Single-bath Electrodeposition of Chromium-Nickel Compositionally Modulated Multilayers (CMM) From a Trivalent Chromium Bath

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Electrodeposition of Cr-Ni compositionally modulated multilayers was investigated. It was realized using the single-bath technique under galvanostatic conditions. The structure was characterized by scanning electron microscopy (SEM) and optical microscopy. Deposit composition was determined by energy dispersive X-ray (EDX) analysis. Cr-Ni multilayers with distinct sublayers can be produced by single-bath electrodeposition. Nickel and chromium layer thicknesses are kept equal and vary from 2 μ m to 0.3 μ m. Nickel sublayers are pure, while chromium sublayers contain a small amount of nickel (< 10 wt pct). These deposits should exhibit improved characteristics compared with chromium without nickel deposits, such as corrosion and wear resistance.

Multilayer films or compositionally modulated multilayers (CMM) consist of alternating layers of two different metals or alloys. Compared with pure metals, such new materials seem to have unusual and enhanced mechanical, electrical, optical and/or magnetic properties when sublayer thicknesses are in the nanometer range. For instance, coppernickel CMM are shown to exhibit greatly enhanced tensile strength for copper layer thickness of less than 0.4 μ m.¹ Ag-Pd multilayers composed of thin Pd-rich layers alternated with thick Ag-rich layers offer the high corrosion resistance of Pd combined with the low electrical resistance and relatively low cost of Ag.²

When ferromagnetic metal/non-magnetic metal superlattices are electrodeposited and individual layers have thicknesses as small as 10 Å or less, an interesting phenomenon can be observed at room temperature: giant magnetoresistance (GMR).^{3,4} When a magnetic field is applied to such a multilayer, its electrical resistivity varies. With no applied magnetic field, an anti-ferromagnetic exchange coupling across the non-magnetic layers means that the magnetization vectors of the magnetic layers are anti-parallel to each other. In a sufficiently large applied field, however, they become parallel. Because the resistance of the parallel configuration is smaller than that of the anti-parallel configuration, the multilayer resistance decreases on application of a magnetic field. These nanostructured materials could be incorporated in magnetic field sensors for magnetic data recording or for monitoring the positions of machine components, for example.5

At present, CMM are essentially elaborated by vacuum deposition techniques, such as evaporation, molecular beam epitaxy and sputtering. Technological difficulties and the cost of such processes are responsible for the development of electrolytic deposition techniques. They are cheaper and well-established industrial processes. They need lower temperature, thus the risk of interdiffusion is low. They offer greater choice of shape and size of the substrate. Besides, higher production rates are obtained.

There are two ways to produce CMM by electrodeposition-the dual-bath technique (DBT) and the single-bath technique (SBT).^{6,7} The DBT involves the use of two different plating baths. The substrate is moved successively from one bath to the other. Layers of pure metals are deposited, but this process has some important drawbacks: (1) it is often accompanied by different phenomena, such as dissolution and reaction displacement; (2) rinsing and depassivation tanks are indispensable to avoid outside pollution and oxidation. For the SBT, only one bath, which contains the two metals salts, is used. The CMM is created by changing the current density or cathodic potential, by controlling the diffusion or by a combination of these different possibilities. This process presents electrochemical limitations for the two-metals choice. The deposition current density or potential of both components must be sufficiently different to allow separate electrodeposition. Alloying of the less noble metal with the other is almost inevitable. Pure layers of the more noble metal can be deposited, while the less noble metal layers will always contain a certain amount of the other.

The SBT offers some advantages, however, compared with the DBT. They are briefly listed in Table 1.² For different reasons, it was decided to work with this technique. The chromium-nickel system was chosen because nickel and chromium coatings have interesting properties.⁸⁻¹⁰ Also, the current study is the first to employ SBT for electrodeposition of a Cr-Ni layered structure.

Experimental Procedure

A concentrated trivalent chromium (Cr⁺³) solution was used. This bath was obtained by reduction of chromic acid by methanol in the presence of hydrochloric acid.¹¹ Its concentration was about 60 g/L, or 1.2 mol/L. A low pH, near zero, was necessary for bath stability. The working temperature was controlled at 50 ± 1 °C. Coatings were deposited on a steel cylinder with a diameter of 1 cm and a length of 4 cm. Steel cathodes were encircled by a shaped cylinder mesh anode of



Fig. 1—Effect of the first 5-10 µm nickel layer.



Fig. 2—Polarization curve of the nickel and trivalent chromium baths. Scan rate 1 mV/sec.



Fig. 3-Square-wave double-pulse current waveform.



heat treatments were carried out in an argon atmosphere. The cylinders were air-cooled and were cut and polished. The structure was characterized by optical microscopy and SEM. The microhardness was then measured. Thus, the structure and hardness evolution of Cr-Ni multilayer was observed as a function of the heat treatment temperature.

Fig. 4—EDX analysis of Cr sublayers deposited at 80 A/dm².

platinized titanium. A PVC cell 5 dm³ in capacity was used. At 80 A/dm², the chromium deposition rate was $3.5 \,\mu$ m/min, corresponding to a current efficiency for chromium of 28.4 percent. Thick, dense deposits were plated. A small amount of nickel (0.2 mol/L of NiSO₄ \cdot 6H₂O) was added to the concentrated solution of trivalent chromium.

Nickel is nobler than chromium (standard potentials of both systems: $E_0[Ni^{+2}/Ni] = -250 \text{ mV/SHE} > \hat{E}_0[Cr^{+3}/Cr] =$ -740 mV/SHE).¹² At a sufficiently low cathodic potential, the reduction rate of nickel is slow and controlled by diffusion, while chromium is deposited rapidly. At a higher polarization potential, only nickel is reduced.¹³ Polarization measure-

Results & Discussion

Chromium & Nickel Kinetic Analysis

The polarization curve is shown in Fig. 2. Chromium reduction begins when cathodic potential is above about 1.6 V vs. SCE (absolute value). Below a cathodic potential of 1.6 V vs. SCE, pure nickel is reduced. When the current density is lower than 45 A/dm² (absolute value), pure nickel layers are expected, while a rich chromium alloy is deposited with higher current density.¹⁵ The fabrication of Cr-Ni CMM was achieved by using a square-wave, double-pulse current (Fig.

ments were carried out at a scan rate of 1 mV/ sec. A standard saturated calomel electrode (SCE) was used as a reference.

The trivalent chromium bath has low throwing and covering power. Chromium deposits are very sensitive to structural defaults of the substrate. Each pit on the surface has a corresponding transverse crack. If a first nickel layer is plated on the surface, it could reduce structural asperities and decrease the quantity of transverse cracks. Before each Cr-Ni CMM deposition, therefore, a 5-10 µm nickel coating was deposited in the same bath. In Fig. 1, the effect of this first nickel layer can be observed (nickel sublayers are the lighter). The nickel fills the hole on the substrate surface.

Optical microscopy and scanning electron microscopy (SEM) were used to characterize the structure of the Cr-Ni multilayers. The cylinder samples were cut across midlength and polished in an automatic metallographic polishing set-up.^a Energy dispersive X-ray analysis (EDX) was used to determinate the deposits chemical composition in conjunction with SEM observations of the coatings.

The Cr-Ni CMM microhardness measurements were carried out with a Vickers indenter at a load of 100 g on cross-sections. The hardness of chromium deposits in a trivalent chromium bath, without nickel, could be increased up to 1700-1900 HV₁₀₀ by an appropriate heat treatment at 300-500 °C for 2 hr.14 Two multilayers with different sublayer thicknesses were heated for 2 hr at a temperature range of 200 to 700 °C. These different

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Advantages	of	SBT	Compared	with DBT

	SBT	DBT
Minimum layer thickness	< 1 nm	~25 nm
Wastewater generation	low	high
Process rate	medium	low

3). The current density was switched between 40 and 80 A/ dm^2 to form, respectively, pure nickel layers and layers of chromium with a small amount of nickel (< 10 wt pct by EDX analysis [Fig. 4]). The working conditions are listed in Table 2. The deposition rate of nickel was 10 times lower than for chromium.



Fig. 5—SEM photos of Cr-Ni CMM deposits obtained from the single-bath process under galvanostatic conditions: (a) $e_{Ni} = e_{Cr} = 2 \ \mu m$; (b) $e_{Ni} = e_{Cr} = 1 \ \mu m$, $t_{Ni} = 100 \ sec = 10 \ t_{Cr}^{-1}$; (c) $e_{Ni} = e_{Cr} = 0.5 \ \mu m$, $t_{Ni} = 50 \ sec = 10 \ t_{Cr}^{-1}$

Table 2
Working Conditions

	Current Density A/dm ²	Deposition Rate µm/min
Nickel	40	0.3
Chromium	80	3.5

Cr-Ni Multilayer Microstructure

The thickness of rich-chromium and nickel sublayers were kept equal. Four different Cr-Ni CMM were realized with nickel and rich-chromium sublayer plating times, t_{Ni} and t_{Cr} , equal, respectively, to 200 and 20 sec; 100 and 10 sec; 50 and 5 sec; 30 and 3 sec (Figs. 5 and 6). These sublayer plating times should produce sublayer thicknesses, e_{Ni} ($\approx e_{Cr}$), respectively equal to 2, 1, 0.5 and 0.3 µm. The four different cycles ($t_{Ni} + t_{Cr}$) were repeated until the total coatings thickness was 50 µm. The first nickel layer of 5-10 µm can be seen in each picture of Figs. 5 and 6. Good regularity of the multilayers can be seen, as well as good adhesion between rich-chromium and nickel layers.

Trivalent chromium deposits are often crossed by cracks. The nickel layers insertion, in a chromium coating, clearly reduces the macrocrack concentration, whatever the sublayer thicknesses may be. They will exhibit higher corrosion resistance than chromium deposits from a trivalent chromium bath without nickel. This property is all the more important inasmuch as the nickel sublayers are thick. The quantity of cracks decreases with decreasing thickness of rich-chromium and nickel sublayers, as can be seen in Fig. 5, but in the



Fig. 6—SEM photos of Cr-Ni CMM with sublayer thickness of 0.3 $\mu m (t_{_{Ni}} = 30 \text{ sec} = 10 t_{_{CV}})$ for two different magnifications.



Fig. 7—Microhardness evolution of Cr-Ni multilayers with increasing sublayer thickness ($e_{_{Ni}} = e_{_{Cr}}$).



Fig. 8—Microstructure evolution of Cr-Ni multilayers with sublayer thickness of 0.5 μ m after heat treatment for 2 hr, showing structure preservation: (a) 200 °C; (b) 400 °C.

same way, crack length increases. For instance, in Fig. 5a ($e_{Ni} = e_{Cr} = 2 \mu m$), the cracks measure on average 6 μm and in Fig. 5c ($e_{Ni} = e_{Cr} = 0.5 \mu m$), they reach a length of 20 μm . The cracks do not cross the whole deposit; they are microcracked. In Fig. 6a ($e_{Ni} = e_{Cr} = 0.3 \mu m$), a large area with only one crack can be observed. Also, at higher magnification (Fig. 6b), distinct and continuous sublayers can be seen.

Cr-Ni Multilayer Microhardness

The hardness of Cr-Ni multilayers decreases with increasing thickness of rich-chromium and nickel sublayers, as shown in Fig. 7. On the one hand, the maximal value, about 800 HV₁₀₀, is twice the hardness of nickel deposits, 400 HV₁₀₀. On the



Fig. 9—Microstructure evolution of Cr-Ni multilayers with sublayer thickness of 0.5 μ m after heat treatment for 2 hr, showing chromium and nickel diffusion: (a) 600 °C; (b) 700 °C.



Fig. 10—Microhardness evolution of Cr-Ni multilayers for two different sublayer thicknesses (2 and 0.5 μ m), with increasing heat treatment temperature.

other hand, it is lower than that of chromium without nickel coatings: 1000 HV_{100} . The wear resistance is all the more important, as the sublayers are thin. A compromise should be reached between hardness and corrosion wear, in view of their opposite evolutions with sublayer thickness. A greater microhardness could perhaps be obtained if rich-chromium sublayers were thicker than those of nickel.

Heat Treatment

The effect of heat treatment was studied for two different Cr-Ni CMM with sublayer thicknesses of 2 and 0.5 μ m. The coatings had a total thickness of 45 μ m. They were heated for

2 hr at 200 to 700 °C in an argon atmosphere to avoid oxidation. In Figs. 8 and 9, the evolution of the morphology can be observed for the thinner sublayers (0.5μ m). From 600 °C upward (Fig. 9), the multilayer structure begins disappearing because of nickel and chromium diffusion, and the first nickel layer diffuses towards the substrate. During each heat treatment, the cracks of the coating grow wider and the substrate becomes oxidized. These events are common to every heat-treated coating. In Fig. 10, it can be seen that the increase of heat treatment temperature in the range 200-500 °C caused an increase of hardness up to 1000 HV₁₀₀ for the thinner structure. The microhardness approaches that of nonheat-treated chromium deposits. Their wear resistance is improved to the detriment of their corrosion resistance.

Conclusions

This study demonstrates that the single-bath electrodeposition technique can result in trivalent chromium-nickel multilayers with distinct and continuous sublayers. The insertion of nickel improves the trivalent chromium coating characteristics. Indeed, the decrease of cracks will induce improvement of corrosion wear. The alternation of hard (chromium) and soft (nickel) sublayers can enhance the wear properties resulting from the lubricating effect of the soft sublayers between the hard sublayers.

The Cr-Ni multilayer microhardness increases after an appropriate heat treatment (T < 500 °C). Chromium coatings obtained in a standard chromic acid bath do not have this property—their microhardness decreases after any heat treatment.

It must be noted that all Cr-Ni multilayer properties depend on bath composition (organic additives, Cr^{3+} and Ni^{2+} concentrations); electrodeposition temperature; current density and/ or cathodic potentials; sublayer thicknesses; the ratio of nickel sublayer thickness to that of rich-chromium; and total thickness.

Future investigations will comprise study of corrosion and wear resistance of Cr-Ni multilayers as a function of the previously mentioned parameters. Since GMR is such an interesting and potentially useful phenomenon, we will investigate whether this deposition technique could be used to grow materials showing significant GMR.

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References

- 1. D. Tench & J. White, Metal Trans. A, 15A, 2039 (1984).
- U. Cohen, F.B. Koch & R. Sard, J. Electrochem. Soc., 130(10), 1987 (1983).
- 3. M.N. Baibich et al., Phys. Rev. Lett., 61, 2472 (1988).
- 4. W. Schwarzacher & D.S. Lashmore, *Trans. IEEE Mag.*, **32**(4), 3133 (1996).
- 5. R.L. White, Trans. IEEE Mag., 30(2), 346 (1996).
- M. Eis Benzon, P. Leisner, C.N. Panagopoulos & V.D. Papachristos, in Dépôts Métalliques avec Particules, Recueil Conferences Acts, ENSMSE (1996).
- 7. J. Electrochem. Soc., 141(1), 230 (1994).
- Y. Bade, Techniques de l'Ingénieur, Traité Matériaux Métalliques, M5, M1610
- P. Benaben, Techniques de l'Ingénieur, Traité Matériaux Métalliques, M5, M1615
- 10. P. Morisset, Chromage dur et décoratif, CETIM, Senlis (1993).
- 11. P. Benaben, Plat. and Surf. Fin., 76, 60 (1989).
- M. Pourbaix, Atlas d'équilibres électrochimiques à 25 °C, Gauthier-Villars & Cie, Eds., Paris (1963).
- Chun-Chen Yang & Huk Y. Cheh, J. Electrochem. Soc., 142(9), 3034 (1995).
- F. Durut & P. Benaben, *Characterization of Trivalent Chromium Deposits Structure after Hardening Thermal Treatment*, Final Report on the Summer Research Project funded by AESF (1996).
- A. Rousseau, Conception, élaboration et propriétés de dépôts multicouches chrome/nickel, DEA, ENSMSE-INPG, 1997.

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