular direction. A qualitative evaluation revealed that this direction is at an angle to the [010] rolling direction of the recrystallized copper substrate, however, the specific crystallographic orientation for each deposit was not identified. The surface of these large nodules was covered with finer nodules (<1 \( \mu \text{m} \)).

### Table 1

<table>
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<tr>
<th>Disc #</th>
<th>Cu composition (mM)</th>
<th>pH</th>
<th>( t_{Ni} ) (s)</th>
<th>( t_{Cu} ) (s)</th>
<th># cycles</th>
<th>Cu addition</th>
<th>( \lambda_{Ni}^c ) (nm)</th>
<th>( \lambda_{Cu}^c ) (nm)</th>
<th>( \lambda_{Cu}^c / \lambda_{Ni}^c )</th>
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<td>3</td>
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<td>3</td>
<td>15</td>
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### Table 2

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<th>Solution side</th>
<th>Nodule size (( \mu \text{m} ))</th>
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<td>.52</td>
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<tr>
<td>7</td>
<td>.22</td>
<td>.87</td>
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</tr>
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</table>

*No or very small (200) peak
**No or very small (111) peak
3.2 Tensile strength/fracture behavior correlation

Table 3 shows the tensile strength of the Ni/Cu layered structures investigated in this study. For the purpose of consistency, all specimens were cut with the tensile axis parallel to the rolling direction of the substrate. At least two samples were tested from the same deposit, and the results are presented as columns a and b in Table 3. There was a large variation in the strength of specimens from the same deposit as well as samples from different deposits fabricated under similar conditions (discs 5, 6, and 7). Consistent with Menezes and Anderson\textsuperscript{11} findings, our results suggest that the tensile strength is improved with increasing the copper content of the electrolyte from 4 to 7 mM.

Figure 3 presents SEM pictures from the fracture surface of samples from discs 1, 4, and 7, with tensile strengths of <100, 423, and 812 MPa, respectively. Figure 3(a) is representative of very low strength samples (tensile strength < 150 MPa), which fractured in a complete brittle manner. Except for the very brittle samples, the fracture surface of tensile specimens showed two distinct fracture zones: a brittle zone and a ductile zone (see Figs. 3(b) and (c)). High magnification pictures of these two zones are shown in Fig. 4. The ductile zone developed by microvoid coalescence mechanism and consisted of shallow microvoids. The brittle zone showed relatively large grooves and consisted of semi-round facets of the order of 0.2 to 0.5 μm, similar to the size of fine nodules (see Fig. 2(b)). A fine lamellar structure is also apparent on these round facets. The spacing of these curved lamellae was in the range of 50 to 70 nm. The brittle zone was usually observed near the solution side, however, in some specimens its position varied across the width.

Several other features were observed on the fracture surface of brittle samples. Figure 5(a) presents the fracture surface of the specimen with tensile strength of 265 MPa from disc 2. A columnar grain structure can be detected on the fracture surface. As marked by the arrow, in some areas these columnar grains were not completely connected. A lamellar structure near the substrate side of the deposit (marked as “A”) is evident. A high magnification of this region is shown in Fig. 5(b). Note that the lamination spacing observed on the fracture surface is much larger than the layer thickness, indicating that not every Ni/Cu interface fractured. The ob-
Fig. 3 SEM pictures showing the fracture surface of tensile specimens from (a) disc 1, (b) disc 4, and (c) disc 7. Arrows indicate the deposition direction. Brittle and ductile areas are marked as “B” and “D”, respectively.

Fig. 4 High magnification SEM pictures showing (a) the ductile and (b) the brittle fracture zones on the fracture surface of a specimen from disc 5.

Most tensile specimens broke within the elastic limit. Some samples showed stable microcracking before final fracture, typical of composite materials as noted in Table 3. As can be seen on the fractographs shown in Figs. 3(b) and (c), plastic deformation and necking was associated with the ductile region, however, this behavior was not manifested on the stress-strain curves. In general, the increase in tensile strength was found to be associated with a decrease in the percent of brittle fracture, as demonstrated in Fig. 3. An increase in the deposition time of each layer resulted in less brittle regions and improved tensile strength (see Table 3).

3.3 Microstructure/fracture behavior correlation

In order to understand the microstructural responsible for the brittle fracture zone, cross-sectional metallography samples were prepared from selected specimens. All specimens showed two microstructural zones: a porous and a dense region, which could be detected in the as-polished state and without etching. Figure 6(a) presents a SEM picture showing these two regions. The curvature of the interface between these regions assists in identifying the growth direction. This sample was prepared from a tensile specimen, and consequently, we can see microcracks associated with the porous regions. Note that the stable microcracks have developed parallel to the loading axis as well as perpendicular to it. Of-
ten, the porous regions showed relatively orderly features in two dominant directions and the crack followed in between these features as shown in Fig. 6(b). These parallel features were also apparent on the fracture surfaces as grooves (see Fig. 4(b)). The microstructural units that fit the size and morphology of these parallel features are twins, which have been observed in electrodeposited Ni/Cu laminated nanostructures.\textsuperscript{5} The crack path suggests that the pores developed preferably at twin boundaries and the layer interfaces. Investigation of many samples revealed that similar to the brittle zones observed on the fracture surface, the porous region developed preferentially on the solution side but its position varied from one area to another area on a disc. These results suggest that the porous regions correspond to the brittle zones observed on the fracture surfaces. Therefore, it was concluded that fracture occurred initially in the porous regions, and consequently the load was transferred fast to the dense regions, which immediately necked under this loading condition and fractured in a ductile manner. In order to prove this point, a strip of disc 7, which showed porous regions predominantly on the solution side, was mechanically polished till the porous layer was removed. Then a tensile specimen was prepared from this strip. Figure 7 shows that the removal of the porous region resulted in plastic yielding. The fractograph shown in Fig. 8 reveals that necking occurred on both sides of this sample and the microvoids are much deeper than those observed on the fracture surface of the original sample (see Fig. 3(c)), confirming the proposed fracture sequence. Note that pores always form in electrodeposited metals and they are the initiation sites for development of microvoids.\textsuperscript{20,21} However, the size and possibly the density of them in dense regions are small and cannot cause brittle fracture.

### 3.4 Microprobe analysis

Microprobe analysis was conducted to evaluate the composition, and hence, the thickness of copper and nickel layers. Initially we found significant differences in the compositions measured on the solution side and substrate side of deposits. Therefore, we conducted microprobe analysis through the thickness of selected samples. Figures 9 presents the variation of copper concentration across the cross-sections of disc 5. The porous regions were found to have a much lower copper content than the dense regions. Cross-sectional microprobe analysis from several deposits confirmed, that disregard of the position of the porous region, \textit{i.e.}, on the substrate, in
the mid-thickness or on the solution side, always the dense regions showed a much higher copper efficiency than the porous regions did.

Table 4 presents the calculated layer thickness values based on the average composition measured by microprobe analysis on the surface of deposits. The values in the parentheses were calculated from the analysis of the cross-sectional samples. There is a good correlation between these two sets of results for discs 2 and 5. The cross-sectional samples from discs 6 and 7 were prepared from near the edge of the discs. No porous zones could be detected on these samples and they showed a higher copper content than the copper level detected on the dense surface of samples from the central part of these discs. The results shown in Table 4 reveal that in porous regions the efficiency of copper deposition is very low. These results suggest that the copper layer is thicker in the ductile zone than in the brittle zone. Therefore, contrary to the assumptions made previously, a small $\lambda_{Ni}/\lambda_{Cu}$ does not cause brittleness. It should be noted that the layer thickness values calculated from microprobe results are based on the average bi-layer thickness estimated by dividing the total thickness of the deposit, $\delta$, by the number of cycles. The low efficiency of the nickel layer in the dense region implies that the actual bi-layer thickness is higher than the estimated value in this region. Similarly the relatively high efficiency of nickel in the porous region suggests that the actual bi-layer thickness is smaller in this region.

4. Discussion

Results of this study confirm that nodules play an important role in the brittleness of electrodeposits. The way they cause brittleness is by not joining to each other and leaving
a crack open between them. Therefore, the crack follows an inter-nodular path. Nodules developed at two scales in Ni/Cu laminated structures reported here. The larger nodules as can be seen in Fig. 2(a) usually correlate with columnar growth. The columnar regions develop by growth of islands. These islands when join other create boundaries. A fast growth rate results in a more curved interface and a larger probability of unfilled spaces between the columns. The smaller nodules (0.5 to 0.1 \( \mu \)m) as can be seen in Fig. 2(b) develop within the larger nodules. These growth centers usually have similar crystallographic orientation. Crack propagation in between these nodules is encouraged owing to the development of internal stresses.\(^{22}\)

The inhomogeneous distribution of the porous regions in a deposit suggests that the mechanism responsible for this phenomenon is localized. The low concentration of copper in these regions implies that the efficiency of copper deposition was low in these regions. This can be due to the depletion of Cu\(^{2+}\) ions at the electrode surface or passivation of the nickel layer, which would increase the overpotential required for the deposition of copper. The absence of porous regions and thicker copper layers near the edges of the discs support the former mechanism. Near the edges more ions can be brought to the deposition front, and hence, the efficiency of copper deposition is expected to be higher. On the other hand, hydrodynamic perturbations can reduce the concentration of copper ions brought close to the electrode surface locally. Consequently, the copper layer growth becomes diffusion controlled, which results in formation of a defective deposit. Another explanation can be related to the formation of hydrogen during nickel deposition. If the hydrogen that co-deposits with nickel is not removed locally, it will form bubbles on the Ni/electrolyte surface. These bubbles inhibit the deposition of copper and result in a weak Ni/Cu interface. Also, during deposition, hydrogen can enter the metal and accumulate at defects (vacancies, dislocations, interfaces and twin boundaries) and eventually form gas bubbles.\(^{23}\) The formation of bubbles and the weakness of Ni/Cu interfaces result in brittle fracture, which is responsible for the large scatter in the tensile strength of Ni/Cu laminated structures produced in this study. An increase in the electrolyte copper concentration is expected to reduce the probability of copper depletion at the electrode surface and consistent with the experimental results would reduce the formation of the porous regions. The smaller percent of porous regions in deposits with longer bi-layer deposition time may be attributed to the establishment of stable hydrodynamics at longer times.

Both copper and nickel have FCC (face centered cubic) crystal structure and are inherently ductile, i.e. crack tips in these materials emit dislocations spontaneously.\(^{24,25}\) Therefore, this question arises that how can brittle facets such as those shown in Figs. 4 and 5 form in these metals. First we should consider several facts regarding the deformation and fracture of Ni/Cu laminated nanocomposites:

(a) The brittle fracture is associated with porosity in the material, whether at the inter-columnar boundaries, at the layer interfaces, or in the regions with hydrogen bubbles.

(b) We have shown that the degree of brittleness depends on the stress-state, and indeed near the edges of some samples, where plane-stress condition is achieved, brittle facets are not found and the fracture mechanism changes to microvoid coalescence.\(^6,23\)

(c) The relatively low yield strength of the dense regions (see Fig. 7) suggests that dislocation generation and motion is not very difficult in these regions.

(d) The higher tensile strength of the samples with brittle zones (compare the strength of disc 7 with and without the brittle zone in Table 3) suggests that plastic yielding is more difficult in the porous regions.

(e) The extensive formation of cracks parallel to the loading axis in the porous regions implies that large internal stresses were present perpendicular to the layers. In other words the deposit is under in-plane compression and out-of-plane tensile stresses in these regions. This is consistent with the observation that the porous regions carry larger loads than the dense regions.

Two scenarios may explain the formation of cleavage-like facets on the fracture of Ni/Cu laminated structures. One explanation is that a high density of nano-size pores creates ultra thin ligaments that can tear by generation and motion of screw
dislocations. The tearing of small ligaments is a common observation in TEM thin foils. The other possibility is that plastic deformation is very difficult in these regions and the local stresses are raised high enough to cause cleavage, i.e., breaking of the atomic bonds. The smaller bi-layer thickness due to a low efficiency of copper deposition requires a higher stress for dislocation generation/motion.\(^{27}\) Nano-size pores can increase the yield strength by pinning the dislocations as well as creating a triaxial stress-state. We have shown 6) that the fracture behavior of Ni/Cu laminated structures depends on the stress state in the sample. The formation of cleavage-like facets is encouraged under mode I of crack opening rather than mode III. This observation suggests that these facets may indeed have developed by breaking of the atomic bonds rather than motion of dislocations.

5. Conclusions

We have fabricated Ni/Cu laminated nanostructures using electrodeposition techniques. Analyses of microstructure and fracture behavior of these deposits have led to the following conclusions.

1) Formation of pores play an important role in brittle fracture of Ni/Cu laminated nanostructures. The high density of pores at twin boundaries and layer interfaces creates weak paths for fracture.

2) Local hydrodynamic effects result in accumulation of hydrogen and depletion of copper ions near the deposition front. Consequently, hydrogen is absorbed into the deposit and gathered at boundaries and interfaces, and copper layers grow with many defects in them. Formation of hydrogen bubbles and defective copper layers, create a high density of pores. These porous regions have high out-of-plane tensile internal stresses, which lead to a plain strain condition, despite the small thickness (20 to 45μm) of the deposits. The combination of a high density of nano-size pores, high internal stresses developed due to processing and during deformation, and high yield strength induces cleavage fracture in nickel and copper in laminated nanostructures.

3) An increase in the copper content of the electrolyte decreases the probability of formation of porous regions, and hence, improves the tensile strength.

4) Nodule formation is detrimental to the strength by providing weak inter-columnar paths for fracture.

Acknowledgements

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REFERENCES