## **Technical Article**

# **Electrolytic Codeposition** Of Diamond Particles With Nickel and Cobalt Metals by E.C. Lee\* & I.T. Moon

The electrocodeposition of nickel-cobalt-diamond composite coatings from Ni-Co sulfamate baths was studied using a rotating disc and a wire cathode geometry. The deposition rate of cobalt for the composite coatings was controlled by mass transfer of the cobalt ions through the diffusion boundary layer of the solution. That of nickel however, involved a mixed control mechanism of diffusion and electrochemical reaction. The cobalt content of the composite coatings was approximately 10 wt% when 1.0 wt% Co was present in the Ni-Co sulfamate bath. At this composition, a maximum hardness value was observed. Gradient nickel-cobalt alloy composite coatings could be made by controlling the electrolyte agitation (stirring) and the bath voltage.

The process of electrolytic codeposition of insoluble particles with metals has been developed for diverse engineering applications during the past three decades. These include dispersion-hardening coatings, wear-resistant coatings and self-lubrication coatings. Recently, electrodeposited nickeldiamond wires have been commercialized for the precision cutting of semiconducting silicon ingots. These wire saws have been produced by passing a fine steel wire through sedimented diamond particles in nickel plating baths. The codeposition behavior of suspended diamond particles with nickel on steel from a nickel sulfamate bath has recently been investigated using both rotating disc and wire geometries.<sup>1</sup>

Based on zeta potential measurements and the change of diamond content in the deposits with electrical potential strength, we proposed that diamond particles were electrophoretically attracted to the cathode after an adsorption of positive nickel ions. Mathematical models for the electrolytic codeposition of particles have been developed by several researchers.<sup>2-7</sup> Among them, Gugliemi<sup>3</sup> proposed a mechanism of codeposition which considered two-successive adsorption steps: (1) a loose adsorption, which had an essentially physical character, and (2) a subsequent strong adsorption which was assumed to be electric field assisted.

Celis, et al.6 developed a mathematical formula to calculate the inert particle composition of codepositions. Celis, et al.<sup>8</sup> also published a very good literature survey on the mechanism of electrocodeposition developed over the past few decades and the expected future developments in composite plating.

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Yagodkina, et al.9 studied the phase composition, structure, physicochemical and corrosion-related electrochemical properties of Ni-diamond composite coatings. They reported that the diamond content in coating depended not only on the current density and time of electrolysis, but on the diamond particle size range as well.

Reddy, et al.<sup>10</sup> studied the wear resistance of electroless Ni-P/diamond composite coatings. Their results showed a substantial increase in wear resistance after a coated sample containing 9-10 wt% P containing fine-sized diamond particles was annealed at around 350°C (662°F).

Abi-Akar, et al.11 investigated the electrocodeposition of Ni-diamond and Co-chromium carbide under low-gravity



Fig. 1-Experimental apparatus for electrodeposition using (A) rotating disc and (B) wire geometries.

## Nuts & Bolts: What This Paper Means to You

This work involves a fascinating application, namely plated nickel-cobalt-diamond wires for the precision cutting of semiconducting silicon ingots. The cobalt content of the composite coatings was approximately 10 wt% when 1.0 wt% Co was present in the Ni-Co sulfamate bath, the point of maximum hardness. Better yet, gradient composite coatings could be made by merely controlling the stirring and voltage.

conditions in earth orbit. The results showed that reduced gravity eliminated sedimentation and edge effects, and uniform particle distribution was obtained.

 Table 1

 Chemical Compositions of the Steel Disc Plate & Wire

Al

0.074%

S

0.10%

0.004%

Electrodeposited alloys as matrices for composite coatings give better properties

such as finer grain size, better appearance, higher hardness and mechanical strength and better corrosion resistance than for the parent metals. Cobalt has been a popular constituent of nickel plating baths. In the present work, we attempted to elucidate the mechanism of electrocodeposited Ni-Co-diamond composite coatings using rotating disc geometry. We studied the effects of hydrodynamics, bath temperature and voltage on the deposition rates of nickel and cobalt. We also looked at the variation of the diamond and metal contents in Ni-Co-diamond deposits as related to the deposition rates of nickel and cobalt. Using a wire geometry, we studied the influence of bath voltage, temperature and hydrodynamics on the nickel composition after plating of the composites was carried out over several hours.

Disk

Wire

С

250ppm

0.82%

Mn

0.12%

0.50%

Р

0.012%

0.005%

## **Experimental**

Nickel-cobalt-diamond electrocodeposition experiments were carried out in batches in a 200-mL glass vessel, using a 3-cm (1.2-in.) diameter flat steel rotating disc mounted on a Teflon holder. In the continuous processes, a 0.15-mm (6 mil) diameter steel wire was used in the same container. The electrodeposition cell for the rotating disc electrode is shown schematically in Fig. 1a. A saturated calomel electrode (SCE) equipped with a Luggin capillary probe, was positioned close to the rotating disc. A pure platinum electrode was positioned 2 cm (0.8 in.) below the rotating disc in the plating bath. The disc rotation speed was controlled by an electrode rotator\*\* from 300 to 1200 rpm, under laminar flow conditions.

\*\* Model HR-103A, Hukudo Denko Corporation, Tokyo, Japan.



Ν

13ppm

0

36ppm

Si

0.20%

Fe

Bal.

Bal.

The compositions of the steel disc plate and wire are shown in Table 1. Table 2 shows the composition of the plating bath. The steel disc surfaces were successively polished with emery paper and alumina powder, degreased in an alkaline ultrasonic cleaning bath and pickled in an acid solution.

For the electrodeposition tests, a rotating disc or a steel wire cathode was used with an electrochemical measurement apparatus, including a power supply,<sup>\*\*\*</sup> potentiostat,<sup>\*\*\*\*</sup> and function generator.<sup>\*\*\*\*\*</sup> Artificial diamond particles,<sup>\*\*\*\*\*</sup> in size ranges of 2-4, 4-8, 10-15 and 20-30  $\mu$ m were used in the experiments. The surface morphology and composition of the Ni-Co-diamond deposits were analyzed by scanning electron microscopy, image analysis and atomic absorption spectrophotometry. Unless otherwise stated, the experiments were conducted at 1.35 V (vs. SCE), 500 rpm, 50°C (122°F) and a 4 g/L diamond concentration.

<sup>\*\*\*\*\*\*</sup> General Electric Company, New York, NY.







Fig. 3—Deposition rates of Ni and Co for different disc rotation speeds at 35°C (95°F).

<sup>\*\*\*\*</sup> HP-6642A, Hewlett-Packard Company, Palo Alto, CA.

<sup>\*\*\*\*</sup> Model HA-301, Hukudo Denko Corporation, Tokyo, Japan.

<sup>\*\*\*\*\*</sup> Model HG-104, Hukudo Denko Corporation, Tokyo, Japan.

## Table 2 Chemical Composition of the Plating Bath

<b>Chemical Formula</b>	Concentration, g/L (oz/gal)
Ni(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	500 (66.7)
H <sub>3</sub> BO <sub>3</sub>	40.0 (5.3)
NiCl <sub>2</sub> .6H <sub>2</sub> O	5.00 (0.67)
CoCl <sub>2</sub> .6H <sub>2</sub> O	3.82 (0.50)

### **Results & Discussion**

## Ni-Co-Diamond Composite Coatings Using a Rotating Disc

The effect of metal composition in the Ni-Co sulfamate bath on the metal content of the deposits is shown in Fig. 2. The microhardness of the Ni-Co alloys is also shown. Curve 1 was above the composition-reference line, indicating that cobalt in the nickel sulfamate bath was the more readily deposited metal. Similar results have been observed in sulfate and chloride baths, where the cobalt content in the Ni-Co alloys was much higher than the nickel content (anomalous codeposition).<sup>12</sup> The microhardness of the Ni-Co deposits (Curve 2) rose sharply up to 10 wt% Co and then remained constant as the cobalt content increased. Therefore, 1 wt% Co in the Ni-Co sulfamate bath is all that is required to impart maximum hardness to the alloy.

The effect of disc rotation speed on the deposition rates of nickel and cobalt for the Ni-Co-diamond composite coatings is shown in Fig. 3. The deposition rates of nickel and cobalt showed first-order behavior with a higher rate for cobalt than for nickel. The log-log plots of the rate constants for Ni and Co versus disc rotation speed are shown in Fig. 4. The slopes of the log (k) versus log ( ) curves are 0.45 and 0.37 for cobalt and nickel, respectively. These slope values are less than 0.5, which would be the expected slope for a system under diffusion control.

The effect of potential on the apparent rate constant for nickel and cobalt deposition for the Ni-Co-diamond composite coatings



Fig. 5—Effect of potential on the deposition rate constants of Ni and Co for the diamond composite coatings.

is shown in Fig. 5. These curves did not follow Tafel behavior, according to the equation

 $= a + b \ln I$ ,

and thus the deposition rates of both nickel and cobalt were not fully controlled by the electrochemical reaction. The corresponding polarization curves are shown in Fig. 6. The plots of log (I/A) versus ( $V_{sCE}$ ) were not linear. These results are consistent with the previous ones.

The deposition rates of cobalt increased as the cobalt content in



Fig. 4—Effect of rotation speed on the deposition rate constants of Ni and Co for the diamond composite coatings at  $35^{\circ}C$  ( $95^{\circ}F$ ).

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Fig. 6—Potential-current density diagram for the diamond composite coatings; diamond content in bath, 0.1 vol%.



Fig. 7—Variation of nickel, cobalt and diamond contents of the composite coatings with potential.

the Ni-Co-diamond deposits increased. The metal and diamond compositions are plotted versus potential in Fig. 7. The nickel content increased, while the cobalt decreased up to 1.3  $\rm V_{SCE}$  and then reached a plateau. The diamond content increased up to about 1.0  $\rm V_{SCE}$  and then decreased. The nickel and cobalt contents varied about 15 wt% and diamond content varied about 20 vol% with the potential variation.

The effect of rotation speed on the metal and diamond content are shown in Fig. 8. The nickel content decreased slightly with rotation speed, while the cobalt increased. The diamond content increased and reached a maximum at 500 rpm. As the disc rotation speed was further raised, the diamond content decreased.

The effect of temperature on the apparent rate constant for nickel and cobalt deposition is shown in Fig. 9. Arrhenius activation energy values for the deposition of nickel and cobalt are 20.1



Fig. 8—Variation of nickel, cobalt and diamond contents of the composite coatings with rotation speed.



Fig. 9—Effect of temperature on the deposition rate constants of Ni and Co for the diamond composite coatings.

kJ/mol (4.8 kcal/mol) and 15.5 kJ/mol (3.7 kcal/mol), respectively; these values are nearly the same or somewhat higher than those for mass-transfer controlling systems and the results are consistent with the previous results on rotation speed.

#### Gradient Ni-Co-Diamond Composite Coatings

Gradient Ni-Co-diamond composite coatings were studied by continuously varying the rotation speed and bath voltage, as shown in Fig.10. Details of the experimental apparatus are given elsewhere.<sup>13</sup> The EPMA photomicrographs show that the cobalt content gradually increased as the rotation speed increased from 400 to 1200 rpm (Fig. 10a). The opposite results were obtained at a constant 500 rpm with a gradual increase in applied voltage from 0.5 to 2.0 V<sub>SCE</sub> (Fig. 10b).

#### Continuous Electrodeposition of Ni-Co-Diamond

In order to investigate the surface morphology and the variation of nickel composition of the bath during electrodeposition, continuous electrodeposition of the composite onto a 0.1-mm (3.9-mil) diameter steel wire was carried out for three hours. The surface morphology of the Ni-Co-diamond composite using the wire geometry is shown in the SEM photos of Fig. 11. The diamond particles were uniformly deposited for all sizes ranging from 2 to 30  $\mu$ m. The nickel content of the sulfamate baths did not vary significantly with changes in stirring speed and temperature during the three hours of continuous electrodeposition.

#### Conclusions

The cobalt content of the Ni-Co-diamond deposits was about 10 wt% corresponding to a Ni-Co sulfamate bath composition of 1 wt% Co. This was also the point at which maximum hardness was obtained. The cobalt deposition rate was controlled by mass transfer of the cobalt ions through the diffusion boundary layer of the solution. On the other hand, the rate of nickel deposition was under mixed control via both diffusion and electrochemical reaction. Gradient nickel-cobalt alloys of the Ni-Co-diamond composite coatings were made

by controlling the bath stirring speed and the plating voltage.

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Fig. 11—Surface morphology of Ni-Co-diamond composite coatings; anode diameter, 1.2 cm (0.5 in.); voltage, 0.96  $V_{_{SCE}}$ 



Fig. 10a—Qualitative analysis of the plated Ni-Co-diamond composite by EPMA with changing rotation speed from 400 to 1200 rpm at 1.35  $V_{sce}$  and 50°C (122°F).



Fig. 10b—Qualitative analysis of the plated Ni-Co-diamond composite by EPMA with changing potential from 0.5 to 2.0  $V_{sce}$  at 500 rpm and 50°C (122°F).

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