Corrosion Resistance Of Velour Cu/Ni Electroplates

L. Valentelis, L. Grinceviciene, D. Bucinskiene & M. Gladkovas

Corrosion performance of silvery matte nickel coatings of different thicknesses, single and with matte and velour copper undercoatings, was investigated by the Corrodkote method and compared with the resistance of matte nickel coatings. It was shown that the greatest corrosion resistance is obtained when velour copper and silvery matte nickel deposits are used.

Table 1
Composition of Copper & Nickel Plating Solutions & Operating Conditions

Solution	Composition		Operating Parameter
Matte nickel	$NiSO_4 \cdot 7H_2O$	180 g/L	Temp: 50 °C
	NaCl	50 g/L	i_c: 2 or 4 A/dm^2
	H_3BO_3	30 g/L	pH 3.5 to 5.0
			Air agitation
Silvery matte Ni	$NiSO_4 \cdot 7H_2O$	180 g/L	Temp: 50 °C
	NaCl	50 g/L	i_c: 2 or 4 A/dm^2
	H_3BO_3	30 g/L	pH 3.0 to 5.5
	Limeda NIS-3	6 mL/L	Air agitation
	Limeda NIS-4	0.4 g/L	
Matte copper	$CuSO_4 \cdot 5H_2O$	180 g/L	Temp: 20 °C
	H_2SO_4	120 g/L	i_c: 2-4 A/dm^2
			Air agitation
Velour copper	$CuSO_4 \cdot 5H_2O$	180 g/L	Temp: 20 °C
	H_2SO_4	120 g/L	i_c: 2-4 A/dm^2
	NaCl	0.02 g/L	Air agitation
	Ethylene glycol	0.5 mL/L	
	Limeda NIA*	0.06 mL/L	

** An organic polymer*

Decorative matte coatings (known as velour) have been utilized recently to replace bright coatings. One of the simplest and cheapest ways to produce velour nickel is by epitaxic growth on a velour copper electroplate.[1,2] In earlier studies,[3-6] the nature of velour has been investigated and the physical-mechanical properties of the coatings have been determined. Data on corrosion resistance of velour electrodeposits, however, has not been available.

It is known that nickel electroplate corrosion resistance depends on the structure and on the admixtures contained.[7,8] Inclusion of sulfur in the coating has an especially strong effect on nickel corrosion resistance.[9,10] It has been shown that velour coatings are harder, less stressed, with larger crystallites, and contain an amount of sulfur different from common nickel.[3,6] It would be reasonable, therefore, to expect that the corrosion resistance of velour nickel coatings is different from that of common nickel coatings. The aim of this study was to determine the corrosion resistance of velour nickel coatings, with and without copper underlayers, and to compare it with the corrosion resistance of common nickel coatings.

Experimental Procedure

All coatings for the corrosion tests were obtained from solutions created at the Institute of Chemistry, Vilnius, Lithuania. The solution compositions are listed in Table 1. Matte copper (Cu_m), matte nickel (Ni_m), velour copper (Cu_v), and silvery matte nickel (Ni_s) coatings were deposited from solutions of the same name. Velour nickel coatings were obtained by deposition of a silvery matte nickel coating on a velour copper layer. The coatings were deposited on carbon steel panels, 10 x 5 x 0.1 cm. The steel was given a preliminary coating of a 2-3 µm-thick nickel strike on specimens on which a copper deposit was applied. Five specimens with coatings of the same composition and thickness were prepared.

The corrosion resistance of the coatings was determined by the Corrodkote method.[11] Specimens with Corrodkote paste were exposed in a humidity chamber in which a relative humidity of 85 ±5 percent and a temperature of 38 ±1 °C were maintained. The duration of a cycle was 16 hr. The degree of corrosion damage, in terms of a rating number, was assessed by the standard method,[12] according to the specimen surface area occupied by red rust. The rating numbers and the corresponding surface areas damaged by corrosion are listed in Table 2.

Results & Discussion

The corrosion resistance of nickel coatings without a copper underlayer is not great. The corrosion rating number of specimens with single 13-µm-thick coatings declines sharply as the Corrodkote cycle number increases; the evaluation "0" is obtained after 20 cycles. The same decline occurs when either matte nickel (Fig. 1) or silvery matte nickel (Fig. 2) is used. That means the additives Limeda NIS-3, an aromatic sulfo compound, and Limeda NIS-4, a non-saturated organic compound, added to the nickel plating bath to obtain a silvery effect, do not influence the corrosion resistance of a single nickel coating.

Adding a copper deposit as an undercoating to a matte nickel electroplate strongly improves coating protective quality. For example, the rating number of a Cu_m10 µm/Ni_m9 µm coating after 20 Corrodkote cycles is about 4, and such coatings pass 64-70 cycles (Fig. 1). Comparison of the rating

Table 2
Rating Numbers
& Corresponding Surface Areas
Damaged by Corrosion

Rating Number	Surface Area, %
10	Without corrosion
9	$0 < S \leq 0.1$
8	$0.1 < S \leq 0.25$
7	$0.25 < S \leq 0.5$
6	$0.5 < S \leq 1.0$
5	$1.0 < S \leq 2.5$
4	$2.5 < S \leq 5$
3	$5 < S \leq 10$
2	$10 < S \leq 25$
1	$25 < S \leq 50$
0	$S > 50$

numbers for Cu_m10 µm/Ni_m9 (Fig. 1) and Cu_v10 µm/Ni_m9 µm (Fig.2) coatings shows that the corrosion performance of those coatings is very similar. The latter finding means that changing a matte copper layer existing under a matte nickel deposit to velour copper does not change the corrosion resistance of a Cu/Ni coating. Rating number curves for coatings containing a 9-µm-thick matte nickel layer deposited at 2 and 4 A/dm^2 are very close (Fig. 1). This finding shows that matte nickel deposition current density has no influence on coating corrosion resistance.

An especially great improvement in Cu/Ni coating corrosion performance is observed when velour copper and silvery matte nickel deposits (*i.e.*, velour nickel coatings) are used. The corrosion rating numbers of velour nickel coatings consisting of 10-µm-thick velour copper and 9-µm silvery matte nickel, beginning at the fifth cycle, are 2-3 rating units higher than coatings containing matte or velour copper and matte nickel of the same thickness (Fig. 2). The advantage that velour coatings have over matte coatings increases with increasing thickness of the copper or nickel layer. When copper and nickel layer thickness is 15 and 13 µm, respectively, the difference in rating numbers of velour and matte coatings is about 4 units (Fig. 3, curves Cu_m15 µm/Ni_m13 µm and Cu_v15 µm/Ni_s13 µm).

The cathodic current density of silvery matte nickel coating deposition, like matte nickel deposition, has no influence on the corrosion resistance (see Fig. 2, Cu_v10 µm/Ni_s9 µm and Cuv10 µm/Ni_s9 µm (4 A/dm^2) of coating rating numbers.

Comparison of the corrosion rating of coating Cu_v10 µm/Ni_s9 µm (Fig. 2) with the corrosion ratings of coatings Cu_v15 µm/Ni_s13 µm and Cu_v15µm/Ni_s18 µm shows that increasing velour copper and silvery matte nickel layer thickness improves the corrosion performance of coatings. The rating

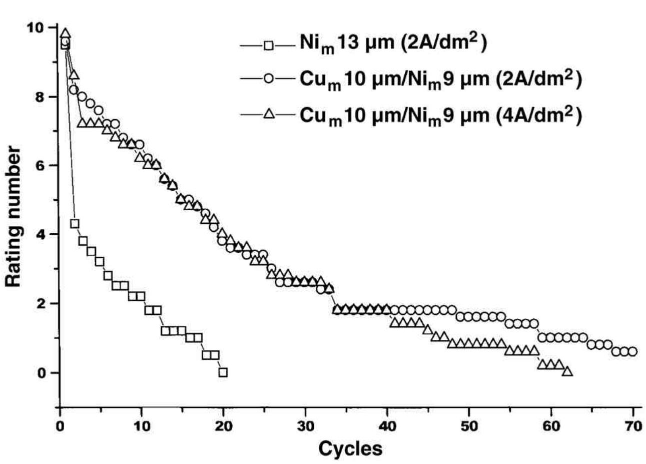

Fig. 1—Corrosion performance of matte nickel and Cu/Ni coatings consisting of 10 µm copper and 9 µm nickel layers.

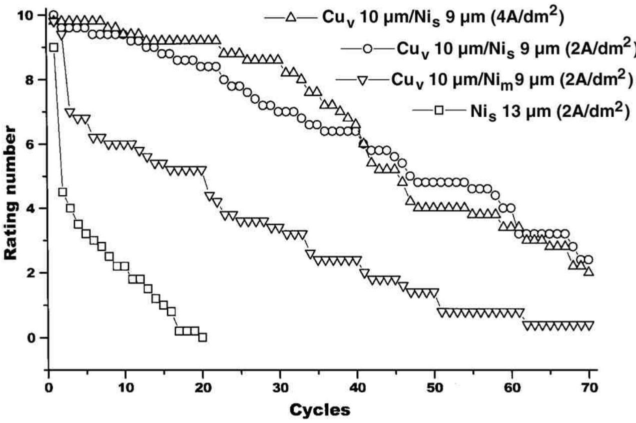

Fig. 2—Corrosion performance of silvery matte nickel and velour Cu/Ni coatings consisting of 15 µm copper and 13 µm nickel layers.

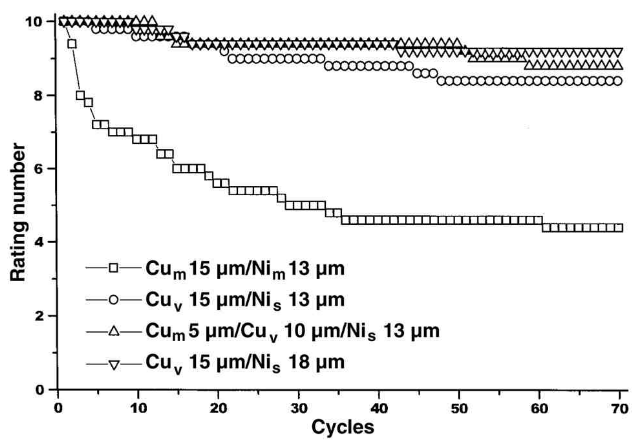

Fig. 3—Corrosion performance of matte and velour Cu/Ni coatings containing 15 µm copper and 13-18 µm nickel layers. Cathodic current density for the nickel layers was 2 A/dm^2.

number of coating Cu_v15 µm/Ni_s13 µm, during 70 Corrodkote cycles, did not decline below 8.2, which means that the specimen surface area damaged by corrosion is just slightly more than 0.1 percent. A coating containing a silvery matte nickel layer of 18 µm thickness keeps its rating number of 9.2 after 70 cycles (*i.e.*, corrosion has damaged less than 0.1 percent of the coating surface area). Good corrosion resistance is demonstrated by a coating in which the copper layer is composed of both matte and velour deposits (*i.e.*, coating Cu_m5 µm/Cu_v10 µm/Ni_s13 µm). That coating withstood corrosion damage for 12 Corrodkote cycles.

From the results, it follows that silvery matte nickel coatings, deposited on the velour copper layer from a solution containing the special additives Limeda NIS-3 and Limeda NIS-4, not only have a decorative appearance, but also are highly corrosion resistant. Velour nickel coatings have an increased corrosion resistance apparently because their structure is very different from that of matte nickel. Common nickel coatings are formed of rhombic twins, while silvery matte nickel coatings are composed of hemispherically shaped aggregates of small crystallites.[4] That type of crystal shape forms, usually, when there is burdened growth of crystallites. The burdening in this instance is caused by adsorption of additives present in the plating solution.

Conclusions

A single silvery matte nickel coating has the same corrosion performance as a matte nickel coating, and the corrosion resistance is not great. A matte or velour copper layer under a matte nickel deposit improves the corrosion performance of a coating. The highest corrosion resistance is achieved when velour copper and silvery matte nickel coatings are used. The effect of velour on coating corrosion performance increases with increasing coating thickness.

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