Characterization of Cu/Ni-B Multilayers Deposited by Dynamic Chemical Plating

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This paper describes the properties of Ni-B/Cu multilayers deposited on low carbon steel substrates by dynamic chemical plating (DCP), a new direct wet plating process that allows the deposition of alternating layers of Ni-B and Cu with an individual layer thickness of 0.2 to 0.3 µm (7.9 to 11.8 µ-in.), at room temperature over the course of a few minutes. Assemblies of five to 20 alternating layers of Ni-B and Cu were obtained and the influence on the total number of layers on the properties of the assemblies was investigated. Analysis by SEM showed that continuous films with a homogeneous thickness distribution were deposited. Results showed that the thickness was dependent only on the deposition parameters and not on the surface properties, after the first deposited layer. The adhesion properties of the Ni-B/Cu multilayers as well as the thickness and the morphology of cross sectional multifilms with and without heat treatment were investigated. Despite the absence of cupronickel alloys even after heat treatment, the results showed that Ni-B/Cu multilayers obtained by DCP improve the corrosion resistance of carbon steel in 5% of sodium chloride.

Alternating metallic layers may show improved mechanical, magnetic or tribological properties when compared to the corresponding pure metals.[1] The properties of multilayers are not only governed by the composition, thickness and nature of each layer but also by the properties and composition of the interfaces.[2,3] The crystal structure, orientation and grain size for instance, characterize the nature of the individual layers.[4] The goal of this work was to deposit Ni-B/Cu multilayers on steel substrates at room temperature by using a new method of deposition called dynamic chemical plating.[5] The principle of this new process is to spray in sequence and simultaneously two or several aqueous solutions on the surface of the substrate.[6] The two solutions are sprayed together, using a double nozzle gun for specific times (msec), followed by off times (msec). Our purpose in preparing such coatings was to improve hardness, wear resistance,[7] thermal stability[8] and, specifically, to provide corrosion protection. It is well known that Ni/Cu (with the copper content about 30 wt%) alloys are highly corrosion resistant in many aggressive environments such as seawater. In order to obtain these desirable properties, many attempts have been made to plate Ni/Cu on metallic bases.[9,10] Different methods are available to deposit Ni/Cu multilayers, including: (1) vacuum techniques (vacuum evaporation, magnetron sputter deposition or molecular beam epitaxy) and (2) electrolytic deposition techniques.[1-11] However, the establishment of alternating layers by classical wet techniques is still industrially difficult. Our study, on the other hand, shows that dynamic chemical plating is a fair and easy way to deposit multilayers on the surfaces of different substrates.

Nuts & Bolts: What This Paper Means to You

Alternating multiple thin metallic layers often possess improved mechanical, magnetic or wear properties when compared to the corresponding pure metals. This has been done by vacuum deposition, among other methods. This work describes an electroplating technique to make these coatings, called dynamic chemical plating. The process is literally "spray plating," and the two metals are alternately applying by switching back-and-forth with a double nozzle spray gun. Nickel-boron/copper deposits are studied in detail here.

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Experimental

Preparation of Cu/Ni-B multilayers on steel.

The substrates used were XC18 low carbon steel samples (100 × 100 × 3 mm; 3.94 × 3.94 × 0.12 in.), mechanically polished with a silicon carbide abrasive disk (800 μm; 0.032 in.), ultrasonically cleaned in ethanol for 5 min and rinsed with doubly-distilled water. After mechanical cleaning, the samples were immersed in a dilute solution of commercial nitric acid (40%) for 5 sec to eliminate the oxides present on the surface and finally rinsed with doubly-distilled water.

Two spray modules were used independently for the alternating deposition of the Ni-B and Cu layers. Each module was integrated with an oil-free air compressor to feed compressed air to the reservoir tanks containing the reducing agent [10 g/L (1.33 oz/gal) potassium borohydride] and the corresponding metal salt (nickel or copper). The compositions were selected from our previously reported results[5-12] to obtain adherent and homogeneous Ni-B and copper films. The air pressure in each tank was independently controlled by using two individual manometers and both tanks were connected to a commercial double nozzle spray gun.** Each module was automated and controlled with software specifically developed for this purpose. The steel samples were vertically fixed at 40 cm (15.7 in.), perpendicular to the double nozzle-spray gun. The spray conditions (spray and relaxation times) were the same for both the Ni-B and Cu films and were 100 msec and 200 msec, respectively.[12]

Multilayer assemblies of 5, 10, 15 and 20 alternating layers of Ni-B and Cu were obtained on the steel substrates by using the DCP integrated modules. When the number of layers was even, the copper layer was the first deposited layer and when the number of layers was odd, the Ni-B layer was the first deposited. In both cases, the final layer was a Ni-B layer in order to avoid the attack of the multilayer assembly, because of the higher susceptibility of copper versus Ni-B to corrode when exposed to air.

The deposition process was carried out at room temperature. Taking into account the kinetic features of the copper and Ni-B deposition process by DCP as previously reported,[12] the spray times were fixed at 2.5 and 1.5 min for each copper and Ni-B individual layers, respectively, in order to obtain deposits with a thickness between 0.2 and 0.3 μm (7.9 to 11.8 μ-in.). In this way, the total plating time to obtain 5, 10, 15 and 20 Ni-B/Cu multilayers was 9.5, 20.0, 29.5 and 40.0 minutes, respectively. Because the reducing agent was the same in both cases and the deposition process stops when the spray is stopped, no rinse was carried out between the deposition of each individual film.

The properties of the as-obtained and annealed DCP films were compared to those of electrodeposited Cu/Ni films and annealed electroless Ni-P films, the latter selected as a reference. The electrodeposited films were obtained at 2.0 A/dm^2 (18.6 A/ft^2) from commercial baths, at room temperature. The copper layer was first deposited on the steel substrates from a cyanide bath [26.0 g/L (3.5 oz/gal) copper cyanide, 41.0 g/L (5.5 oz/gal) sodium cyanide, 2.0 g/L (0.27 oz/gal) sodium hydroxide and additives]. The nickel was subsequently deposited on the copper layer from a Watts-type bath [250 g/L (33.4 oz/gal) nickel sulfate, 40.0 g/L (5.3 oz/gal) nickel chloride, 30.0 g/L (4.0 oz/gal) boric acid and additives). A deposit of 20 Ni/Cu multilayers was produced with a total thickness of 5.0 μm (197 μ-in.). The electroless Ni-P films were obtained on steel substrates by immersion in a commercial medium phosphorus (*i.e.*, 5.0 to 7.0 wt%) bath*** at 90°C (194°F). The immersion time was fixed to obtain deposits with the same thickness (1.3 μm; 51 μ-in.).

Uniformity and thickness distribution

Scanning electron microscopy (SEM) was used to evaluate the uniformity and thickness of the Ni-B/Cu multilayered deposits, because of its ability to show, from cross-sections, the arrangement of the multilayers throughout the thickness of the deposit.[13] For the SEM analysis, the multifilm samples were separated from the substrate by cutting with a rotating diamond disk, embedded in Bakelite which contained a thin layer of graphite on the surface, mechanically polished with 0.05-μm alumina and finally rinsed with distilled water. The samples were then analyzed with the scanning electron microscope.

Adhesion testing

In order to evaluate the adhesion of the multilayers on the steel substrates, an adhesion test according to ASTM D3359 was carried out. The test was performed by scratching on the plated surface followed by a peeling operation using adhesive tape. The percentage of small squares still adhering to the plated surface was determined. The adhesion scale covers a range from 5B (100% adhesion) to 1B (poor adhesion, more than 60% of the deposit peeled and transferred to the tape).

Corrosion testing

The corrosion resistance was evaluated in a Q-panel salt spray chamber, according to ASTM B117. A 5% NaCl spray solution [35°C (95°F), pH 6.5 to 7.0] was focused vertically and then diffused from the top of the salt chamber in order to limit the direct projection of the NaCl solution on the samples. The backside and edges of the samples were masked in order to limit the exposed areas to the multilayer side.

Electrochemical corrosion measurements were also carried out, according to ASTM G05. The corrosion rate was determined in a 5% NaCl solution, using the classic Tafel slope method. A potentiostat-galvanostat and an electrochemical cell with a three-electrode configuration were used, with a saturated calomel electrode as the reference electrode.

Results and discussion

Morphological characterization

The SEM images shown in Fig. 1(a, b) correspond to the cross sections of the as-deposited and the annealed multilayers, respectively. In both cases, alternating, uniformly-thick Ni-B and Cu layers, observed as clear and dark layers, respectively, are seen. The layers are also easily distinguished because of their differences in thickness.

The average individual thicknesses of the Ni-B (0.15 μm; 5.9 μ-in.) and Cu films (0.39 μm; 15.4 μ-in.) were determined by increasing the magnification of the SEM cross-sectional images. The total thickness was also evaluated using several measurements performed on the SEM cross-section (Fig. 2) and the results are shown in Table 1. The value of the total thickness agreed with the expected total thickness calculated from the individual layer thicknesses. This confirmed our previously reported results,[12] indicating that the thickness was independent of the substrate and depended only on the spray conditions and the nature of the deposited layer. The effect of the substrate surface preparation was observed for the first deposited layer with a distribution reflecting the inhomogeneities in the substrate surface, fixing the growth pattern of the subsequently deposited layers.

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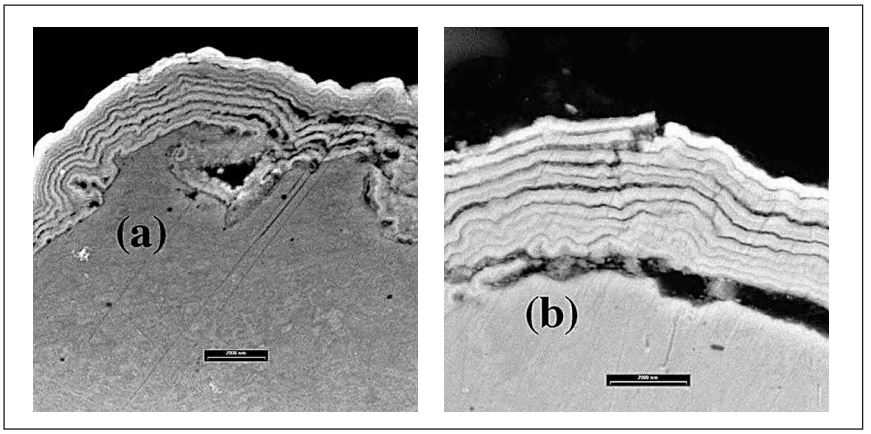

Figure 1—Cross-section observed by SEM of a 20-NiB/Cu multilayer assembly deposited by DCP: (a) as deposited; (b) annealed at 300°C (572°F) for 1 hr.

The pattern distribution of the layers was not affected by annealing, indicating the absence of intermixed layers of Cu-Ni compounds. On the other hand, annealing caused longitudinal cracking of the multilayers, as observed in Fig. 1(b). This effect was attributed to the transition of Ni-B from an amorphous to a crystalline state (Fig. 3) by thermal treatment effects and to the difference between the thermal expansion coefficient of the copper and Ni-B layers and the steel substrate. The latter induced localized mechanical stress in the deposit, thus generating cracking, fracture and discontinuities.

Adhesion testing

The adhesion performance of the Ni-B/Cu multilayers and the deposits of Ni/Cu and Ni-P on steel were all evaluated by the cross hatch adhesion test for comparison. The results are shown in Table 2. The results indicate that the poorest adhesion (Class 1B) was exhibited by the electrodeposited Ni/Cu coating. No significant differences in adhesion were observed between the Ni-P coating and the as prepared-DCP multilayers. The effect of annealing (1 hr at 300°C; 572°F) was unclear. The only effect was observed for the ten-multilayer sample where a decrease in adhesion was observed after annealing. This particular behavior may be related to the SEM cross-sectional observations that revealed the presence of cracked areas which could be more important at intermediate thicknesses.

Corrosion testing

The salt spray corrosion resistance was defined as the time to the appearance of the first pits on the exposed side. The results are shown in Fig. 4 showing the influence of the total number of layers on the corrosion resistance.

As observed in Fig. 4, the corrosion resistance of the DCP multifilms increased with the number of layers, confirming the protective properties of the multilayer deposits. The increase in the protective power of the multilayers can be associated with the increase in total thickness. In comparing these results with those obtained for electrolytic Cu/Ni multilayers and Ni-P electroless layers at equivalent thicknesses (approx. 5 μm; 197 μ-in.) a similar corrosion resistance was observed between the DCP Ni-B/Cu and the electrolytic Ni/Cu multilayers. The electroless Ni-P layer showed the poorest corrosion resistance. The observed differences could be attributed to the very compact structure of the deposits obtained by DCP or by electrodeposition. Annealing caused a decrease in corrosion resistance (from 552 to 168 hr) in the DCP 20 Ni-B/Cu multilayers, which was associated to the cracking of the assembly of layers. This is in concert with the effect of annealing on the loss of adhesion.

On the other hand, the corrosion potentials (E_{corr}) evaluated by electrochemical techniques (Table 3) show the effect of the presence of the deposited layers on the relative resistance to oxidation. As summarized in Table 3, the electrodeposited Cu-Ni multilayers had the highest value of E_{corr} while the E_{corr} value of the DCP Ni-B/Cu multilayers and the electroless Ni-P were similar. After annealing, an increase in E_{corr} for the DCP 20 Ni-B/Cu multilayers

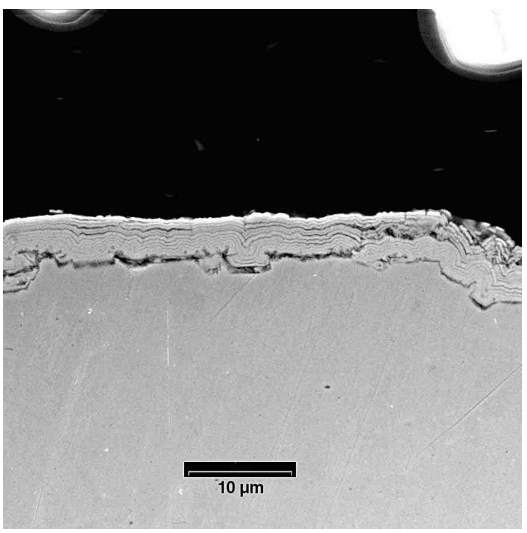

Figure 2—General cross-section observed by SEM of a 20-NiB/Cu multilayer assembly.

Table 1
Thickness of NiB/Cu multilayers with and without annealing, as evaluated by SEM cross-section observation

Total number of NiB/Cu layers	20		15		10		5	
Annealing (300°C, 1 hr)	No	Yes	No	Yes	No	Yes	No	Yes
Thickness, μm	5.1	5.7	3.5	3.9	2.5	2.7	0.95	1.05
Thickness, mils	0.20	0.22	0.14	0.15	0.10	0.11	0.04	0.04

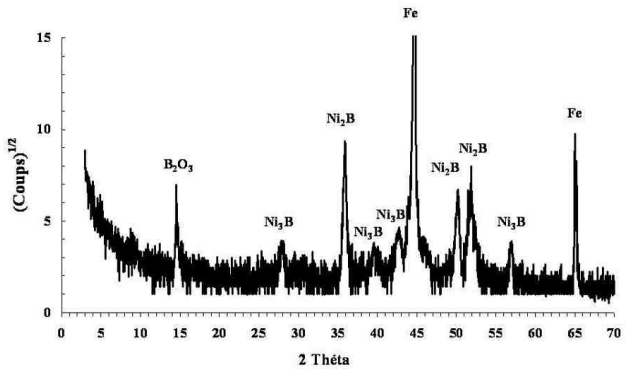

Figure 3—X-ray diffraction spectra of an annealed DCP Ni-B film.

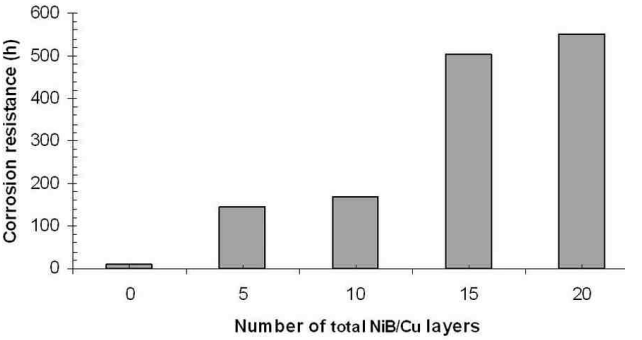

Figure 4—Corrosion resistance of DCP NiB/Cu multilayers in 5% NaCl.

was observed, probably related to the structural changes in Ni-B by thermal effects that were known to have a positive effect on the corrosion resistance of electroless layers.[14] The results indicate the protective effect of the deposits, because a more positive value of E_{corr} was observed in all cases, as compared with the substrate.

Conclusion

The results show that DCP can be used to obtain Ni-B/Cu multilayers on steel, with controlled thicknesses, using two different double nozzle spray modules, at room temperature. The multilayers thus obtained were homogeneously distributed on the substrate, uniform in thickness and had excellent adhesion properties. The corrosion resistance of the DCP multilayers was similar to that of electrodeposited Ni/Cu multilayers and superior to that of electroless deposits. Therefore, DCP is a more attractive technique than other wet methods because of the lengthy preparation steps involved. The combination of properties (good corrosion resistance and adhesion) of the deposits obtained makes DCP an excellent technique for preparing protective coatings where corrosion resistance and adhesion are required.

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Table 2
Adhesion results for different multifilms

Deposit tested	Total thickness, μm (mils)	Adhesion Classification
20 Ni-B/Cu DCP	5.1 (0.20)	5B-4B
20 Ni-B/Cu DCP annealed	5.7 (0.22)	5B
15 Ni-B/Cu DCP	3.5 (0.14)	5B
15 Ni-B/Cu DCP annealed	3.9 (0.15)	5B
10 Ni-B/Cu DCP	2.5 (0.10)	5B-4B
10 Ni-B/Cu DCP annealed	2.7 (0.11)	3B
5 Ni-B/Cu DCP	0.95 (0.04)	5B
5 Ni-B/Cu DCP annealed	1.05 (0.04)	5B
20 Ni/Cu Electrolytic	5.0 (0.20)	1B
Ni-P Electroless	1.3 (0.05)	5B

Table 3
Corrosion resistance of multilayers in 5% NaCl

Sample	Thickness, μm (mil)	Salt Spray Corrosion Resistance (hr)	Corrosion potential V_{SCE}
DCP 20 Ni-B/Cu multilayer	5.1 (0.20)	552	- 0.365
Annealed DCP 20 Ni-B/Cu multilayer	5.7 (0.22)	168	- 0.218
Electrolytic 20 Ni/Cu multilayer	5.0 (0.20)	528	- 0.120
Electroless Ni-P	5.0/1.3(0.20/ 0.05)	185/48	- 0.349
Substrate	---	10	- 0.565

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