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COLD PRESSING AND HEAT TREATMENT OF BULK Ni-P-B DEPOSITS ON MILD STEEL SUBSTRATES FOR BETTER CORROSION PROTECTION

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ABSTRACT

Bulk deposits of Ni-P-B alloys on mildsteel were obtained up to 0.8 mm thickness, by prolonging the time of deposition. The formability of these deposits was studied by following the percentage reduction in thickness, during cold-pressing. The electrochemical properties of these coated surfaces were studied before and after cold-pressing. Cold-forming and heat treatment improves the corrosion resistance properties.

Key words: Cold pressing, heat treatment, Ni-P-B alloy, corrosion protection

INTRODUCTION

It has been reported [1-5] that metals like nickel and cobalt may be successfully codeposited with phosphorous, or boron, either by chemical reduction or electrodeposition techniques. It has been shown that electrodeposition of Ni-P-B is possible from the conventional chemical baths [5-7]. The unique properties and possible industrial exploitation of these coatings, possessing resistance to wear, corrosion and tarnishing have brought these class of materials, in the technological forefronts. Bulk deposits of Ni-P-B on mildsteel substrate have been developed to a thickness of 0.8 mm, by extending the time of deposition. The electrochemical properties of the bulk Ni-P-B coating have been studied before and after cold-deformation and heat treatment. Microstructural analysis has also been conducted by using both scanning electron and optical microscopes. Deposits are obtained on this mildsteel plates, so that bulk deposits of Ni-P-B may be easily retrieved, by the preferential dissolution of the thin mildsteel substrate. The alloys retrieved as such may be used to fabricate components requiring high corrosion resistance and hardness.

EXPERIMENTAL

Pretreatment

Rectangular specimens (3.5 x 7.5 x 0.5 cm) of mild steel are polished to −000 − emery and degreased in trichloroethylene, followed by the conventional cathodic and anodic processes, using a solution of NaOH and Na_2CO_3. The cleaned specimens are washed thoroughly in dilute hydrochloric acid and distilled water, before immersing in the plating bath.

Plating of Ni-P-B coating

The plating bath is prepared from nickel sulfate, nickel chloride, phosphoric acid, sodium hypophosphite and sodium borohydride. Mild steel cathodes are placed in between two nickel anodes for plating on both sides in the 5-litre capacity P.V.C. bath. The deposition was conducted continuously for various periods of time, namely, 1/2, 1,2,3 and 4 hours, to build up thickness (bulk-depsoit). Coatings of 0.5 to 0.6 mm were obtained.

Cold pressing of the bulk Ni-P-B depsoit

The specimens coated on both sides are cold-pressed at a load of 4-tonnes, using a hand-operated press for a period of 1 hr. increasing the loading rate at 50kg/min.

Heat-treatment of the coated and pressed specimens

Heat treatment is conducted at 400° C using a muffle-furnace in a controlled atmosphere.

Electrochemical studies

The plated specimens are immersed in 1.5% NaCl and potential values are followed up by using a V.T.V.M. with respect to saturated calomel electrode. Corrosion-rate values are determined on weight loss basis in 10% HCl solution for a period of 60 minutes. Potentiodynamic studies are also conducted in 1.5% NaCl solution.

S.E.M. examination

Mildsteel specimens, coated with Ni-P-B deposits are examined in scanning electron microscope at 1000 x.

RESULTS AND DISCUSSION

Table I provides the optimum conditions for nickel-phosphorous-boron alloy-deposition, along with the hardness and compositions of the deposits. Experiments were conducted at 25° C, 60° C and 80° C and pH = 1,2,3,4,5 and c.d. was varied between 5 $A.dm^{-2}$ and 15 $A.dm^{-2}$ with duration of plating 30 mins, 45 mins, 60 mins and 90 mins. The concentration of phosphoric acid was varied from 50 ml/L to 150 ml/L and concentration of sodium borohydride was varied between 2.5 gpl and 7.5 gpl. It is observed from the above studies that satisfactory bright adherent deposits with unaffected edges, can be produced by using a c.d. of 15 $A.dm^{-2}$ at 60° C for 60 mins at a bath pH of 2, the concentration of phosphoric acid being 150 ml/L and that of borohydride being 7.5 g/L. The hardness of the deposit varies from 1200 B.H.N. to 1206 BHN. However the hardness values varied from 1455 to 1465 BHN for the heat treated specimens (400° C for 1 hr.). The composition of the deposits, as analyzed by the atomic absorption spectroscopy, after stripping from the mild steel plate has a phosphorous content of 8.8% and boron content of 2.5%. Table I also reveals the bulk deposition of Ni-P-B on mildsteel substrates produced by extending the time of deposition up to 4 hours, using the bath parameters as standardized above. A 5-litre capacity bath is employed for building of nickel-phosphorous-boron deposit, up to a thickness of 0.8mm. The bath is highly agitated due to the liberation of hydrogen at cathode. It is clearly seen that the coating weight and coating thickness progressively increase up to 3.5 hours of plating, followed by a reduction of coating thickness and weight beyond that. The open circuit potentials of these coatings are identical and the appearance varies between lustrous and dull-bright. The O.C.P values appear to be highly positive in comparison to uncoated specimens, indicating higher corrosion resistance for the coated surface.

Table I: Composition and hardness of Ni-P-B deposits and its bulk-deposition on mild steel substrates

Bath composition: Nickel sulphate 150g, nickel chloride 45g, sodium hypophosphite 135g, sodium borohydride 7.5g and phosphoric acid (sp.gr 1.75) 150 ml—All made upto 1L.

Plating conditions: Temp. 60 ± 5°C; pH 2 ± 0.5; c.d. 14-15 A.dm^{-2}, Time 60 mins.

Composition of deposit (%)		Hardness, kg/mm^2		
P	B	As plated	Pressed to 6% reduction	Heat treated 400°C, 1hr.
8.8	2.5	1200-1206	1350-1360	1455-1465

Sl. No	Time of deposition (hr)	Coating thickness (mm)	Coating weight (g/sq. mm)	O.C.P. vs. S.C.E (1.5% NaCl soln) uncoated	O.C.P. vs. S.C.E (1.5% NaCl soln) coated	Appearance of deposit	Agitation of bath
1	0.5	0.05	0.034	−450	−150	Bright	The bath
2	1.0	0.12	0.054	−450	−150	Bright	is in a
3	1.5	0.39	0.155	−450	−150	Dull bright	very much agitated
4	2.0	0.66	0.236	−450	−155	-do-	state due
5	2.5	0.70	0.258	−450	−155	-do-	to the
6	3.0	0.74	0.283	−450	−155	-do-	liberation
7	3.5	0.80	0.245	−450	−155	-do'	of hydrogen
8	4.0	0.64	0.215	−450	−155	-do'	at cathode

Table II, reveals the percentage deformation of NI—P—B coated mild steel attaining a maximum value at a coating thickness of 0.66 mm.

Table II: Cold-forming of Ni-P-B on mild-steel
Rate of load, 50kg/min.

Sl No.	Coating weight g/cm^2	Plating time (hr.)	Cold-forming load (tonnes)	O.C.P. mV vs S.C.E. (1.5% NaCl solution) Coated	O.C.P. mV vs S.C.E. (1.5% NaCl solution) Coated & pressed	Percentage reduction in thickness due to pressing	Microscopical-observation (S.E.M.)
1.	0.0543	1.6	4	−150	−150	5.7	Reveal
2.	0.1553	1.5	4	−150	−225	15.2	deforma
3.	0.2360	2.0	4	−155	−250	24.5	tion
4.	0.2586	2.5	4	−155	−265	22.1	lines
5.	0.2838	3.0	4	−155	−300	21.0	(after pressing) and voids and cracks

Scanning electron microscopical examination of the cold-pressed surfaces reveals the presence of deformation lines, voids and cracks. However the open circuit potential, before and after pressing, reveals that with increase of cold-pressing beyond 6%, the values of O.C.P. become more and more negative. It is seen from Table III that the potential values become progressively positive, as the heat treatment time is increased from 1 to 2 hours. Two hours's heat treatment results in macro-crystallinity, revealing highly negative potential values. It is also seen that cold-pressing of 6% appears to make the potential values more positve in comparison with those having higher percentage deformation. Heat treatment of the cold-pressed specimens makes the potential values more negative. The positive trend in potential values shown after heat treatment and 6% cold-deformation is attributed to the sealing up of the pores on the coated surface. Longer duration of heat treatment and higher deformation result in complete macro-crystallinity and formation of voids and cracks. Table IV reveals the weight loss corrosion rate values. One hour heat treatment reduces the corrosion rate values, while it is drastically increased after heat treatment for 2 hours, due to complete macro-crystallinity. Specimens, cold pressed upto 6% reduction in thickness, reveal lower corrosion rate values in comparison with those of 21% and 24% cold-pressed specimens. The pressed specimens reveal marginal improvement in corrosion resistance values, which is increased with heat treatment time. It is seen that plain Ni-P-B coated mild steel reveals a corrosion resistance value almost 5 times that of mild steel.

Potentiodynamic studies (Table V) show that potentials, corrosponding to various current values, are less positive for cold-pressed (21% and 24% reduction in thickness) and heat treated specimens. The open circuit potential values, also reveal this trend. S.E.M. microphotographs (Fig. 1,2 and 3) show the morpohlogy of Ni-P-B deposit on mild steel surface before and after cold-pressing and heat treatment. The specimen without any cold-deformation and heat treatment (Fig. 1) reveals the absence of crystal grain boundaries, indicating microcrystallinity. Fig. 2 shows the specimen cold pressed by 6% reduction in thickness and heat treated at 400°C for 1 hr. The micro-crystalline nature of the deposits appears to be somewhat modified by cold-pressing and heat treatment.

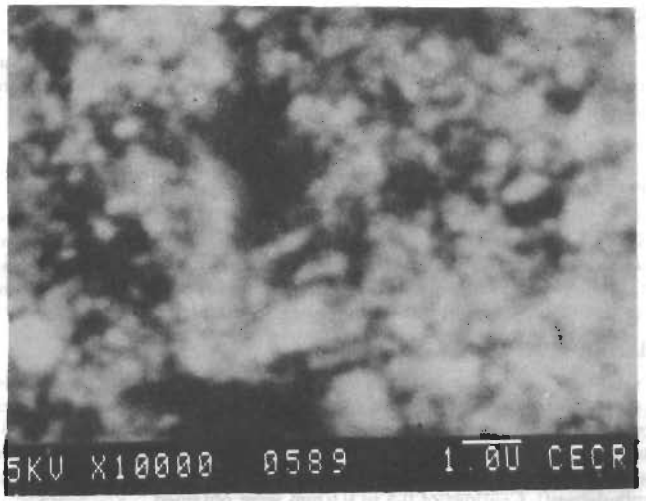

Fig. 1: SEM photomicrograph of Ni-P-B deposit on mild steel without any cold deformation and heat treatment

Fig. 3 shows that after cold pressing (21% reduction) and heat treatment crystal grain boundaries and cracks are visible, indicating complete macro-crystallinity.

Table III: Potential-time relationship of Ni-P-B coated mild steel plates as a function of heat-treatment time (400°C) and cold pressing (under a pressure of 4 tonnes) in 1.5% NaCl-solution

Time (min)	Potential in "mV" w.r.t. S.C.E.								
	Percentage cold pressing = 0 %			Percentage cold pressing = 6 %		Percentage cold pressing = 25 %		Percentage cold pressing = 21 %	
	Heat treatment time (hr)			Heat treatment time (hr)		Heat treatment time (hr)		Heat treatment time (hr)	
	0	1	2	0	2	0	2	0	2
0	−150	− 80	−400	−150	−250	−250	−400	−300	−310
15	−265	−205	−520	−160	−300	−480	−485	−530	−380
30	−305	−200	−535	−160	−290	−510	−485	−525	−390
45	−308	−200	−535	−165	−280	−510	−465	−500	−395
60	−318	−205	−530	−160	−250	−500	−450	−450	−400
75	−318	−200	−530	−160	−240	−400	−400	−400	−415
90	−320	−200	−540	−150	−250	−300	−300	−400	−425

Table IV: Corrosion-rate values on weight loss basis for Ni-P-B coated mild steel panels with and without cold-pressing and heat treatment in 10% HCl solution

Treatment	Corrosion-rate (g/sq mm) X 10^{-5}		
	Time of heat treatment = 0 hr	Time of heat treatment = 1 hr	Time of heat treatment = 2 hr
Without cold-pressing	4.65	3.1	15.50
6% Cold-pressing	3.10	2.5	4.65
21% Cold-pressing	5.43	5.0	7.75
24% Cold-pressing	5.43	5.2	7.75
M.S. without cold-pressing and heat treatment	6.20	—	—

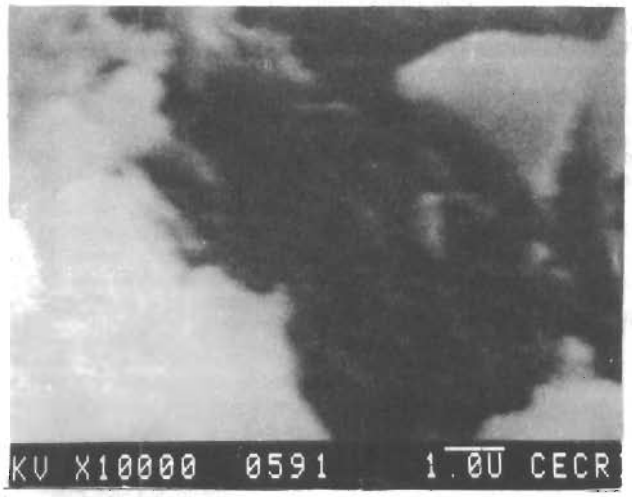

Fig. 2: SEM photomicrograph of Ni-P-B deposit on mild steel 6% cold pressed and heat treated at 400°C for 1 hr

Table V: Potentiodynamic studies in 1.5% NaCl solution vs S.C.E.
Scan rate = 10 mV/sec.

Current (mA)	Potential in "mV"		
	Ni-P-B coating on M.S.-No pressing, no heattreatment	Ni-P-B coating on M.S.−24% cold pressing, heat-treatment at 400°C for 2 hrs	Ni-P-B coating on M.S.−21% cold pressing, heat treatment at 400°C for 2 hrs
8.30	+ 50	−300	−340
12.45	+100	−280	−320
16.60	+120	−260	−300
24.90	+170	−220	−280
33.20	+190	−200	−260
41.50	+200	−180	−250
49.90	—	−140	−240
	O.C.P = −150 mV	O.C.P = −300 mV	O.C.P = −400 mV

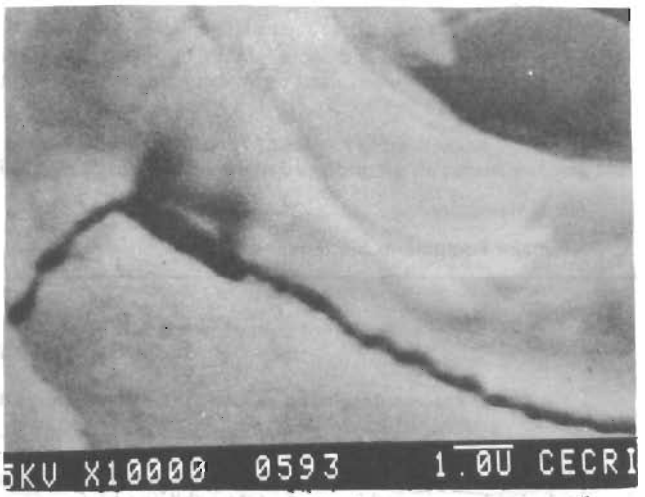

Fig. 3: SEM photomicrograph of Ni-P-B deposit on mild steel 21% cold pressed and heat treated for 1 hr

CONCLUSION

Satisfactory bulk deposit of Ni-P-B up to a thickness of 0.8 mm may be obtained on mild steel surface, by extending the time of coating to 3-4 hours duration, using a 5-litre capacity bath. The coatings obtained as such may be deformed by cold-pressing technique, although cracks and voids appear beyond a deformation of 6% reduction in thickness.

Heat treatment of the Ni-P-B coated mild steel reveals an initial improvement in corrosion – resistance, followed by drastic reduction as a result of macro-crystallinity. Lower percentage of cold pressing also results in an improvement in corrosion resistance. Cold pressing beyond 6% reduction in thickness, followed by heat treatment results in reduction in corrosion resistance properties.

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