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Electrochemical Corrosion Behaviour of Electroless Ni-P-CNF Nano-coatings in Peracid Solutions

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ABSTRACT

In the current work, Ni-P-CNF nano-coatings are deposited successfully on a mild steel (AISI 1040) substrate material by an electroless method. After coatings on the coupons, the basic composition and microstructure of as-coated and heated coupons were investigated by SEM method. The SEM micrograph of as-coated coupon reveal amorphous and uniform structure with hollow tubes of diameter roughly 20 to 90 nm range while heated coupons turn out to be more close packed with no major change in diameters of CNF hollow tube. The scanning electron microscope results specify attachment of carbon nano fibers into an electroless Ni-P matrix. The electroless Ni-P-CNF (as-coated) coupon shows better corrosion resistance than Ni-P-CNF (heated) coupons.

Keywords: electroless, coating, Ni-P-CNF, SEM, electrochemical, corrosion etc.

I.INTRODUCTION

Paper manufacturing industry is executing non-chlorine chemicals e.g. hydrogen peroxide, peracids, ozone etc. for bleaching with the endeavor of reducing greenhouse gasses and toxic wastes. The peracids explicitly peracetic acid (P_a), Caro's acid (P_x) and (P_{xa}) mixture of P_a and P_x, have been used as brightening driving force and as activating agent for lignin. Chemically, Pa is CH_3COOOH with molecular weight of 76.05 and active oxygen as 21% whereas, P_x is peroxymonosulfuric acid (H_2SO_5) having molecular weight of 114.08 gram and 14% active oxygen content. The peracids are favored for bleaching over the latter two substitutes on description of their superiority with regard to associated safety hazards, ingredient costs and effluent loads [1, 2]. The efforts are still continuing on to search possible futuristic materials of construction for bleach plant section which is also the most corrosive section of paper industry. In recent time, electroless (EL) coatings have set on extensive popularity in all industries such as petrochemicals, automobiles, space, nuclear, textile and paper etc. owing to its capability to produce uniform, hard, wear, friction and corrosion resistant surfaces [3-10]. Among the electroless coatings with different nano-particles, the CNF nano-particle is the most important chemical due to its low cost, high hardness, wear/corrosion resistance and important physical properties. Considering the above useful properties of CNF nano-particles, the Ni-P-CNF nano composite coatings are synthesized by electroless method. To understand the corrosion protection mechanism of these coatings, electrochemical corrosion tests are performed on EL Ni-P-CNF nano composite coated coupons in per acid solutions under alkaline condition (simulating to future bleach plant condition).

II.MATERIAL AND METHODS

2.1. Materials

The electroless Ni-P-CNF coated cylindrical coupons were used for electrochemical corrosion tests. All the test samples were solution annealed as per ASTM specification A240 [4]. All the cylindrical coupons have dimension 10 mm × 11 mm. For non-conventional materials (EL Ni-P-CNF nano-composite coatings), the elemental composition of base mild steel (MS) coupon (used as substrate material for coatings) is listed as; carbon (0.181 %), silicone (0.042 %), manganese (1.64 %) and rest iron (Fe balance).

2.2. *Electroless unit (EU)*

The coating unit has a magnetic stirrer (Remi model), a heater having temperature ranges 0 to 100 °C also an agitator have a rate 0 to 400 rpm. A glass beaker (500 ml volume) with electroless bath solution (300 ml volume) is positioned upon a heating base. The agitator rate and bath temperature are set with assist of speed setting and temperature sensing grip respectively. The intention of magnetic agitator is to adopt nano particles dispersion in underneath of glass beaker [5-9].

2.3 Characterization of surface coatings

The microstructure examination of as-plated and heated coupons of Ni-P-CNF was analyzed with the help of SEM methods. The adequate grain magnitudes of deposits were calculated by Scherer equation ($t = 0.9\lambda/ B \cos \theta_B$) where factor ‘$\lambda$’ is Cu K_α ($\lambda = 1.51$ A^0) wavelength, ‘B’ is extension of absolute width at half maximum and ‘θ_B’ is Bragg’s angle by burly Nickel (111) peak (subsequent elimination of instrumental broadening grounds [7, 8-10].

2.4 Composition and Concentration of Peracetic Acid (P_a) Solutions

The test samples are exposed into peracid solution namely peracetic acid (P_a) prepared as described previous [11]. Consequently, P_a was prepared by adding glacial acetic acid to hydrogen peroxide (1 molar ratio each) containing 1 ml. of concentrated sulfuric acid as a catalyst. The mixture was then warmed to 45^{0}C, held at this temperature for two hours, and stored overnight in a refrigerator to allow the mixture to come into equilibrium. The % A.O. was calculated as mentioned by [11]. The NaCl was added in the solutions to get desired level of Cl^- ions. The pH of these solutions is kept as pH 8.0 (best bleaching range of pH is 5 to 9 for peracids by adding required amount of 10% NaOH solution. Table -1 gives test conditions and composition of solutions.

Table 1: Chemical composition of the Peracid solutions

Solution	**Chemical Charge (%A.O.)***	**pH**	**Chloride (ppm)**	
			0 ppm	400 ppm
Peracetic acid (Pa)	0.40±0.05	8.0±0.2	P_{ao}	P_{acl}

* A. O. – Active Oxygen

2.5 Electrochemical Corrosion Tests

The electrochemical corrosion tests namely E versus time (OCP), potentiodynamic and cyclic polarization tests were conducted in peracetic acid ($P_{a)}$ solutions having pH 8.0. For electrochemical tests, a potentiostat PGZ 301 and polarization cell (having five necks meant for a working electrode, two counter electrodes, a reference electrode; SCE and one for gas purging) was used. Open circuit potential (OCP), Corrosion (E_{corr}), pitting (E_p) and re-passivation potential (E_c) were evaluated from these electrochemical corrosion tests

III.RESULTS AND DISCUSSIONS

3.1 Characterization of coatings

The microstructure photograph of electroless Ni-P-CNF (heated) depositions, before exposure in solutions is shown in Figure 1. The SEM micrograph of electroless Ni-P-CNF (as-plated) nano-composite coated coupon divulge compressed, nebulous and consistent flakes structure with void tubes of diameter 20 to 90 nm range. When coated coupons are heated at 400 ^{0}C for one hour duration under Argon atmosphere, globules of (Ni) nickel and (P) phosphorus with fine discrete CNF nano-particles twirl out to close packed (Figure 1) and these consequences are also in agreement of prior studies [3-10].The small quantity of surfactant (SDS) into Ni-P electroless bath is major motive for homogenous allotment of CNF nano-particles on the base surface.

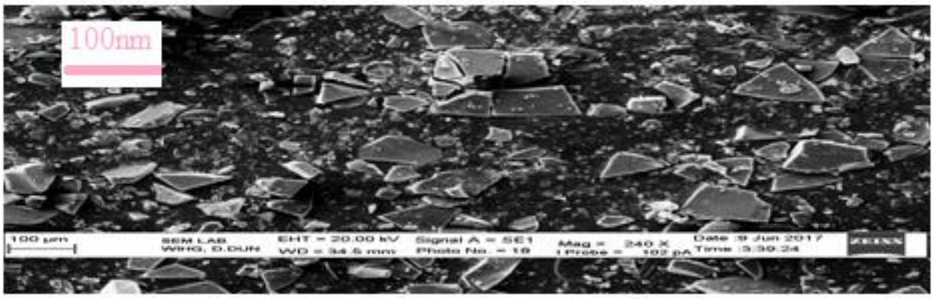

Figure 1: SEM image of Ni-P-CNF (Heated) electroless nano coated coupon

3.2 Corrosivity of solutions

The anodic/cyclic polarization curves along with corrosion values are specified in table 2 and figure 2. The table 2 shows that the OCP's of different materials are higher than their respective E_{corr} in all peracid solutions. The OCP's of all coupons in P_{ao} solution are nobler than P_{acl} solution, which indicates lesser corrosivity of P_{ao} solutions. In P_{ao} solutions, no pitting was observed under microscope (6.5X), in all samples. However, the anodic polarization curves in these solutions show a kink indicating onset of pitting around 950 to 1100 mV in most cases. Cyclic polarization curves, in these cases, also show hysteresis behavior when polarization scan reverses to cathodic direction on reaching vortex potential. This is an indication that pits were formed and now have started passvating. Probably the pits formed were not observable under the microscope, due to their small size, but their effect is clear in polarization curves. In general, P_a solutions are very corrosive due to the nature of peracetic acid solution. The polarization curves of EL Ni-P-CNF (As-plated) depositions illustrate steady passive character seeing that almost erect passive section. The character of heated curves is not vertical any longer which indicate elevated currents at given potential. The EL Ni-P-CNF (Heated) depositions depict low corrosion resistance in compare to as-plated coupons. Although heated depositions can be suggested for application in cases where impulse is for improved triobological behavior along with not so corrosive environment.

Table 2: Electrochemical corrosion parameters (in mv)

Materials	**Corrosion parameters (mv)**	**Solution (P_{ao})**	**Solution (P_{acl})**
Ni-P-CNF (As-plated)	OCP	127	101.2
	Ecorr	81	93
	E_p	994	962.1
	Passivation (E_c - Ecorr)	928.5	880
	Corrosion rate (mpy)	0.53	1.8
Ni-P-CNF (Heated)	OCP	112	110
	Ecorr	87	89.4
	E_p	944	862
	Passivation (E_c - Ecorr)	901	843
	Corrosion rate (mpy)	0.74	2.1

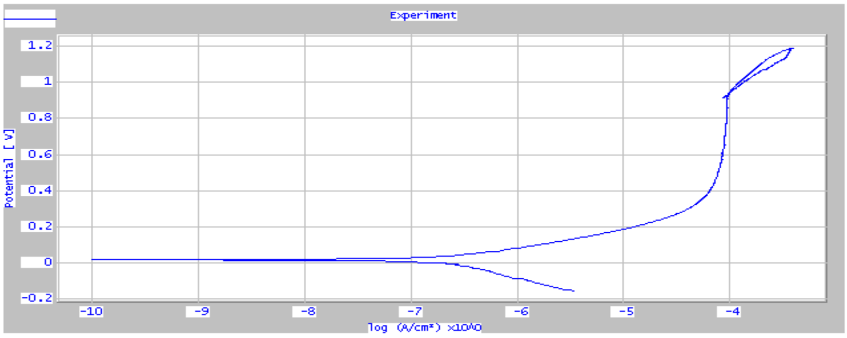

Figure 2: Electrochemical curve of Ni-P-CNF (Heated) in Peracid (Pacl) solution

IV. CONCLUSIONS

Thus result obtained from electrochemical corrosion tests in terms of corrosion rate, pitting potential (E_p) and passivation range for all samples in peracid solutions reveals degree of corrosion resistance varies as Ni-P-CNF (as-plated) > Ni-P-CNF (heated). The use of EL Ni-P-CNF nano composite coated coupons is doubtful in view of the electrochemical measurements so Immersion and in-plant corrosion test should also be performed for better understanding.

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