# A Zero Emission Electrochemical Flow Reactor For Electrodeposition of Multilayer Nano-Structures

N.V. Myung, M. Schwartz & K. Nobe

A flow reactor system providing zero emission effluents has been developed to electrodeposit nano-structured Ni/ Cu multilayers. Advantages of this system are: (1) fabrication of distinct nano-structured multilayers with precise layer thicknesses, (2) electrodeposition of the less noble metal (Ni) without co-deposition of the more noble metal (Cu), (3) preclude formation of oxides at the interfaces by depositing under an inert environment and applying a low cathodic current during the rinsing step, and (4) virtually complete recovery of metals from rinsewaters with three-dimensional reticulated vitreous carbon (RVC) electrodes. Dilute copper sulfate and nickel sulfamate plating solutions containing 0.005 M CuSO<sub>4</sub> +  $2 \text{ M H}_{3}\text{SO}_{4}$  + brightener and 0.01 M Ni(NH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> + 0.5 M H.BO, respectively, were examined. Contiguous twodimensional nano-thick copper and nickel films with high current efficiencies (90-100 percent) can be electrodeposited by applying low current densities (< 2.5 mA/cm<sup>2</sup>). Both copper and nickel electrodeposition were strongly influenced by mass transfer resulting from low metal ion concentrations. Distinct Ni/Cu multilavers were electrodeposited utilizing the electrochemical flow reactor. **RVC** electrodes were used to achieve zero emission by recovering Ni and Cu from rinsewaters. The Cu recovery rate increased with increased applied current density and volumetric flow rate. At 1.8 mA/cm<sup>2</sup>, bright copper was uniformly deposited on the RVC electrode. As the current density increased from 1.8 to 3.6 mA/cm<sup>2</sup>, the Cu recovery rate was mass-transfer controlled. The Ni recovery rate was independent of volumetric flow rate, but increased with increasing current density. Higher recovery rates of Ni were achieved by increasing the D/L (diameter/length) electrode ratio and employing dual anodes. Dual anodes permitted more uniform Ni deposition, probably because of more uniform current distribution. The recovery rate of Ni was reduced, compared to Cu as a result of high rates of hydrogen gas evolution.

Since discovery in 1988,<sup>1,2</sup> giant magnetoresistive (GMR) materials have attracted the attention of the scientific and engineering communities because of their important properties and potential applications in sensor and computer technologies. The GMR effect, which is the change in electrical resistance in response to a magnetic field, has been reported with microengineered materials such as multilayers<sup>3,4</sup> and granular structures.<sup>5</sup> Multilayer materials consist of alternating magnetic layers, such as ferrous metals or alloys, and nonmagnetic layers, such as copper or silver, in nanometer-range thicknesses. The granular GMR structure is composed of nanometer-size ferromagnetic granules dispersed in a nonmagnetic metal matrix. Ross<sup>6</sup> and Schwarzacher and Lashmore<sup>7</sup> have recently published comprehensive GMR reviews. Sensors based on GMR technology can be applied to automobile components, such as engines, suspension and



Fig. 1—Schematic of zero-emission electrochemical flow reactor.

anti-brake systems.<sup>8</sup> Electrodeposition can produce both multilayer and granular alloys, and its advantages have been elaborated by Ross.<sup>6</sup> She describes the two approaches used to fabricate nano-size multilayer GMR films by electrodeposition: the single-bath and the dual-bath methods.

Single baths consist of at least two metal ions in which one can be deposited at a more negative potential, such as ferrous metals (less noble metals), and the other at a less negative potential, such as copper or silver (more noble metals). The electrodeposition of multilayers can be achieved by periodically varying the current or potential. As an example, for Ni/ Cu multilayers, periodically pulsed current or potential is used with a Ni plating bath to which small amounts of Cu ions have been added. A non-magnetic Cu layer is obtained at low current densities (more positive potentials), while a Ni-Cu alloy was obtained at higher current densities (more negative potentials). Potential pulse methods have been successfully used to prepare various multilayer deposits, such as Ni/Cu,<sup>9,10</sup> Co/Cu,<sup>9</sup> and Ni<sub>80</sub>Fe<sub>20</sub>/Cu.<sup>11</sup>

There are limitations to the single-bath method. The metal ions in the electrolyte must have reduction potentials that are sufficiently separated so that nearly pure layers can be selectively deposited. Another limitation is that it is impossible to deposit pure less-noble metal layers because the more-noble metal always co-deposits to some extent during the lessnoble metal deposition phase; this can result in films with poorer magnetic properties, including the GMR effect. Moreover, partial dissolution of the less-noble metal can occur during the deposition of the more-noble metal, and oxides may form between metal layers.

In the dual-bath method, the substrate is repeatedly transferred between different electrolytes. Because the two materials in the multilayers are not deposited from the same plating solution, compatibility of the electrolytes and wellseparated deposition potentials are not required. Nevertheless, the dual-bath technique also has limitations. In addition to the tedious procedure of transferring the substrate from one bath to another, undesired surface reactions, such as formation of metal oxides during the intermediate rinsing and transferring steps, can adversely affect magnetic properties.



Fig. 2—Three-dimensional RVC reactors: (a) reactor #1 (D = 1 cm, L = 2.3 cm, D/L = 0.44); (b) reactor #2 (D = 2.5 cm, L = 0.3 cm D/L = 8.5); (c) reactor #3 (D = 2.5 cm, L = 0.3 cm, D/L = 8.5).

system was developed in the UCLA Electrochemical Laboratory (AESF Project # 79); separation and recovery of heavy metals from dilute waste streams in the potentiostatic mode was achieved.<sup>17-19</sup> This process not only reduces environmental pollution but also recovers for reuse valuable products.

We have developed a zero-emission electrochemical flow reactor to eliminate heavy metal waste effluents from fabrication of metal multilayers by electrodeposition. The electrodeposition of Ni/Cu multilayers in this novel process is similar to the dual-bath technique, except that deposition occurs in an inert environment with alternating flow of plating solutions and rinsewaters, instead of transferring the substrate between plating baths. A low cathodic current is applied during the rinsing steps to eliminate interfacial metal oxide formation. The rinsewater is directed to the metal recovery units for removal and recovery of the metal ions. After removal, the rinsewaters are returned to the rinsewater reservoir and reused. In this study, we show the feasibility of producing nanostructured Ni/Cu multilayers with zero emission of heavy metals from the effluents.

#### Experimental Procedure

Figure 1 shows the schematic of our electrodeposition process, which consists of the flow reactor system and the metal recovery unit. The former consists of the electrochemical reactor, a potentiostat or a power supply, pumps, two 3-way switches, and three reservoirs. The reservoirs contain the Ni plating solution, the Cu plating solution, and deionized rinsewater, respectively. The recirculating metal recovery units are divided into nickel and copper recovery units consisting of sets of porous electrode reactors and wastewater reservoirs. The recovery units are separated to permit recovery of the individual pure metals.

With the evergrowing problem of waste disposal, increasingly stringent governmental restrictions have been imposed on emissions of hazardous/toxic materials to the environment.

Porous flowthrough electrodes have been reported to be effective in recovering metal ions from aqueous effluents.12 Various metals have been removed from dilute waste streams, including copper, silver, lead, mercury and antimony.13-16 Between 1990 and 1993, a multistage, segmented porous electrode



*Fig. 3—Current efficiency of unstirred and agitated copper electrodeposition as a function of current density.* 



Fig. 4—Dependence of the current efficiency of unstirred copper electrodeposition on bath acidity.

The detailed deposition process is as follows: First, the Ni layer is electrodeposited on a gold-sputtered glass substrate, with the nickel plating solution circulating between the electrochemical flow reactor and the nickel plating solution reservoir. When the desired thickness of nickel is achieved, the valve is adjusted so that rinsewater flows into the reactor, displacing the remaining Ni plating solution. A low cathodic current is applied to prevent oxidation of the film during the rinse step. The displaced nickel plating solution and rinse water are directed to the nickel recovery unit. The Cu plating solution is then circulated between the reactor and copper plating solution reservoir, and the Cu layer is electrodeposited on the nickel deposit to the desired thickness. This is followed by another rinse step, with the flow directed to the copper recovery unit. Multilayer films are deposited by repetitive cycling.

When electrodeposition of the multilayer is completed, recovery of pure copper and nickel is initiated from the copper and nickel rinsewaters collected in separate reservoirs. For Cu recovery, the Cu rinsewater is recirculated between the Cu recovery unit and the Cu rinsewater reservoir with a constant current applied between the porous cathode and the platinum-coated titanium anode. When copper removal is complete, the reclaimed rinsewater is returned to the rinsewater reservoir for reuse. Ni is recovered from the Ni rinsewater in the same way as Cu, and this reclaimed rinsewater is also returned to the rinsewater reservoir for reuse.



Fig. 5—Plot of limiting current density of Cu deposition vs. square root of rotation rate;  $0.005 \text{ M CuSO}_4 + 2 \text{ M H}_2\text{SO}_4 + \text{brightener.}$ 



Fig. 6—Dependence of current efficiency of unstirred Ni electrodeposition on current density and  $Ni^{+2}$  ion concentration.

As indicated, three-dimensional RVC (reticulated vitreous carbon) electrodes are used to recover the metals. RVC has a honeycomb structure that provides a high surface-areato-volume ratio. It is inexpensive and readily available commercially (ERG, Oakland, CA) and can be obtained with surface-area-to-volume ratios ranging from 4.9 to 66 cm<sup>2</sup>/ cm<sup>3</sup>. In addition, the RVC can be stripped and reused because of its inert nature.

Three different RVC reactors were evaluated for their effect on metal recovery rates. Detailed schematics of the porous flow-through electrodes with the various configurations are shown in Fig. 2. A 60-pore-per-inch (ppi) RVC sheet (surface-area-to-volume ratio of 36.1 cm<sup>2</sup>/cm<sup>3</sup>) was cut into cylinders having the following dimensions: 1.00 cm diam. and 2.25 cm length (reactor #1) and 2.54 cm diam. and 0.3 cm length (reactors #2 and #3). Diameter-to-length ratios for reactor #1, and for reactors #2 and #3 were 0.44 and 8.5, respectively, with the total surface areas fixed at 64 cm<sup>2</sup>.

For reactors #1 and #2, the cylindrical cell was constructed from stainless steel, and a platinum-coated titanium mesh served as the anode. The flow was directed upward, with the anode positioned above the cathode. The stainless steel tube was capped at the ends with o-ring-sealed polymethylmethacrylate covers. Tapered joints with Tygon<sup>™</sup> tubing



*Fig.* 7—Dependence of current efficiency of Ni electrodeposition on charge in unstirred solutions; 20 mA/cm<sup>2</sup>.

(0.95 cm diam.) were inserted at the ends of each cover connecting the cell to the rinsewater reservoir. A variable-flow pump pumped rinsewater to the porous reactor. Volumetric flow rate was varied from 540 to 950 mL/min, and the volume of rinsewater was fixed at 100 mL. Reactor #2 (Fig. 2b) contained a glass bead bed in the section below the RVC electrode to provide a uniform flow pattern, offsetting the differences in tube and electrode diameters. Reactor #3 is similar to a parallel plating cell with two anodes placed at the cell wall and a cathode in the center of the cell (Fig. 2c).

Samples were taken from the reservoirs at regular time intervals and analyzed with an atomic absorption spectrophotometer (AA). After each experiment, the cell was disassembled and washed thoroughly with deionized water. The RVC electrodes were stripped of the deposits by soaking in 30-percent v/v nitric acid.

The copper sulfate bath consisted of  $0.005 \text{ M CuSO}_4$ , 2 M  $\text{H}_2\text{SO}_4$ , and a brightener. The brightener was required to obtain contiguous two-dimensional copper layers. The nickel sulfamate bath consisted of 0.005-0.02 M nickel sulfamate and 0.5 M boric acid. Brighteners were not required to obtain contiguous two-dimensional nickel layers. All solutions were prepared with analytical grade reagents and deionized water and maintained at room temperature (~25 °C).

After preliminary evaluation of copper and nickel electrodeposition from dilute solutions in unstirred and paddleagitated systems,<sup>20</sup> individual copper and nickel layers were electrodeposited in the recirculating electrochemical flow reactor, galvanostatically, with fixed charge (one coulomb). The deposits were thoroughly rinsed and dried. They were dissolved with 30-percent nitric acid, and deposit weights were calculated from analysis by AA. The current efficiencies (C.E.) were determined by the ratio of the actual deposit weight divided by the theoretical weight at 100 percent current efficiency times 100. For example, the weight of electrodeposited copper and nickel with 100 percent C.E. at fixed charge of one coulomb (1 C) are 0.329 mg and 0.304 mg, respectively.

C.E. of  $Cu = (actual deposit weight/0.329 mg) \times 100 (for 1 C)$  (1)

The partial current densities (i) of copper and hydrogen gas evolution were determined by:



Fig. 8—Dependence of current efficiency of copper electrodeposition on current density and volumetric flow rate.

$$i_{Cu} = i_{appl} x \text{ C.E./100}$$
(2)  

$$i_{H2} = i_{appl} x (100 - \text{ C.E.})/100$$
(3)

Volumetric flow rates of 100 mL/min and 147 mL/min were selected to examine hydrodynamic effects on copper and nickel electrodeposition. Several Ni/Cu multilayer deposits with various layer thicknesses were prepared, utilizing the electrochemical flow reactor. The current density and volumetric flow rate of copper and nickel were fixed at 2.5 mA/cm<sup>2</sup> and 147 mL/min. Current efficiencies ranged from 90-100 percent.

X-ray diffraction in the  $\theta$ -2 $\theta$  mode using Cu-K $\alpha$  radiation determined the crystal structure of the electrodeposits. To examine the cross section of Ni/Cu multilayers, samples were cold-mounted and mechanically polished sequentially with different (440 to 1200) grit papers, followed by diamond paste (6, 1, 0.5 and 0.1  $\mu$ m) on a polishing wheel. Copper layers were slightly etched with a solution of 0.0157 M chromic acid + 0.012 M HCl + 0.36 M H<sub>2</sub>SO<sub>4</sub> for 120 sec to distinguish the nickel and copper layers. The cross-sectional mounts were examined by scanning electron microscopy (SEM).

Resul	ts&Di	scussion	

Electrodeposition of Ni/CuMultilayers

The main focus of our initial studies was to develop an environmentally friendly low metal ion concentration plating solution from which contiguous nano-thick copper and nickel layers could be deposited. It was determined that such copper layers can be electrodeposited from dilute copper sulfate solutions containing 0.005 M of copper ions and a brightener. Without the brightener, electrodeposited copper layers were not contiguous.

The current efficiency is relatively low compared to common copper plating baths as a reult of the low concentration of copper ions. In both unstirred and reciprocating paddleagitated baths, the current efficiency decreased from 35 to 9 percent and 51 to 9.5 percent, respectively, as the current density increased from 2.5 to 30 mA/cm<sup>2</sup> (Fig. 3). Bath agitation increased the current efficiency.

The effects of  $H_2SO_4$  concentration on the structure of copper deposits and on the deposition rates were studied at  $H_2SO_4$  concentrations of 2 and 0.05 M, with constant copper ion concentrations and brightener. Dull, poor quality copper



Fig. 9—Dependence of current efficiency of nickel electrodeposition on current density and volumetric flow rate.

films were deposited from 0.05 M  $H_2SO_4$ . Electrodeposited copper films from 2 M  $H_2SO_4$  baths, however, were contiguous two-dimensional films. Figure 4 shows current efficiencies for the two  $H_2SO_4$  concentrations as a function of current density for unstirred conditions, indicating practically no difference above 10 mA/cm<sup>2</sup>.

To develop information about copper electrodeposition in dilute  $\text{CuSO}_4$  concentrations, linear sweep voltammetry (2 mV/sec) on rotating Pt disk electrodes was performed from 300 to 2000 rpm. The limiting current density increased with rotation rate. Linear plots of limiting current density vs. the square root of the rotation rate through the origin (Fig. 5) indicate mass transfer control following the Levich relation,

$$i_{\rm r} = 0.62 \rm{n} F D^{2/3} v^{-1/6} \omega^{1/2} c \tag{4}$$

where  $i_L$  is the limiting current density, n is the number of equivalents per gram-atom, F is Faraday's constant, D is the diffusion coefficient of  $Cu^{+2}$ , v is the kinematic viscosity of the solution,  $\omega$  is the rotation rate (rad/sec) and c is the concentration (mol/cc).

Our studies show that contiguous nano-thick nickel layers can be electrodeposited from a simple nickel sulfamate bath containing low nickel ion concentrations (0.005 to 0.02 M Ni<sup>+2</sup>). In contrast to electrodeposition of nano-thick copper layers, a brightener was not required to promote two-dimensional growth.

The current efficiency was low compared to a conventional nickel sulfamate plating bath containing approximately 1.4 M Ni<sup>+2</sup>. The dependence of the current efficiency on nickel ion concentration and applied current density in unstirred solutions is shown in Fig. 6. Current efficiency increased substantially from 20 to 70 percent as the nickel ion concentration increased from 0.005 M to 0.01 M at 10 mA/ cm<sup>2</sup>. A smaller increase in current efficiency was obtained from 0.01 M to 0.02 M. The experimental results indicate that nickel can be electrodeposited from unstirred, dilute nickel sulfamate baths (0.01 M) with relatively high current efficiency (~70%). Bright metallic deposits were obtained up to 15 mA/cm<sup>2</sup>. Burnt deposits were obtained above 20 mA/cm<sup>2</sup>.

The dependence of current efficiency on charge (Fig. 7) using a sputtered-gold glass substrate was studied to gain information on the growth of the nickel deposit in a 0.01 M nickel sulfamate bath at 15 mA/cm<sup>2</sup>. A two-dimensional



Fig. 10—SEM micrograph of electrodeposited Ni/Cu multilayers; 147 mL/min,, 2.5 mA/cm<sup>2</sup>,  $\delta_{cu} = 60 \text{ nm}, \delta_{Ni} = 120 \text{ nm}.$ 



Fig. 11—X-ray diffraction of electrodeposited Ni/Cu multilayers (a,b) on gold and pure Ni film (c) on brass from unstirred solutions: (a)  $\delta_{Ni} \approx 90$  nm and  $\delta_u \approx 45$  nm, 2.5 mA/cm<sup>2</sup>, 147 mL/min; (b)  $\delta_{Ni} \approx 45$  nm and  $\delta_{Cu} \approx 45$  nm, 2.5 mA/cm<sup>2</sup>, 147 mL/min; (c)  $\delta_{Ni} = 3.7 \mu m$ , 10 mA/cm<sup>2</sup>. (S = X-ray diffraction peak for brass substrate).

contiguous thin film rapidly formed with current efficiency decreasing from 52 to 46 percent with increasing charge. The average thickness increased linearly with charge. The dependence of the current efficiency of copper deposition on current density and volumetric flow rate in the flow reactor is shown in Fig. 8. Current efficiency increased substantially with increasing volumetric flow rate, attaining almost 100 percent at 2.5 mA/cm<sup>2</sup> and 147 mL/min. Current efficiency decreased sharply, however, to 20 percent at 10mA/cm<sup>2</sup> and to 10 percent at 20mA/cm<sup>2</sup>. In unstirred solution, current efficiency was approximately 15 percent at 15 mA/cm<sup>2</sup>, decreasing to 5 percent at 20 mA/cm<sup>2</sup>.

Figure 9 shows the dependence of nickel deposition current efficiency on applied current density and volumetric flow rate. Current efficiency increased with increasing solution flow rate and decreasing current density as for copper.

Ni/Cu multilayers were electrodeposited on gold-sputtered glass substrate at 2.5 mA/cm<sup>2</sup> and 147 mL/min. The low applied current density and precise control of the charge passed, permitted tailored individual deposition layer thicknesses. Figure 10 shows the cross sectional SEM micrograph of the Ni/Cu multilayers with Ni and Cu layer thicknesses of 120 and 60 nm, respectively. Cu was selectively etched to distinguish the Cu and Ni layers. A well-defined lamellar structure was obtained.



Fig. 12—Effect of volumetric flow rate on the removal of Cufrom rinsewater in reactor #1 (initial  $Cu^{+2}$  concentration = 323 ppm, 1.8 mA/cm<sup>2</sup>).

X-ray diffraction of the Ni/Cu multilayers on gold-sputtered glass shows four distinct diffraction peaks, Cu(111), Ni(111), Cu(200) and Ni(200), indicating good crystallinity of the Ni/Cu multilayers (Fig. 11a & b). The Ni (220) diffraction peak was not observed in Ni/Cu multilayers compared to pure nickel films deposited on a brass substrate from unstirred solutions, indicating that the presence of the copper layer suppressed the (220) orientation of nickel (Fig. 11c).

## Recovery of Cu & Ni from Rinsewaters

There are a number of recycle technologies suitable for metal finishing operations, including membrane, electrolysis, crossflow filtration, reverse osmosis, ion exchange, diffusion dialysis, electrodialysis, vacuum evaporation and electrodeposition, to recover metals from waste streams.<sup>21</sup> The major advantage of electrodeposition is that metal can be recovered directly in a relatively pure state. There are many different reactor configurations that generally are either two-dimensional flat or three-dimensional porous or packed bed reactors. Three-dimensional electrodes have the advantage of a large surface area per unit volume of reactor to permit faster recovery compared to the more conventional flat electrode. Three-dimensional electrodes can have significant current distribution limitations, however, because of ohmic, geometric, and mass transfer effects. Two approaches can be utilized with three-dimensional flow-through electrodes: (1) parallel current and solution flow, and (2) perpendicular current and solution flow.

To develop optimum recovery conditions, current density, volumetric flow rate, and reactor geometries (diameter-tolength ratio, D/L) were investigated. Three different reactors were used (Fig. 2). Reactors #1 and #2 are three-dimensional flow-through, with the same total surface area (66 cm<sup>2</sup>) but different D/L ratios (0.44 for reactor #1 and 8.5 for reactor #2). Reactors #2 and #3 have the same D/L ratio (8.5), but reactor #3 is an open unstirred parallel plating cell with two anodes placed at the cell walls with the cathode in the center.

In reactor #1, copper removal was faster as the volumetric flow rate increased from 540 to 756 mL/min (Fig. 12) but was essentially unchanged, with an increase to 950 mL/min. At  $1.8 \text{ mA/cm}^2$  and the two higher flow rates, the concentration



Fig. 13—Effect of applied current density on removal of Cu from rinsewater in reactor #1 (initial  $Cu^{+2}$  concentration = 323 ppm, 756 mL/min).

of copper decreased from 323 ppm to less than 10 ppm after 25 min.

The effect of applied current density on the copper recovery rate in reactor #1 is shown in Fig. 13. As the applied current density was increased from 1.8 to 3.6 mA/cm<sup>2</sup>, the rate of copper recovery also increased. The recovery rates converged, however, within 20 min.

A linear decrease in the ln  $[C(t)/C_o]$ -time plot at 3.6 mA/ cm<sup>2</sup> (Fig. 14) indicates that copper recovery was under mass transfer control, according to the model of Pletcher *et al.*<sup>15,16</sup> They developed the relationship,

$$\ln \left[ C(t)/C_{o} \right] = -V_{e}k_{m}A_{e}t/V$$
(5)

where  $C_0$  is the initial concentration of metal ions, C(t) is the concentration of metal ions at time t, k<sub>m</sub> is the mass transfer coefficient, V<sub>e</sub> is the cathode volume, A<sub>e</sub> is the surface-areato-volume ratio and V is the total volume of the solution. The mass transfer coefficient of copper in the RVC electrode was determined to be 0.22 cm/sec, where  $V_a = 1.77$  cm<sup>3</sup>,  $A_a = 36$  $cm^{-1}$ , V = 100 cm<sup>3</sup>. At 1.8 mA/cm<sup>2</sup>, however, the ln[C(t)/C<sub>0</sub>]time plot was not linear. At 1.8 mA/cm<sup>2</sup>, the RVC was covered uniformly with bright copper, independent of the volumetric flow rate (Fig. 15). Above 1.8 mA/cm<sup>2</sup>, copper deposits were dull, covering only the upper half of the RVC, just below the anode. The effect of volumetric flow rate on the removal of nickel in reactor #1 was also investigated at 1.8  $mA/cm^{2}$  (data not shown). In contrast to copper, the recovery rate of nickel was not dependent on the volumetric flow rate, and the recovery rate was much slower than for copper. At 950 mL/min, the concentration of nickel was reduced from 253 to 200 ppm in 50 min. The recovery rate of nickel improved by increasing current density from 1.8 to 3.6 mA/ cm<sup>2</sup>. Only ten percent of the RVC electrode had been utilized to recover nickel at both current densities.

Both reactors #2 and #3 have higher cross sectional areas with smaller lengths than reactor #1. The nickel recovery rate of reactor #2 was also independent of flow rate, as was reactor #1, but increased with increase in current density as reactor #3 (open unstirred parallel cell with dual anodes). The Ni recovery rate at 3.6 mA/cm<sup>2</sup> after 50 min increased in the order: reactor #3 > reactor #2 > reactor #1. By increasing the D/L ratio, more of the RVC electrode was utilized for nickel recovery. Enhancement was achieved by a second anode



Fig. 14— $ln[C(t)/C_{a}]$ -time plots of experimental data given in Fig. 13.

positioned opposite the first anode. A dull nickel deposit was concentrated in 30 percent of the RVC electrode adjacent to the anode in reactor #2, whereas a uniformly distributed bright nickel deposit on RVC was obtained with reactor #3.

Dimensionless concentration  $[C(t)/C_o]$ -time plots for nickel and copper indicate a much lower recovery rate of nickel compared to copper at 3.6 mA/cm<sup>2</sup> (Fig. 16) because of considerable hydrogen gas evolution during nickel recovery, reducing the current efficiency.

## Summary & Conclusions

Ni/CuMultilayers Deposited

By an Electrochemical Flow Reactor

- Nano-structured Ni/Cu multilayers have been electrodeposited by a zero-emission electrochemical flow reactor system. Advantages of this system are:
- 1. Fabrication of distinct nano-structured multilayers with precise layer thicknesses.
- 2. Electrodeposition of the less-noble metal (Ni) without co-deposition of the more-noble metal (Cu).
- Formation of metal oxides at the interface is prevented by deposition under an inert environment and by applying a low cathodic current during the rinsing step.
- 4. Virtually complete recovery of metals from rinsewaters with three-dimensional reticulated vitreous carbon (RVC) electrodes.
- Nano-thick films have been electrodeposited from plating solutions containing low concentrations of copper and nickel. A brightener was required to obtain contiguous two-dimensional copper films. No brightener was required for nickel films. The solution compositions used were:

1. Copper:  $0.005 \text{ M CuSO}_4 + 2 \text{ M H}_2\text{SO}_4 + \text{brightener}$ 2. Nickel:  $0.01 \text{ M Ni}(\text{NH}_2\text{SO}_3)_2 + 0.5 \text{ M H}_3\text{BO}_3$ 

- Multilayer nano-structures of copper and nickel have been electrodeposited from dilute plating solutions with high current efficiency at low current densities and higher solution flow rates. Contiguous nano-thick films of copper and nickel were obtained under these conditions.
- X-ray diffraction shows that Ni/Cu multilayer electrodeposits were randomly oriented compared to the (220) preferred orientation of pure nickel films.
- SEM micrographs reveal sharply demarcated multilayered deposits.



*Fig.* 15—*Effect of reactor configuration on the recovery rate of nickel at* 3.6 *mA/cm<sup>2</sup>: (A) reactor #1, (B) reactor #2 and (C) reactor #3.* 

Heavy Metal Recovery from Rinsewater

- Ni and Cu were sucessfully recovered from rinsewater by reticulated vitreous carbon (RVC) electrodes.
- Cu recovery rate was influenced by both applied current density and volumetric flow rate.
- Ni recovery rate was independent of volumetric flow rate, but increased as the applied current density increased. Higher recovery rates of Ni were achieved by increasing the D/L (diameter/length) ratio of the reactor and employing dual anodes.
- The recovery rate of Ni was lower than Cu because of high hydrogen gas evolution rates.

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Fig. 16—Dimensionless concentration of Cu and Nivs. time at 3.6 mA/cm<sup>2</sup>.

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