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EFFECT OF PRE-AND POST-STRESS RELIEVING ON THE ELECTRO-CRYSTALLIZATION OF Ni-P-B ALLOY

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It has been widely mentioned that the incorporation of metalloids like P and B, in the nickel matrix, improves the physicochemical properties of nickel. An attempt has been made in this study to produce a coating of Ni-Fe-P-B, on mild steel substrate, which is more cost-effective than Ni-P-B coating.

Bath formulation and current density for obtaining good deposit have been arrived at by voltammetric technique. The duration of heat treatment of the substrate-surface, before and after coating, temperature and time of deposition were adjusted for obtaining good deposits. The physicochemical properties of the deposited panels were also studied and compared.

Key words: Stress relieving, Ni-Fe-P-B coating, corrosion resistance

INTRODUCTION

It has been widely reported that the incorporation of metalloids like P and B, in the nickel-matrix, improves the physico-chemical properties of nickel. The high cost of nickel, gives scope to substitute nickel by less costly metal. It has been reported [1] that nickel-iron alloy-deposit with a copper undercoat and a microporous chromium topcoat is comparable to the conventional nickel coating, from corrosion resistance view point.

Therefore, an attempt has been made in this study to substitute nickel in Ni- P-B coating by iron, using the reported Ni-Fe [1] and Ni-P-B [2,3,4] bath formulations.

EXPERIMENTAL

(a) Material: Mildsteel used was of commercial quality and chemicals were of A.R. quality, pure nickel anode of 99.9% purity, was employed.

(b) *Electroplating:* Plating of Ni-Fe-P-B on mild steel substrate was done, from bath composition, comprising of Ni-P-B and Ni-Fe [1] formulations as in Table IA, in the ratio 2:1 at room temperature.

TABLE-IA: Bath parameters from cyclic voltammogram using the bath formulations of Ni-Fe [1] and Ni-P-B [2, 3, 4]

Solution A:

It is prepared by removing nickel salts from the Ni-P-B [2, 3, 4] bath formulations as shown below:

H_3PO_4	180 cc/l
$Na_2H_2PO_4$	140 g/l
$NaBH_4$	7.5 g/l

Solution B:

It is based on Ni-Fe [1] bath formulation as shown below:

$NiSO_4$	75 g/l
$NiCl_2$	75 g/l
$FeSO_4$	15 g/l
H_3BO_4	45 g/l
Stablilizer	30 g/l

(c) *Pre - and post-stress relieving:* Pre stress relieving of the mild steel cathode and post-stress relieving of the plated specimens, were conducted respectively at 200°C and 400°C for 2 hrs, using a thermostatically- controlled oven.

(d) *Diagonostic studies in cyclic voltammetry:* Triangular sweep cyclic voltammetric technique was employed at scan rates of 10 mV, and 100 mV/sec, to determine the composition of the plating bath for good bulk deposition and the equivalent current. The current density has been obtained from ther recorded graph.

(e) *Electrochemical studies:* Anodic and cathodic polarization, of as-plated and heat-treated specimens were conducted in 3% NaCl solution, using galvanostatic technique. The values of the i_{corr} and E_{corr} were also analyzed by cyclic voltammetric technique in 3% NaCl solution, with 1 mV/sec and 100 mV/sec scan rates. The effect of pre-stress-relieving of the mild steel specimen and that of post- stress relieving on the coated specimens on the electro-catalytic behaviour of the above coating, were assessed from these data.

(f) *Thickness of the coating:* The thickness of the coating of Ni-Fe-P-B on mild steel substrate was assessed by magnetic thickness meter.

(g) *Micro structure:* The coated specimens were analyzed for their micro structures, using Neophat-21, Metallurgical Microscope.

RESULTS AND DISCUSSION

Table IB reveals the composition of the solution and test parameters like agitation, temperature, amount and the form of the voltammogram. It is clear that a solution prepared by mixing 100 c.c. of solution A and 50 c.c. of solution B gives maximum current of 13.2 mA at—550 mV (double the standard electrode potential of nickel at room temperature). The deposition is accompanied with gas evolution and a flat region or plateau is observed in the voltammogram within a potential range of —350 to —750 mV. The flat region also indicated the possibility of obtaining a bulk deposit, which may be of interest bearing on its electro-catalytic behaviour.

Table II reveals the bulk deposition of the coatings mentioned in Table IB.

TABLE-IB : Composition of the test solutions.
The solution agitated by stirring; Room temperature

Solution A	Solution B	Ratio A:B	Observation from the voltammogram			
			Scanning rate (mv/sec)	Current at -550 (mv/sec)	Gas evolution at electrode	State of the voltammogram
100	0	—	10	2.8	Gas evolved on mild steel electrode	No flat region or plateau observed
100	10	10:1	4.8	4.8	-do-	-do-
100	50	2:1	-do-	13.2	More evolution of gas	Distinct flat region or plateau observed between —350 and —750 mV
100	100	1:1	-do-	8.64	Increased gas evolution	No flat region

Table II: Deposition of Ni-Fe-P-B coating on mild steel substrates using a C.D. of 13 ma/cm^2 and bath composition comprising of the basic solution and Ni-Fe solution in the ratio 2:1 (as detailed in Table IA)

Material	Bath temp. (°C)	Pre-stress relieving	Time of deposition (Hr)	Post-heat treatment	Thickness of coating (micron)	Visual examination
Plated mild steel	Room temp.	Nil	0.5	Nil	—	Partial coverage of the surface
	-do-	-do-	1.0	-do-	—	-do-
	-do-	-do-	1.5	-do-	2	Complete coverage
	60	-do-	1.5	-do-	—	Powdery coating
	Room temp.	0.5 hr at 200°C	1.5	-do-	2	Complete coverage
	-do-	1 Hr at 200°C	1.5	-do-	2	-do-
	-do-	2 Hrs at 200°C	1.5	-do-	4	-do-
	-do-	0.5 Hrs at 200°C	1.5	2 Hrs at 200°C	2	Surface of the coating is oxidised
	-do-	1 Hr at 200°C	1.5	2 Hrs at 200°C	2	-do-
	-do-	1.5 Hr at 200°C	1.5	-do-	4	-do-
	-do-	0.5 Hr at 200°C	1.5	2 Hrs at 200°C and 2 Hrs at 400°C	2	Surface of the coating is oxidised and blackened.
	-do-	1 Hr at 200°C	1.5	2 Hrs at 200°C and 2 Hrs at 400°C	2	-do-
	-do-	2 Hrs at 200°C	1.5	2 Hrs at 200°C and 2 Hrs at 400°C	4	-do-
Unplated mild steel	—	2 Hrs at 200°C		—	—	—

A current density of 13 ma/cm^2 and a solution comprising of 100 c.c. of solution A and 50 c.c. of solution B, have been employed. It is clearly seen that increasing the temperature of this bath to 60°C did not give satisfactory coating. Good adherent coating was obtained after coating for a period of 1 ½ hours at room temperature. However the prestress relieving of the mild steel specimens at 200°C for 2 hours appeared to improve the thickness of the coating. Post-stress relieving at 200°C and 400°C for 2 hours each did not further improve the coating thickness. The dull colour of the coating changes to black after post-stress relieving at 400°C for 2 hours.

Table III gives the physical and chemical properties of these coatings.

TABLE-III: Physical and chemical properties of the coated mild steel panels: Coating thickness: 4 microns

Materials	O.C.P. (mV)	i_{Corr} $\mu A/cm^2$	E_{corr} (mV)	Micro examination
	(3% NaCl solution)			
Pre-stress relieved mild steel	—500	100	—510	Ferrite grains are pearlite
Pre-stress relieved mild steel + coatings	—460	65	—525	Coating with some porosities are visible
Pre-stress relieved mild steel coated + post-stress relieving at 200°C for 2 hrs	—460	65	—575	Coating with less number of pores are visible
Pre-stress relieved mild steel coated + post-stress relieving at 200°C for 2 hrs and 400°C for 2 hrs	—525	65	—575	Coating with oxidised products are visible

The i_{corr} values of the pre-stress relieved mild steel is approximately double that of pre-stress relieved, coated specimen. The O C P value of the pre-stress relieved coated specimens at 200°C is more positive than pre-stress relieved mild steel specimens. It indicates that the corrosion resistance of pre-stress relieved mild steel has been improved by coating in Ni-Fe-P-B bath formulation. Post-stress relieving at 200°C further improves the surface properties of the coating. On micro-examination it is seen that some porosities are present on the coated panels while post- stress relieving at 200°C reduces the number of porosities while at 400°C results in oxidation of the coated surface. This explains the more negative O.C.P. value of the coated specimens, post-stress relieved at 400°C.

Table IV shows the potential-current relationship for both forward and backward scan at a scan rate of 1 mV/sec in 3% NaCl solution.

TABLE-IV: Cyclic voltammetric potential-current relationship for both forward and backward scan at low-scan rate
Scan rate = 1 mV/sec in 3% NaCl solution

S.No.	Potential (mv)	Thickness (micron)		Current (Micro-ampere)							
		Before cyclic voltammetric test	After cyclic voltammetric test	Mild steel		Mild steel pre-stress relieved + coating with Ni-Fe-P-B		Mild Steel pre-stress relieved + coated with Ni-Fe-P-B + Post stress relieved at 200°C		Mild Steel pre-stress relieved + coated post stress relieved at 200°C + post stress relieved at 400°C	
				Forward scan	Backward scan	Forward scan	Backward scan	Forward scan	Backward scan	Forward scan	Backward scan
1	-500	4	3.5	26.6	6.6	30.0	6.6	30.0	13.3	20.0	20.0
2	-550	4	3.5	26.6	13.3	23.3	13.3	40.0	16.6	26.6	26.6
3	-600	4	3.5	50.0	16.6	50.0	16.6	50.0	20.0	40.0	33.3
4	-650	4	3.5	63.3	26.6	63.3	20.2	66.6	30.0	46.6	36.6
5	-700	4	3.5	80.0	36.6	76.6	30.0	83.3	83.3	50.0	43.3

Comparing the current values at equivalent potentials it is observed that the pre-stress relieved, coated and post-stress relieved at 200°C and 400°C (2hrs) specimens reveal lower corrosion current, during the forward scan i.e. during oxidation cycle. This trend is not observed during the reverse scan or during reduction. It indicates that for slower reactions, the oxidation process is favoured by post-stress relieving of the coated panels. Pre-stress relieving of the mild steel panel improves the coating thickness. The deposited mild steel panels reveal higher corrosion resistance than mild steel. The corrosion resistance of the coated panel is not improved by post- stress relieving. Post-stress relieving appears to favour oxidation processes for slower reactions, while for faster reactions both oxidation and reduction reactions are favoured.

TABLE V: Cyclic voltammetric potential-current relationship for both forward and backward scan at high scan rate. Scan rate = 100 mV/sec in 3% NaCl solution

S.No.	Potential (mv)	Thickness (Micron)		Current (Micro-amphere)							
		Before cyclic voltammetric test	After cyclic voltammetric test	Mild steel Forward scan	Mild steel Backward scan	Mild steel pre-stress relieved + coating with Ni-Fe-P-B Forward scan	Mild steel pre-stress relieved + coating with Ni-Fe-P-B Backward scan	Mild Steel pre-stress relieved + coated with Ni-Fe-P-B + Post stress relieved at 200°C Forward scan	Mild Steel pre-stress relieved + coated with Ni-Fe-P-B + Post stress relieved at 200°C Backward scan	Mild Steel pre-stress relieved + coated post stress relieved at 200°C + post stress relieved at 400°C Forward scan	Mild Steel pre-stress relieved + coated post stress relieved at 200°C + post stress relieved at 400°C Backward scan
1	-500	4	3.5	23.3	46.6	30.0	40.0	6.6	40.0	10.0	3.3
2	-550	4	3.5	43.3	43.3	40.0	36.6	30.0	36.6	10.0	3.3
3	-600	4	3.5	60.0	40.0	56.6	33.3	46.6	33.3	13.3	50.0
4	-650	4	3.5	36.3	43.3	70.0	23.3	63.3	16.6	16.6	50.0
5	-700	4	3.5	36.6	6.6	76.6	6.6	80.0	—	56.6	46.6

Table V depicts the same behaviour at a scan rate of 100 mV/sec, except that during reduction cycle also, the prestress relieved, coated and post-stress relieved specimens show, lower current values at comparable potentials. It indicates that for faster reactions, both oxidation and reduction processes are favoured by the post-stress relieving of the coated panels.

CONCLUSIONS

In conclusion the authors observe that the electrocrystallization parameters like bath composition and current density which are obtained from cyclic voltammogram, may be used subsequently for bulk deposition from a solution comprising of nickel chloride, nickel sulphate, ferrous sulphate, phosphoric acid, sodium hypophosphite, boric acid, sodium borohydride and citric acid.

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