

DEPOSITED AND DIFFUSED COATINGS OF NICKEL-CHROMIUM

D MUKHERJEE, R MAHALINGAM and S GURUVIAH

Central Electrochemical Research Institute, Karaikudi 623 006

ABSTRACT

The nickel and chromium were deposited on mild steel substrate from the conventional electroplating baths to $3\ \mu$ and $6\ \mu$ respectively. Aluminium oxide was codeposited with nickel to improve the corrosion resistance properties, after annealing. The annealed and non-annealed deposits were examined in Scanning Electron Microscope (SEM) and the hardness values were also determined. The change in potential of the annealed specimen in 3% NaCl was also assessed.

Key words: Diffused coatings, Annealing, Corrosion resistance, Electrodeposition

INTRODUCTION

It is well known that electroplating is the most common method for applying metallic coatings, like chromium and nickel. However such coatings, often undergo cracking [1], due to the tensile stresses induced on the surface during plating. Heat treatment like stress or vacuum [2] annealing, sometimes improves, the coating performance and enhances the bonding between the coating and the substrate. Studies [3] have revealed that diffusion annealing of porous chromium plated mild steel specimens improve the corrosion resistant characteristics.

In this paper, the authors have studied the aspect of diffusion of nickel and chromium coating, deposited from the conventional electroplating baths. Particulate material, like alumina (Al_2O_3), were codeposited with the nickel undercoating to improve the corrosion resistant properties after annealing. The galvanic relationship among mild steel, nickel and chromium helps to protect the mild steel surface by the dissolution of nickel, which is anodic to chromium overcoat. Such coatings [4] possess high corrosion resistance and have good adhesion to the substrate. Subsequent annealing treatment is to improve the bond strength of the coating and reduce the tensile residual stresses from the coated substrates and finally form an inter-diffusional alloy layer. The coating thickness of Ni and Cr on mild steel substrate, may be controlled, so as to obtain an interface of nickel-chromium and iron after annealing. Diffusion coatings produced as such revealed high corrosion resistance. Moreover the nickel content of the coating has been brought down from the usual 25-30 μm to 3 μm level. It was reported in literature that optimum corrosion resistance, had been obtained from a combination of 25 μm nickel and 0.1 to 0.2 μm Cr.

EXPERIMENTAL

Electrodeposition

a. Pre-treatment

The following preplating sequence was followed:

- (1) Solvent degreasing with trichloroethylene
- (2) Electro cleaning in a solution of sodium hydroxide (35 gpl) and sodium carbonate (25 gpl) at 70°C , at a current density of $70\ \text{A}/\text{m}^2$, cathodically for 2 minutes and anodically for 1 minute.
- (3) Washing well in running tap water.
- (4) Dipping in 5% (by volume) H_2SO_4 acid for 10 seconds.

For all experiments, a 500 ml capacity bath was used, with cylindrical anode and specially designed attachment for the cathode.

b. Nickel plating

Nickel plating was conducted using the conventional watts bath, as shown below:

Nickel sulfate	300 gpl
Nickel chloride	60 gpl
Boric acid	40 gpl
Sodium lauryl sulphate	0.1 gpl
Temperature	$30^\circ - 32^\circ\text{C}$
Current density	3 A/sq.m.
Al_2O_3 (250 mesh - size)	3 - 18 gpl

c. Chromium plating

Conventional chromic acid bath had been employed for chromium plating over the nickel undercoat as shown below:

Chromic acid (CrO_3)	300 gpl
Sulphuric acid (1.8 sp.gr)	2.5 gpl
Temperature	50°C
Current density	14.5 A/sq. m.
Cylindrical lead anode	

Details of annealing

- The plated specimens have been annealed in vacuum furnace for a period of 1 hour at a temperature of $1000^\circ\text{C} - 1100^\circ\text{C}$ and a pressure of 5×10^{-5} torr.

Properties of electrodeposits

(a) Physical properties

(i) Thickness

The thicknesses of the electrodeposited specimens, were measured with a pencil type magnetic thickness meter at 6 or 7 points on the specimen and the average value was taken.

(ii) Hardness

Hardness was determined with the help of Rockwell testing machine and reported in BHN scale.



Fig.1. Ni + Cr, No Al_2O_3 in Watt's bath and no annealing
coating thickness $10\ \mu\text{m}$

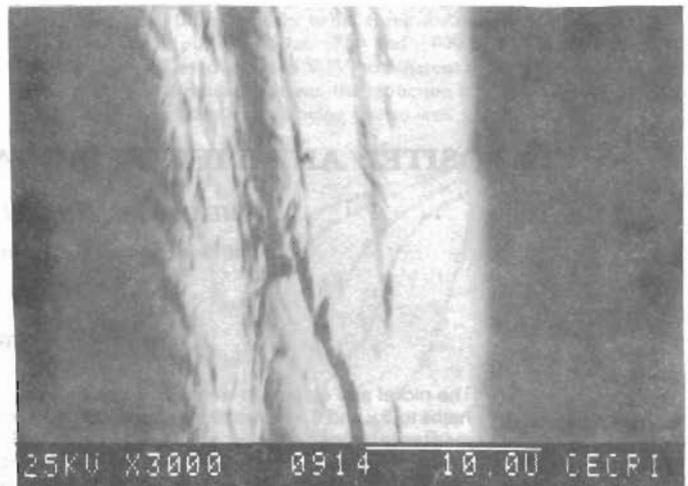


Fig.2. Ni + Cr, 9 gpl Al_2O_3 in Watt's bath and no annealing, coating
thickness $10\ \mu\text{m}$



Fig.3. Ni + Cr, 9 gpl Al_2O_3 in Watt's bath and no annealing, coating thickness $20\ \mu\text{m}$



Fig.4. Ni + Cr, 18 gpl Al_2O_3 in Watt's bath and no annealing,
coating thickness $10\ \mu\text{m}$

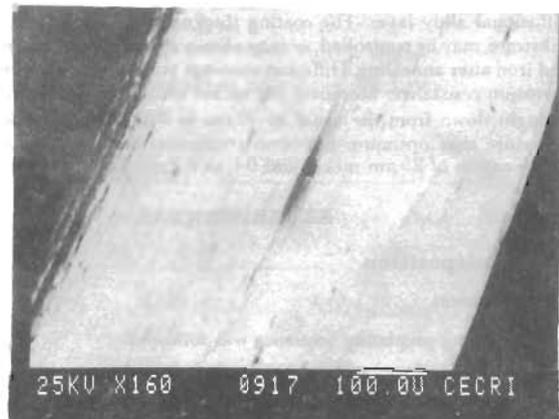


Fig.5. Ni + Cr, 18 gpl Al_2O_3 in Watt's bath and no annealing,
coating thickness $30\ \mu\text{m}$

Details of the SEM Photographs

(iii) Photomicrograph

SEM micrographs have been taken from the 1% nital etched specimens at magnifications, 100 X, 1000 X and 3000 X.

(b) Electrochemical properties

Potential vs time data was obtained with reference to SCE in 3% NaCl solution using a micro-voltmeter.

RESULTS AND DISCUSSION

It is seen from Table I, that nickel-chromium is not bright after annealing in air and a maximum nickel coating of 2.8 μm is used for obtaining uniform coating. Moreover the ratio of the coating thickness and depth of penetration, before and after annealing decreased with increase in nickel layer thickness, indicating better diffusion, after annealing for the coatings having higher nickel thickness.

Table I: The properties of nickel-chromium coating deposited on mild steel and diffused in air

Before annealing

Coating thickness plated (μm)	0.7 Ni + 6.0 Cr	1.4 Ni + 6.0 Cr	2.1 Ni + 6.0 Cr	2.8 Ni + 6 Cr

After annealing

Depth of penetration (μm)	22	45

Visual examination	Oxidized and cracked coating	Oxidized and cracked coating	Uniform coating. Edges affected. No more bright	Uniform coating. Edges affected. No more bright

Ratio of coating thickness and depth of penetration before and after annealing	0.37	0.20

Table II shows the effect of Al_2O_3 in the nickel chromium coating deposited on MS and diffused in vacuum. The specimens appear dull bright after vacuum annealing. The ratio of the coating thickness and the depth of penetration, before and after annealing, also reveal a decreasing trend, with increase in the alumina (Al_2O_3) content in the nickel coating. It indicates that diffusion is more after incorporation of Al_2O_3 particulates in the coating. This may be attributed to the cracking of the nickel coating, by the oxide particulates, resulting in better intermixing and diffusion of chromium.

The hardness value increases from Rockwell superficial Hardness 45 to 51 due to the incorporation of the Al_2O_3 particulates and decreases to 40-41 after annealing.

Table III reveals the potential vs time for the coated and annealed specimens in 3% NaCl vs S C E. It is seen that the annealed specimens without Al_2O_3 incorporation in the nickel under layer, reveal more negative potential than those incorporated with Al_2O_3 . The specimen, with 18 gpl Al_2O_3 in the bath reveals more positive potential than that of 9 gpl in the solution after 24 hours exposure. However, both specimens behaved identically after 360 hours exposure.

Table II: The effect of Al_2O_3 in nickel-chromium deposited on M.S. and diffused in vacuum

Before annealing

Coating thickness (μm)	3.0 Ni + 6.0 Cr	3.1 Ni + 6.0 Cr	3.2 Ni + 6.0 Cr	3.3 Ni + 6.0 Cr

Al_2O_3 in Watts bath (gpl)	3.0	6.0	9.0	18.0

After annealing

Depth of penetration (μm)	10	17	20	30
Visual examination	Lightly tarnished appearance	Dull bright appearance	Bright	Bright

Ratio of coating thickness and depth of penetration before and after annealing	0.90	0.54	0.46	0.31

Table III: Potential vs time for the coated and annealed specimens in 3% NaCl with reference to SCE

Coating system	Potential in mV. with different periods of time in 3% NaCl solution with reference to SCE				
Thickness (μm)	Initial	1 1/2 hr	24 hr	216 hr	360 hr
1. 2.8 μm Ni + 6 μm Cr (Al_2O_3 - Nil)	-3.00	-3.00	-180	-350	-400
2. 2.8 μm Ni + 6 μm Cr (9 gpl Al_2O_3 in watts bath)	-1.00	-0.10	-170	-220	-250
3. 2.8 μm Ni + 6 μm Cr (18 gpl Al_2O_3 in watts bath)	-1.00	-0.11	-70	-220	-250

SEM Photographs, Fig. 1 to Fig. 5 show that the coating thickness is not affected by Al_2O_3 incorporation in nickel-matrix. However, annealing of this coating, results in the substantial depth of penetration of the coating. For the 9 gpl incorporated specimen, the depth of penetration increases from 10 μm to 20 μm after annealing, while for the 18 gpl Al_2O_3 incorporated specimen, the depth of penetration is very high from 30 μm to 100 μm in some places. The depth has been measured by comparing it with 10 μ line given under each photograph. This indicates that annealing results in increase of the depth of penetration, through diffusion at elevated temperature. Particulate

materials like Al_2O_3 enhance such alloy formation.

CONCLUSION

In conclusion, the authors observe that incorporation of Al_2O_3 particulates in the nickel coating, improves the corrosion resistance of the surface, after annealing. The hardness of the Al_2O_3 incorporated surface increases slightly and the depth of penetration of the coating is also increased after annealing.

Acknowledgement: The authors thank Sri K. Chandran, Scientist, for his help in the plating experiments.

REFERENCES

1. F A Lowenheim, *Modern Electroplating*, John Wiley and Sons Inc., New

York, (1974), p 118-123, 135 and 287

2. G V Karpenko, V I Pokhmuruvskii, V B Dalisov, V S Zamikhovskii, *Trans-Tech Publication* Trans Tech House, C.H = 4711. AEDERMANSORF, Switzerland, (1979), p 13

3. D Mukherjee, C.Rajagopal, R Arghode, K Chandran and S Guruviah, *Preprints of Third National Conference on Metal Finishing and Electroplating*, Organised by SAEST and Metal Finishers' Association of India, Nov. 30 to Dec. 2, 1983, p 79

4. S A Watson, *Trans Inst Met Fin*, **39**, (1961) 91

5. V E Carter, *Metallic coatings for corrosion control*, Nues Butterworth, London (1977) p 113