

Multi-Layered Ni in Ni-Cr Coating System for High Decorative and Corrosion Resistance

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In an attempt to replace the traditional Cu-Ni-Cr coating, which is commonly used for decorative and corrosion-resistance purposes, a multi-layered Ni-Cr coating process and its additives have been developed by Wuhan Research Institute of Materials Protection (WHRIMP) in Wuhan, China. To assess its effectiveness as a corrosion resistance coating, the new process and its additives have been tested both in Korea Institute of Industrial Technology (KITECH), Korea, and WHRIMP, China.

The traditional Cu-Ni-Cr coating has been known for some shortcomings. For the Cu sub-layer coating, a cyanide bath is used, which is hazardous to humans and the environment. The process of Cu-Ni-Cr coating has low deposition efficiency. When pores exist on the coating layer, the Cu-Ni-Cr layer tends to cause accelerated corrosion of the base metal, which is believed to be due to the galvanic current between the coating layer and the substrate.

The testing of the multi-layered Ni-Cr coating process with its additives was performed in a pilot plating line in KITECH and in Electroplating Lab of WHRIMP. The effectiveness of the additives in aiding the coating process, structure and thickness of the coating layer, surface morphology and topography, and effectiveness of the coating layers in corrosion protection have been the major test items.

Results show that the multi-layered Ni-Cr coating is superior to the traditional Cu-Ni-Cr in protecting against corrosion of the metal substrate. The results of the "copper-accelerated acetic acid salt spray" (CASS) test, per ISO 3770, showed no sign of corrosion up to 134 hours.

Keywords: Ni-Cr coating, Multi-layered nickel, Plating, Micro-pores, Chromium coating, CASS test

1. INTRODUCTION

1.1 Copper-nickel-chromium system

An improvement in the decorative and corrosion resistance coating has been made by depositing copper-nickel-chromium layer since the discovery of the corrosion mechanism of bright nickel-chromium layer.^(1,2)

However, there exist three principle shortcomings in the conventional copper-nickel-chromium plating. Firstly, environmental pollution is unavoidable in the process of plating copper sub-layer through copper cyanide bath. Secondly, copper-nickel-chromium system provides a sort of cathodic protection to Fe-substrate. This system may accelerate corrosion rate of the substrate instead of protecting it once porosity or crack was induced on the coating during the production or in service. Thirdly, deposition efficiency of copper is low; but the high degree protection of substrate with copper-nickel-chromium system increases with increasing thickness of the coating. These features further increased the processing time and production cost, thereby reducing the productivity. Moreover, the coating with cracks or pores could not provide a sufficient protection of the substrate under severe conditions, even though its thickness is very great.

1.2 Multi-layered nickel systems

As alternative coating systems, multi-layered nickel systems were developed⁽³⁻⁹⁾, which eliminates the cyanide process for the plating copper. The multi-layered nickel may be either double-layer coatings (semi-bright nickel + bright nickel) or triple-layer coatings (semi-bright nickel + high-sulfur nickel + bright nickel). In the latter system, a special thin layer of high-sulfur nickel is deposited between the semi-bright nickel and the bright nickel.

It has been also reported^(1,10,11) that a very considerable improvement in the corrosion-resistance of multi-layered nickel and chromium coating could be obtained by depositing the chromium with a controlled microporous structure where chromium layer has dispersed micro-pores or micro-cracks. A lot of micro-sized pores or cracks in chromium layer can spread the corrosion current, resulting in a very low current density per unit surface area, and thus a decreased corrosion rate. Such a protective measure is referred to as "a protection by dispersion of corrosion."^(8,9) A schematic diagram of the multi-layered nickel and chromium coating is shown in Fig. 1.

The total coating thickness of this multi-layered structure can be greatly reduced, owing to excellent corrosion resistance attributed to the combinative effect

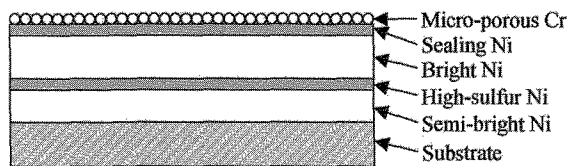


Fig. 1 A schematic of a multi-layer Ni-Cr coating with triple-layer nickel and a top layer of chromium with micro-pores.

of a sacrifice of bright nickel layer and a dispersion of corrosion by chromium layer. The excellent decorative property lies in the special additive containing special intermediates in the bath, which have high leveling capacity and great throwing power during plating.

The motivation for the present research was to estimate the corrosion resistance of those products and their micro-structural differences. It was also of interest to see whether a great quantity of micro-pores or micro-cracks could be introduced in chromium layer by using those additives made by Wuhan Research Institute of Materials Protection (WHRIMP) in Wuhan, China..

2. EXPERIMENTAL PROCEDURE

Plating was conducted on to three different substrates - carbon steel (C: 0.45%), copper and aluminum, each having a dimension of 100mm in length, 50mm in width and 1mm in thickness. Prior to plating, specimens were prepared through series of cleaning processes including ultrasonic cleaning, hot water cleaning (50°C~60°C), cathodic electrolytic degreasing, anodic electrolytic degreasing, two-stage countercurrent rinsing, acid dipping, and three-stage countercurrent rinsing. Double layered nickel consisting of semi-bright nickel and bright nickel was deposited with and without sealing-nickel layer, followed by chromium deposition over it, in order to explore the effect of sealing nickel on the corrosion resistance. Substrate for double layered nickel was carbon steel (C: 0.45%). Triple layered nickel made up of semi-bright nickel, high-sulfur nickel and bright nickel were plated on copper and aluminum substrates with sealing nickel and chromium layer.

The additive agents developed by WHRIMP were selected for the present research. The composition of bathes and plating condition including pH, Temperature (T) and current density (D_K), were exhibited in table I.

Appearance of plated surface was evaluated by visual examination. Coatings thickness of overall nickel layers as well as chromium layer was determined by optical microscopy. To examine the growth morphology of semi-bright nickel, bright nickel and sealing nickel during the plating, the cross section of the coatings were etched in a solution of 50 vol.% nitric acid and 50 vol.% acetic acid at room temperature.⁽¹²⁾ Electrode potential difference of individual layer was measured by using a thickness-potential of multi-layer nickel plating tester (model; DJH-D/E).⁽¹³⁾ Micro-pores or micro-cracks on the plane surface of chromium layer was observed by M-type microscope and their quantity was determined according to ISO 1456⁽¹²⁻¹⁴⁾ by using a computer-aided Numeric Surface Pattern Treating System. Adhesion of coatings was evaluated by either the file test or the thermal shock test specified in ISO 2819-1.⁽¹⁵⁾

Copper-accelerated acetic acid salt spray (CASS) test in accordance with ISO 3770⁽¹⁶⁾ using a salt spray tester (model 12L-ISO) was conducted to determine corrosion resistance of plated specimens.

Table I Composition of bathes and operation conditions.

Type	Composition of bathes	Operation conditions
Semi-bright Ni	nickel sulfate 250~300 g/L nickel chloride 40~50 g/L boric acid 40~50 g/L Wetting agent 1~2 ml/L Softening agent 3~4 ml/L Brightening 1.5~2.5 ml/L Adhesion agent 4~6 ml/L	pH 3.8~4.2 T 50~60°C D_K 2~6A/dm ²
High-sulfur Ni	nickel sulfate 250~300 g/L nickel chloride 35~40 g/L boric acid 35~40 g/L Wetting agent 1~2 ml/L starting agent 8~10 ml/L	pH 3.8~4.2 T 45~55°C D_K 2~3A/dm ²
Bright Ni	nickel sulfate 250~300 g/L nickel chloride 40~50 g/L boric acid 40~50 g/L Wetting agent 1~2ml/L Brightening 0.8~1ml/L Softening agent 8~10ml/L	pH 3.8~4.2 T 50~60°C D_K 2~6A/dm ²
Micro-porous Ni (sealing Ni)	nickel sulfate 250~300 g/L nickel chloride 60~70 g/L boric acid 35~45 g/L Brightening 0.5~1.0ml/L Softening agent 8~12ml/L Emulsion 10~15ml/L Dispersing agent 4~6ml/L Wetting agent 1~2ml/L	pH 3.8~4.2 T 50~60°C D_K 2~5A/dm ²
Chromium	CrO ₃ 250~300 g/L SO ₄ ²⁻ 2.5~3.0 g/L Cr ³⁺ 2~4 g/L	T 50~55°C D_K 15~20A/dm ²

3. RESULTS AND DISCUSSIONS

3.1 Microstructure of multi-layered nickel

Fig. 2 illustrates the metallographic structures of semi-bright nickel after etching, produced by using the additives of WHRIMP.

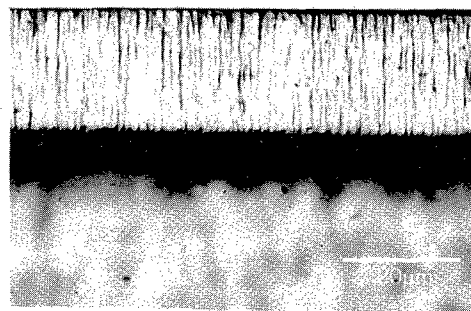


Fig. 2 Micrograph of semi-bright nickel after etching.

The microstructure of semi-bright nickel layer was an array of closely packed columns nearly perpendicular to the coating/substrate interface which agreed well with that in literature.⁽⁶⁾ The columnar grain morphology is known to exhibit a good adherence to the substrate.

However, the grains appeared to be less bonded to each other in the lateral direction.

The metallographic structures of bright nickel after etching are shown in Fig. 3. The metallography of bright nickel was different from that of semi-bright nickel and exhibited layered-structural morphology, which also agreed well with that in literature.⁽⁶⁾ Layer uniformity was found and no porosity was observed.

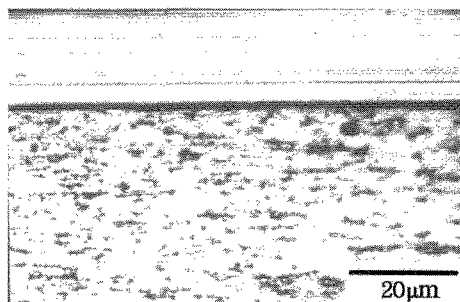


Fig. 3 Micrograph of bright nickel after etching.

Microstructural morphology and potential difference between semi-bright and bright nickel strongly depended on the amount of sulfur content, owing to the varying electrochemical behavior of nickel layer with sulfur content. The layered structural morphology and the higher potential of bright nickel layer was afforded by a higher sulfur content, while the columnar structure of semi-bright nickel was attributed to a lower sulfur content. The mechanism of elongated grains grown normal to the substrate plane or layered on the plane with increasing sulfur content is not firmly established for the present research.

Figure 4 shows the metallographic structure of sealing nickel after etching. It should be noted that sealing nickel was allowed to be plated up to 20~30µm thickness on the carbon steel (C: 0.45%) in order to observe its micro-structural morphology to a visible magnitude. However, the thickness of sealing nickel layer in multiple layered nickel for the present research was approximately 0.3µm which is nearly the same as in the actual application.

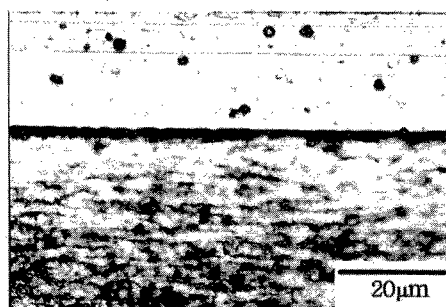


Fig. 4 Micrograph of sealing nickel after etching.

Sealing nickel is a sort of composite coating since it was obtained by co-depositing of nickel and non-soluble micro-sized particles. Thus, there existed a lot of dispersed foreign matters of micro-sized particles in the sealing nickel coatings. When chromium is deposited on the sealing nickel layer, it can not be deposited on the

top of these particles since they are not electrically conductive. Therefore, the chromium coating on the top of sealing nickel has a lot of micro-sized pores, and is called "micro-porous chromium."

3.2 Micro-pores chromium layer

Discontinuities in the chromium were induced during regular chromium plating process, which is due to the non-conductive property of dispersed particles in the sealing nickel layer. The porous structure of plane surface of chromium layer observed by M-type microscope was exhibited in Fig. 5.

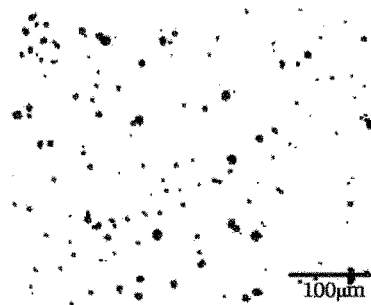


Fig. 5 Micro-pores of the chromium layer.

The quantity of pores determined by a special computer-aided Numeric Surface Pattern Treating System was presented in table II. The porous chromium structure is known to relieve internal stress that exists in a regular crack-free chromium coating, thereby reducing stress corrosion of the coatings.

The more important effect of the micro-porous chromium is that a great number of micro-pores allows the underlying nickel layer to be exposed to actuating corrosive medium over large areas. Under the corrosion environment, chromium and nickel are treated as a unit of corrosion cell having the chromium layer as cathode and the nickel layer as anode. In this corrosion cell, the larger anodic area lowers the corrosion current density. Thus, the rate of penetration of corrosion at each site of micro-pores is considerable reduced.

3.3 Protective properties of multi-layered nickel and chromium coatings

The high decorative and corrosion resistant multi-layered nickel-chromium coatings are required to meet all specifications of ISO 1456⁽¹⁴⁾ as follows,

- (1) Bright, highly leveling and mirror-bright appearance;
- (2) A range of electrode potential difference of semi-bright nickel versus bright nickel to be from 125mV to 140mV, and that between semi-bright nickel and high-sulfur nickel from 20mV to 50mV;
- (3) A minimum of 10,000 pores per square centimeter for micro-porous chromium, or 300 to 400 cracks for micro-cracked chromium;
- (4) High corrosion resistance with protection rating equal to or larger than 9 evaluated through the CASS testing as specified in ISO 1456.⁽¹³⁾

Table II presented the appearance, thickness of nickel and chromium layers, potential difference, adhesion, quantity of micro-pores on the chromium layer, and the results of CASS test. The overall thickness of nickel layers was 20µm to 40µm and the chromium layer

0.19 μm to 0.28 μm . The coatings of as-plated specimens were mirror bright and adhered to the substrate well. The coatings also exhibited micro-pores in the range of 10,000 to 30,000 per square centimeter of chromium layer; the double-layered nickel without sealing nickel did not exhibit any pores. The results of CASS test of specimen show that the double layered nickel with sealing nickel was superior to that without sealing nickel even though they had approximately an equivalent thickness of individual layer and potential difference. This is due to the fact that significant amount of micro-pores existed in the chromium layer deposited on sealing nickel layer. It has been also reported⁽¹¹⁾ that completely crack-free chromium is impossible to be achieved without applying a much thicker deposit of it because there is always the tendency to crack. Therefore, few cracks existing in double-layered nickel layer without sealing nickel layer increased corrosion current density, resulting in lowering protection rating of CASS test. The results of CASS test suggested that a significant improvement of corrosion resistance was achieved by applying sealing nickel layer on various substrates including carbon steel (C: 0.45%), copper, and aluminum. The sealing nickel layer in the multi-layered nickel-chromium coating was found to be unique in corrosion resistance, due to its characteristics to produce micro-pores of 10,000 to 30,000 per square centimeter in chromium. Although very slight corrosion was observed in aluminum substrate from the appearance test, it still satisfied the technical standard of ISO 1462⁽¹⁷⁾ regarding the quantity of micro-pores ($\geq 10,000$) as well as the protection rating (≥ 9).

Table II Results of measurement of properties of multi-layer Ni-Cr coatings

Descriptions	Double-layer Ni+Cr		Double-layer Ni+sealing Ni+Cr	Triple-layer Ni+sealing Ni+Cr	
	Ni	Cr	Fe	Cu	Al
Substrate	Fe		Fe	Cu	Al
Thickness (μm)	Ni	34.5	34.9	25.0	28.8
	Cr	0.20	0.18	0.22	0.28
Potential difference between semi-bright & bright Ni (mV)	110~130		135	135	135
Quantity of micro-pores of Cr per cm^2	-		10,000~30,000	10,000~30,000	10,000~30,000
CASS test [ⓐ]	Duration of test(hr)	44	44	24	24
	Corrosion	yes	no	no	slight
	Protection rating [ⓑ]	4	10	10	9

[ⓐ] CASS test was carried out according to ISO 3770^[16].

[ⓑ] The protection rating was determined with ISO 1462^[17].

4. CONCLUSIONS

Significant micro-pores level of 10,000 to 30,000 per square centimeter of chromium layer was achieved by depositing chromium over the sealing nickel layer. The corrosion resistance of layered nickel-chromium coating with sealing nickel was far superior to that without sealing nickel even though they had approximately an equivalent thickness of individual layer and potential difference. It was found that the

multi-layered Ni-Cr coating employing sealing nickel could be a substitute for the conventional Cu-Ni-Cr coating system having shortcomings such as the use of hazardous copper-cyanide bath and low deposition efficiency.

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