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Corrosivity of Sulphide Solutions Against Ni-P-TiO_2-ZrO_2 Electroless Nanocomposite Coatings

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Abstract

In surface engineering it is found that to incorporate nano particle into Ni-P matrix is very useful. In recent investigation, the electroless Ni-P-TiO_2-ZrO_2 nano-composite plating has been deposited upon mild steel substrate (AISI 1040). The 2.5 gpl each TiO_2 and ZrO_2 nano-particles were incorporated into an acidic electroless Ni-P matrix as a second phase material and were reduced by a reducing chemical called as sodium hypophosphite (Na_2HPO_3). The coating thickness is in micrometer range. After the coating, as-prepared Ni-P-TiO_2-ZrO_2 EL deposition were heated at 400 °C in Argon atmosphere for one hour duration to investigate the heat effect on coatings and were analyzed by SEM/XRD/EDX methods. A homogeneous and weighty consistent allocation of TiO_2 and ZrO_2 nano-particles into EL Ni-P matrix is recognized through analysis of SEM and EDAX methods. From the corrosion test result it observed that he sulphide solutions with chloride are more corrosive than without chloride. Sodium sulphide, thiosulphates and sodium chloride is suggested to be main corrosive chemicals. The corrosion resistance of the conventional materials and Ni-P-TiO_2-ZrO_2 coated samples are in following order as SS2205 > Ni-P-TiO_2-ZrO_2 (As-plated) > Ni-P-TiO_2-ZrO_2 (Heated) > MS.

Keywords- Electroless, FESEM-EDAX, Ni-P-TiO_2-ZrO_2, Corrosion.

1. Introduction

In paper industry for making of paper by kraft pulping process roughly 85% of chemical pulping and 65% of other pulping (mechanical, semi-mechanical) processes are adopted. The Kraft pulping process uses alkaline sulfide solutions for the purpose of delignification of wood/non wood species in order to draw cellulose fibers from them. Further these fibers are used in making of paper. The alkaline sulfide liquor consists mainly NaOH and Na_2S chemicals and the pH of this liquor is 13.8 approximately (Smook, 1982). Now days the selective delignification of wood chips is achieved by cooking them in liquor of slight higher sulfidity (Na_2S amount in gram per litre/Na_2S + NaOH amount in gram per litre) than which is being practiced in the normal kraft pulping process earlier. Naturally the cooking liquors with higher sulfidity will perceptibly have prominent concentration of the sulfur ions which is expected to consequence in increased corrosivity of pulping liquors. Therefore, it seems that the corrosion in pulp digesters depends very strongly on the relative amount of the different sulfur species in cooking liquor, which is likely to be different in different mills, rather than simply on temperature, pH and sulfide content only (Audouard et al,1980; Bennet et al, 1983; Wensley, 2004). In surface science and engineering technology, in literature review it is found that the employment of micro/nano-composite coatings prepared by electroless (EL) method have been recommended by many researchers (Brenner and Riddell, 1946; Agarwala and Agarwala, 2003) to protect industrial materials against corrosion. Also a number of hard and soft second phase micro/nano-particles have been incorporated into EL Ni-P matrix and studied for their corrosion, wear resistant and other tribological properties (Sharma et al., 2002; Sudagar et al.; 2013). From above many soft and hard nano particles, the inclusion of TiO_2 and ZrO_2 nano particles as a combination of nano-particles into the EL Ni-P matrix and measurement of their corrosion and triobological properties is shown hardly. Therefore, addressing above stern issues it is necessary to carry out a long term corrosion experiments in sulphide solutions taking conventional and non-conventional materials. These corrosion tests further will help in understanding of corrosion cause, development of corrosion protection mechanism and will predict the probability of possible use of non-conventional (nano coated) materials in sulphide solutions.

2.1 Material Selection

Carbon steels have been the principal material of construction for kraft batch/ continuous digesters since last many decades. Now day's C-steel digesters have been provided with protective layer of the above mentioned resistant materials by cladding/ weld overlaying/ thermal spraying while duplex SS 2205 is a modern addition. Considering useful applications of nano- composite coatings and among many coatings options a newly developed electroless Ni-P-TiO_2-ZrO_2 nano composite coatings is considered for the current corrosion experiments. Accordingly, mild steel, austenitic grade SS304L, SS316L, duplex grade SS2205 stainless steels and Ni-P-TiO_2-ZrO_2 nano composite coatings have been selected as a test material for the long term immersion corrosion test (Figure 1). Composition of the steels for tests has been given in Table 1.

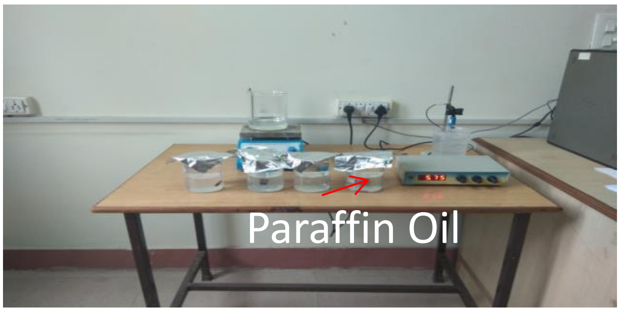

Figure 1. Long term immersion corrosion test representation in sulphide solutions

Table 1. Composition of stainless steels plate samples

Alloy	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu	Ti
MS	0.180	0.040	1.660	-	-	-	-	-	-	-	-
SS 304L	0.036	0.440	1.840	0.024	0.001	18.110	8.010	0.260	0.058	0.460	0.002
SS 316L	0.019	0.500	1.110	0.027	0.002	17.430	11.260	2.030	0.048	0.400	0.001
SS 2205	0.022	0.350	1.470	0.020	0.001	22.130	5.550	3.160	0.188	0.210	0.004

#Fe = Balance

2.2 Preparation of Coatings

For preparations of nano-coatings, mild steel is selected as the base material and its chemical composition is given in Table 1 while the electroless bath components, concentrations and their functions is given in the Table 2. The coating duration is three hours and thickness is in the range of 20 to 100 micro meter range. The microstructure and constituent composition of as-plated in addition to heat treated specimens were planned by the help of SEM and EDAX techniques. Their X-ray diffraction (XRD) study was carried out by source of Cu K_α X- rays for identifying phases present. The sufficient grain dimensions of the deposit were calculated by using Scherer equation ($t = 0.9\lambda / B\text{Cos}\theta_B$) where parameter λ is Cu K_α wavelength (λ=1.54 A^0), B is broadening of full width at half maximum furthermore θ_B is the Bragg's angle by intense Ni (111) peak (after removal of instrumental broadening cause (Sharma et al., 2013).

Table 2. Electroless bath components and their functions

S. No.	Salt/Compound chemical formula	Quantity in gram (g) for 100 ml	Function of chemicals
1	Nickel Sulphate ($NiSO_4$)	3.52 g	Source of Ni^{2+} ions
2	Tri-sodium Citrate	4.80 g	Complexing agent, prevent uncontrolled release of Ni^{2+} ions
3	Sodium Acetate	2.20 g each	Work as basic buffer in the presence of ammonia, to maintain the pH
4	Sod. Hydroxide/ Acetic acid10% Solution	Added drop wise	Maintain pH of the solution ~5.5
5	Sodium Hypophosphite	2.10 g	Reducing agent, provide electrons to the Ni^{2+} ions which on accepting electrons get reduced to Ni^0 and deposited on the catalytic surface
6	Sodium Dodecyl Sulphate	0.01g	Increase the wettability and surface charge
7	Lead Acetate	0.10 mg	Stabilizer
8	Synthesized ZrO_2	0.25g	Work as reinforcement into the matrix
9	Synthesized TiO_2	0.25g	Work as reinforcement into the matrix
10	Bath Operating Conditions	-	pH 5.5; Temperature 85-90 °C; constant stirring is required
11	Annealing Temperature	Up to 400 ^{0}C	Understand the consequence of heat on corrosion and wear resistance

2.3 Solutions for Corrosion Tests

Since cooking liquors in different mills are likely to differ in terms of the relative amount of S^{2-}, $S_2O_3^{2-}$, S_x^{2-} and Cl^- , even though having same pH and sulfidity. Therefore, it was decided to prepare test liquors having varying amount of these species. Accordingly, following composition of liquors was planned on the basis of amount of different species observed in different mills; NaOH 80 gpl, Na_2S 20 to 34 gpl (20% - 30% sulfidity level), $Na_2S_2O_3$ 5 to 35 gpl, S_x^{2-} 2 to 20 gpl and Cl^- 1.21 gpl (corresponding to 2 gpl NaCl). The composition and variation of various test solutions is given in Table 3.

Table 3. Concentration and variations of chemicals of long term immersion corrosion test

Solutions	NaOH	Na_2S	$Na_2S_2O_3$	NaCl	pH
1	80±0.40	19.80±0.20	05±0.20	0	13.40±0.20
2	80±0.12	19.80±0.10	15±0.20	0	
3	80±0.18	19.80±0.20	25±0.20	0	
4	80±0.23	19.80±0.20	35±0.30	0	
5	80±0.20	19.70±0.30	05±0.20	02±0.03	
6	80±0.41	19.70±0.20	15±0.20	02±0.02	
7	80±0.43	19.80±0.20	25±0.30	02±0.02	
8	80±0.40	19.80±0.30	35±0.30	02±0.02	

2.4 Long Term Immersion Corrosion Test

The long term immersion corrosion test was conducted for duration of six months in alkaline sulphide solutions under anaerobic conditions having ~ 20% sulfidity. The variation of chemicals during long term immersion corrosion test is given above in Table 4. The materials considered for the test were: MS (mild steel), austenitic stainless steels 304L, 316L, duplex stainless steel 2205 and some non-conventional materials (as an alternate), e.g. electroless Ni-P-TiO_2-ZrO_2 nano composite coatings. The operating parameters and compositions of nano-coatings are given below in Table 2. The long term immersion corrosion test in sulfide solutions was undertaken to understand the effect of varying $S_2O_3^{2-}$ in the presence/absence of Cl^- in sulfide solutions (pH ~ 14), having ~20% sulfidity. The test materials, including autogenously welded part, of stainless steels 304L, 316L and SS2205 of size 2 cm x 2 cm x 0.4 cm along with mild steel and Ni-P-TiO_2-ZrO_2 nano composite coated coupons of 2 cm x 2 cm and thickness 0.5 cm were used. The test materials were cleaned using emery paper from coarse to fine up to 1200 grit on a polishing machine. The cleaned test materials were weighed and their surface area was measured. The serrated washers were also used on the test materials to know the effect of crevice corrosion, prior to putting in the test solutions. The test solutions had to be covered with a layer of paraffin oil to avoid contact of atmospheric oxygen with the solution. The later was found to change the solutions' composition by oxidizing Na_2S to $Na_2S_2O_3$. Hence these solutions are prepared in nitrogenous atmosphere and the tests are being carried under anaerobic conditions. Since the beginning of the test, parameters e.g. pH, sulfidity, $S_2O_3^{2-}$ and Cl^- were monitored weekly by Scan methods.The long term weight loss immersion corrosion experiment is carried out for corrosion rate assessment, where well cleaned weigh up test specimens were exposed at room temperature. Each coupon was fitted by serrated washers for commencing crevice corrosion and is immersed into test solutions (Table 3). After six-month exposure, corroded specimens were cleaned mechanically pursued by dealing with cold solution of concentrated HCl with 20 gpl $SbCl_3$ and 50 gpl $SnCl_2$ (ASTM G1-10, 1991). Corroded specimens were then weighed for estimating weight loss so as to establish corrosion rate by means of subsequent formula

$$Corrosion\ rate\ (mpy) = \frac{3.45\times10^6\times W}{ADT} \tag{1}$$

Where ‘mpy’ is mils per year, ‘W’ is weight loss in grams, ‘D’ is density of metal in gm/cm^3, ‘T’ is exposure time in hours and ‘A’ is area in cm^2.The corroded along with cleaned specimens were examined underneath optical metallurgical microscope (Riechert Jung, USA make) for evaluating pitting and crevice corrosion attack by measuring utmost depth of attack upon open surface along with under serrated washer area of coupon respectively.

3. Results and Discussion

3.1 Long Term Immersion Corrosion Test

The corroded coupons, after taking out from the test solutions were cleaned initially mechanically and later chemically using solution of 50 gpl $SnCl_2$ +20 gpl $SbCl_3$ in concentrated HCl, as per (ASTM G1-10, 1991). The corroded cleaned test coupons were also analyzed (Balaraju, 2003) for any localized attack namely pitting, crevice corrosion and weld related attacks using metallurgical microscope (Reichert Jung, USA). The results are given in Table 4. A visual examination of the corroded specimens, (Figure 2) after cleaning, shows no observable pitting attack but slight crevice attack is visible in case of mild steel samples only. The extent of uniform attack, assessed from corrosion rate, was obtained on the basis of weight loss observed by the samples during the six months’ test. One observes that mild steel experiences maximum corrosion rate. Corrosion rates on stainless steels and Ni-P-TiO_2-ZrO_2 nano-composite coatings are similar and inconsequential. Further Ni-P-TiO_2-ZrO_2 as plated nano-composite coatings shows less corrosion rate than heated Ni-P-TiO_2-ZrO_2 nano-composite coatings. Among all materials, only mild steel shows crevice type attack. A visual examination too shows the crevice attack to be higher in case of samples immersed in solutions having chloride in comparison to those without chloride. Comparison of corrosion rate on MS (mild steel) shows (i) Increase in $S_2O_3^{2-}$ concentration increases corrosion rate (Table 4). (ii) There appears a sudden increase in corrosion rate when concentration of $S_2O_3^{2-}$ increases from 25 to 35 gpl. (iii) Inclusion of Cl^- in the solution also increases corrosion rate in the solution having corresponding amount of $S_2O_3^{2-}$. Corrosion rates of stainless steels and Ni-P-TiO_2-ZrO_2 nano-composite coatings are small and the variation between their values basically replicates the tentative slip-up. Hence there does not appear any definite correlation between corrosion rate experienced by stainless steels/Ni-P-TiO_2-ZrO_2 nano-composite coatings and the composition of the solutions.

(a) (b) (c)

Figure 2. Photographs of corroded coupon (a) MS (b) Ni-P-TiO_2-ZrO_2 (As-plated) (c) Ni-P-TiO_2-ZrO_2 (Heated) Nano-composite coatings after immersion test

Table 4. Corrosion rate of coupons (mils per year) in alkaline sulfide solutions

Materials	Soln.1	Soln.2	Soln.3	Soln.4	Soln.5	Soln.6	Soln.7	Soln.8
MS	0.601	0.981	0.771	3.260	1.112	1.213	1.012	3.256
SS304L	0.210	0.270	0.340	0.320	0.370	0.410	0.400	0.440
SS316L	0.100	0.210	0.260	0.240	0.280	0.270	0.313	0.300
SS2205	# NMA	0.010	0.014	0.013	0.020	0.021	0.011	0.019
Ni-P-TiO_2-ZrO_2 (As-plated)	0.110	0.200	0.231	0.212	0.217	0.214	0.233	0.310
Ni-P-TiO_2-ZrO_2 (Heated)	0.201	0.216	0.231	0.300	0.304	0.340	0.311	0.342

NMA- No Measurable Attack

4. Conclusions

The microscopic examinations SEM, XRD, EDAX reveal Ni-P-TiO_2-ZrO_2 nano-composite coating is successfully deposited on mild steel base coupon. As-plated coupon is amorphous and heated coupon is crystalline in nature. From long term immersion corrosion test in sulphide solutions, a visual examination of the corroded specimens, after cleaning, shows no significant observable pitting attack but crevice attack is visible in case of mild steel samples only. Further crevice attack is to be higher in case of sample immersed in solutions having chloride in comparison to those without chloride. Comparison of corrosion rate shows (a) Inclusion of Cl^- with $S_2O_3^{2-}$ in the solution increases corrosion rate suddenly. One observes that mild steel experiences maximum corrosion. Corrosion rates on stainless steels and nano composite coated coupons are low as well as show roughly analogous behavior.

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