

Corrosivity of Peracetic Acids Against Electroless Ni-P-CNF Nanocomposite Coatings

Manoj Kumar Dhiman¹, Sulaxna Sharma^{2*}, Awanish Sharma^{1*}

¹(Department of Physics, Graphic Era Deemed To Be University, Dehradun, India)

²(Department of AS&H, THDC, Institute of Hydropower Engineering and Technology, Tehri, India)

*Corresponding Authors: Manoj Kumar Dhiman

Abstract: In recent innovative work, the electroless Ni-P-CNF nano-composite plating has been deposited upon basic mild steel substrate. The 5 gpl activated CNF nano-particles were incorporated into an acidic electroless Ni-P matrix as a second phase material and were reduced by a reducing agent named as sodium hypophosphite. After plating, as-prepared Ni-P-CNF EL deposition were heated at 400 °C in Argon atmosphere for one hour period and were analyzed. A low bulk allocation of CNF nano-particles into EL Ni-P matrix is recognized through analysis of SEM and EDAX. The peracetic acid solutions with chloride are more corrosive than without chloride. The corrosion resistance of the conventional materials and Ni-P-CNF coated samples are in following order as SS2205 > Ni-P-CNF (As-plated) > Ni-P-CNF (Heated) > 316L > MS.

Date of Submission: 31-08-2018

Date of acceptance: 15-09-2018

I. Introduction

Paper manufacturing industry is implementing non-chlorine chemicals e.g. hydrogen peroxide, peracids, oxygen, ozone etc. for bleaching with the endeavour of reducing green house gasses and toxic wastes. The peracids explicitly peracetic acid (PA), caro's acid (PX) and (PXA) mixture of PA and PX, have been used as driving force for lignin removal from pulp. Chemically, PA is peracetic acid (CH₃COOOH) with molecular weight of 76.05 gram and active oxygen as 21% whereas, PX is peroxy-mono-sulfuric acid (H₂SO₅) having molecular weight of 114.08 gram and 14% active oxygen content. The peracids are well thought-out as a very effective chemical for bleaching of pulp as peroxide and ozone. The peracids are favoured over the latter two substitutes on description of their superiority with regard to associated safety hazards, ingredient costs and effluent loads, Amini et al,¹ and Liebergott². It has been observed that with the use of these newer chemicals, their corrosive consequences on industrial equipments have also been occurred. Varjonen et al,³ while studying corrosion of Ti in peroxide found that MgSO₄ was not an effective inhibitor, in contradiction to Macdiarmid et al.,⁴. Pehkonen et al.,⁵ studied corrosion of stainless steel in ozone and peracetic acid without Cl⁻. Singh et al.,^{6,7} and Sharma et al.,⁸ recently studied corrosive effect of peracids with acidic and alkaline pH under different chloride concentration. The efforts are still continuing on to search possible futuristic materials of construction for bleach plant section (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 surfaces⁹⁻¹⁸. This coating method can incorporate soft particles (PTFE, MoS₂, HBN and graphite etc.) and hard particles (SiC, WC, Si₃N₄, CeO₂, TiO₂, ZrO₂, CNF, CNT and diamond etc.) for receiving higher hardness, wear, friction and corrosion resistance and to provide better lubricant^{9,10,12-15,16-22}. With the intention of further improving tribological and corrosion resistance properties, recent attempts have been made to incorporate nano sized hard particles such as TiN, CNF, ZrO₂, TiO₂ and Al₂O₃ etc. into EL Ni-P matrix. Among above these 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, the long term weight loss test plus electrochemical corrosion tests are performed on EL Ni-P-CNF nano composite coated coupons and conventional materials (mild steel, SS 316L, SS2205) in per acid solutions under alkaline condition (simulating to bleach plant condition). All the corroded samples after exposure in per acid solutions were evaluated for localized and uniform corrosion for their possible use in per acid bleach plant section.

II. Experimental

Materials Selection: For corrosion tests, plate coupons of mild steel (MS), austenitic stainless steel 316L, EL Ni-P-CNF coated and duplex stainless steel 2205 were selected for the weight loss test and coupons of above materials (except mild steel) were used for electrochemical corrosion tests. The compositions of all stainless steels for plate coupons are given in Table-1. All the test samples were solution annealed as per¹⁹. Before exposure, the coupons of all steels were fine polished up to 1200 grit SiC emery paper, then degreased using acetone solution and weighed in case of weight loss test. All the base coupons have dimensions 20 mm × 20 mm × (3 to 4) mm and cylindrical coupons have dimension 10 mm × 11 mm. For non-conventional materials (EL Ni-P-CNF nano-composite coatings), the elemental composition of 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).

Table 1 : Composition of plate type test materials for immersion corrosion test

| Alloys | C | Cr | Ni | Mo | P | Cu | Mn | S | Si | N |
|--------|-------|-------|-------|------|-------|------|------|-------|------|-------|
| MS | 0.180 | - | - | - | - | - | 1.66 | - | 0.04 | - |
| SS316L | 0.019 | 17.43 | 11.26 | 2.03 | 0.027 | 0.40 | 1.11 | 0.002 | 0.50 | 0.048 |
| SS2205 | 0.022 | 22.13 | 5.55 | 3.16 | 0.02 | 0.21 | 1.47 | 0.001 | 0.35 | 0.188 |

Fe balance

Preparation of EL Ni-P-CNF Nano-composite Coatings: The Ni-P-CNF (5 gpl CNF nano-particles well disperse into acidic EL Ni-P medium) nano-composite depositions are plated on base coupons of mild steel material through the electroless method. The detailed procedure of EL coating method is given elsewhere^{10,21}. For the heat behaviour study, the EL nano composite coupons (base and cylindrical) were put at 400 °C in tube heating system (1h period, Ar inert gas atmosphere) as well as then were cooled into furnace up to surrounding temperature.

Composition and Concentration of Peracetic Acid (PA) Solutions: The test samples are exposed into peracid solution namely peracetic acid (PA) prepared as described earlier, Amini¹. Accordingly, PA 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 45⁰C, held at this temperature for two hours, and stored overnight in a refrigerator to allow the mixture to come to equilibrium. The % A.O. was calculated as mentioned by¹. 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 peracids¹, by adding required amount of 10% NaOH solution. Table-2 gives the test conditions and composition of the solutions.

Table 2: Chemical composition of the peracid solutions

| Solution | Chemical (%A.O.)* | Charge | pH | Chloride (ppm) | |
|---------------------|-------------------|--------|---------|----------------|---------|
| | | | | 0 ppm | 400 ppm |
| Peracetic acid (Pa) | 0.40±0.05 | | 8.0±0.2 | PA (O) | PA(Cl) |

* A. O. – Active Oxygen

Immersion Corrosion Test: An immersion corrosion test was conducted in the present investigation. In this test, all the well prepared base coupons were exposed in peracid solutions for duration of six months at room temperature (Figure-1). Each coupon was immersed in the solutions with the serrated washers for initiating crevice corrosion. During the immersion test, % active oxygen (% A.O.), Cl⁻ and pH of the test solutions were monitored and maintained each day. While pH and Cl⁻ did not change much (±0.2 and ±30 ppm respectively), decrease in % A.O. was compensated, to keep it within limit as per Table-2, by adding requisite amount of peracetic acid (PA). After the exposure, the corroded coupons were cleaned mechanically and by treating with cold solution of concentrated HCl with 50 gpl SnCl₂ and 20gpl SbCl₃^{9,16,17,23}. The corroded coupons were then weighed for determining weight loss and corrosion rate (formula) and viewed under the optical metallurgical microscope for estimating the extent of localized attack.

$$\text{Corrosion Rate (mpy)} = \frac{534W}{DAT} \quad (i)$$

Where 'W' is equal to weight loss in mg, 'D' is density of steel 7.8 gm/cm³, 'A' area of coupons in inch square and 'T' is time exposure in hours Table-3.



Figure 1: Photographs of long term immersion corrosion test



(a) (b) (c)

Figure 2: Corroded coupons after long term corrosion test (a) MS (b) Ni-P-CNF (As-plated) and (c) Ni-P-CNF (Heated)

Table 3: Corrosion attack on coupons exposed in peracetic acid (pH 8.0) solution

| Solutions | Corrosion Parameters | Samples for Immersion Test | | | | |
|-----------|----------------------|----------------------------|--------|----------------------|-------------------|--------|
| | | MS | SS316L | Ni-P-CNF (As-plated) | Ni-P-CNF (Heated) | SS2205 |
| PA(0Cl) | Corrosion rate (mpy) | 15.27 | 0.32 | 0.23 | 0.34 | 0.003 |
| | Pitting attack(μm) | NMA | 33 | 28 | 31 | NVA |
| | Crevice attack(μm) | 51 | 38 | 26 | 34 | NVA |
| PA(Cl) | Corrosion rate (mpy) | 19.49 | 0.41 | 0.29 | 0.37 | 0.02 |
| | Pitting attack(μm) | 60 | 35 | 31 | 36 | 13 |
| | Crevice attack(μm) | 65 | 34 | 32 | 38 | 15 |

NMA No Measurable Attack

NVA No Visible Attack

III. Results and Discussions

Characterization of Composite Coatings

Microstructures photograph of materials MS, SS316L, SS2205, EL Ni-P-CNF (As-plated) and Ni-P-CNF (Heated) depositions, before exposure in solutions are shown in Figure 3. The main results of XRD, SEM-EDAX study are discussed below.

The SEM micrograph of Ni-P-CNF (As-plated) EL nano-composite coated coupon reveal low dense, amorphous structure with some tubes. When the nano composite coated coupons are heated at 400 °C for one hour duration under Argon (Ar) atmosphere, the globules of nickel and phosphorus with well dispersed CNF nano-particles turn out to be more close packed with no major change in diameters of CNF hollow tubes (Figure 3) and these consequences are also in accordance of earlier studies^{12,16,18}.

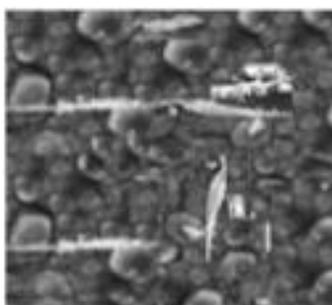
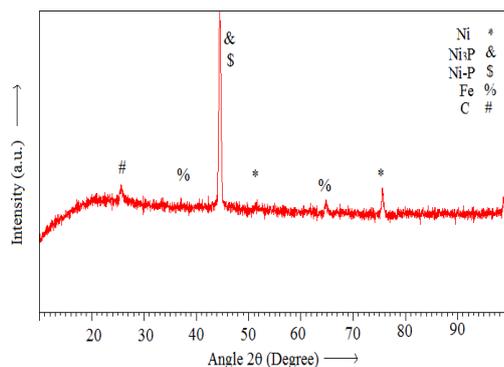


Figure 3: SEM micrographs of Heated; EL Ni-P-CNF coatings



Figures 4: XRD micrograph of Ni-P-CNF (Heated) nano-composite coating

Table 4: EDAX analysis of Ni-P-CNF nano-composite coatings

| Elements | Weight % | |
|----------|----------------------|-------------------|
| | Ni-P-CNF (As-plated) | Ni-P-CNF (Heated) |
| Ni K | 85.28 | 83.73 |
| P K | 9.51 | 9.34 |
| Fe K | 3.0 | 4.76 |
| C K | 2.21 | 2.17 |
| Total % | 100 | 100 |

The EDAX analysis (Table-4) recognized that EL Ni-P-CNF nano-composite coating (As-plated) consisting of 5 gpl of CNF nano-particles have 85.28 wt% of nickel, 9.51 wt% of phosphorus, 3.0 wt% Fe and 2.21 wt% of C while the heated coating have 83.73wt% of nickel, 9.34 wt% of phosphorus, 4.76 wt% Fe and 2.17 wt% C. It is noticeable from the EDAX analysis that quantity of coating elements Ni, P and C decreases on heating while that of Fe increases. This result suggests diffusion of coating element towards interface of coating and substrate surface and increased corrosion in heat treated coupons⁹⁻¹⁷. The XRD patterns of Ni-P-CNF (As-plated) EL nano-composite coatings reveals that coating is amorphous in character as a single wide peak is available at the diffraction angles (2 θ) 43.8 $^{\circ}$ and a small peak of CNF appears at approximately 26.1 $^{\circ}$. The single broad peak at 43.8 $^{\circ}$ is an indication of Ni and Fe presence. The XRD pattern (Figure 4) of Ni-P-CNF EL nano-composite coating (heat treatment at 400 $^{\circ}$ C for one hour duration) demonstrates the transformation of amorphous phase into characteristic crystalline phase. The flutter peak of CNF appears at approximately 26.2 $^{\circ}$ and it is exceedingly co-identical with the graphite peak. The Ni₃P phase is also formed in the Ni matrix. The peaks of Ni are observed at diffraction angles of 52.4 $^{\circ}$ and 76.1 $^{\circ}$ and for Fe as a substrate at 36.3 $^{\circ}$ and 65.2 $^{\circ}$. The uppermost peak of Ni₃P is observed at diffraction angle of 44.4 $^{\circ}$. The evidences identical to (111), (200) plus (220) planes and FCC phase of Ni can be experienced. The grains are in variety between 12 nm to 35 nm for CNF nano particles. The grains get roughness because of heating which assist in growing hardness plus wear resistance of depositions¹⁶⁻²³. In Figure 4 for heated sample, the entire reflections are almost equal by means of orientation of (JCPDS 01 to 1260; FCC Ni) and (JCPDS 34 to 0501; BCC Ni₃P),(JCPDS 75-2078; CNF) (JCPDS 35-0772; Fe₃C) and (JCPDS 13-0534; Fe). The low quantity plus high dispersion of CNF nano-particles into EL Ni-P medium is responsible for small peaks as well as Ni-P peaks are not shifted^{9-12,16-18}. The breadth of main peak of Ni (111) point out grain proportions are in range of 7.2 to 16.1 nm^{9-12,16-18}.

Corrosivity of Solutions

Corrosion rates of mild steel, EL Ni-P-CNF nano composite coated coupons and stainless steels, determined on the basis of long term immersion test, in general, show PA (Cl) solutions to be more corrosive than PA (Cl) solutions. The results of this test reveal high degree of uniform corrosion on mild steel (15.27 and 19.49 mpy) as is evident from corrosion rates (Table -3). So, mild steel has to be ruled out as a material of construction for handling these media at alkaline pH. In case of EL Ni-P-CNF nano composite coated coupons and SS316L, SS2205 stainless steels, uniform corrosion is low (variation is from 0.003 to 0.41mpy) hence suitability of these materials has to be checked on the basis of localized corrosion attack. On the basis of degree of pitting and crevice corrosion, EL Ni-P-CNF (Heated) coupon and SS316L show similar resistance (variation is from 26 μ m to 38 μ m pit depth) while SS2205 exhibit maximum resistance against localized corrosion attack (variation is from 13 μ m to 15 μ m pit depth). The EL Ni-P-CNF (As-plated) coupon also shows better resistance than Ni-P-CNF (Heated) and SS316L coupons. One observes higher degree of pitting attack on all samples, except SS2205. In one such case, maximum pit depth of 52 μ m was observed on SS316L sample in PA (Cl) solution. Thus in common, PA (Cl) solutions are very corrosive. This can be understood on the basis of equation

prevailing reduction reaction which in turn affect the corrosion of materials and the nature of peracetic acid. Following reduction reactions can be considered to be responsible for corrosion in these solutions:



From the reduction reaction (ii) one negative ion of CH_3COOO^- are responsible for consumption of 2e^- and are considered to be more oxidizing than hydrogen peroxide solutions due to the capability of PA showing electrophilic/ nucleophilic character which is not shown by the peroxides¹. Further a comparison of kinetics of several peroxyacids/peroxides¹, shows that electrophilicity of (PA) CH_3COOOH is greater than that of H_2O_2 . Accordingly, peracetic acid, at a given pH, is likely to show higher corrosivity than peroxides.

Corrosion resistance of Ni-P EL depositions depends largely on three features (i) quantity of amorphous configuration (ii) quantity of P chemical substance in EL plating and (iii) occurrence of inner stresses nm^{9-12,16-23}.

Consequently, examination of decreased corrosion resistance of heated depositions as compared to as-plated can be endorsed to subsequent factors: (i) inspection of wide peaks in as-plated coupons and progressively more pointed peaks in heated depositions point out a greater crystallinity than before. The heating at 400 °C detect crystallization of inter-metallics of Ni-P, Ni-CNF, CNF-P etc. These transformations are outcome of decreased corrosion resistance because of (a) superior grain border region (compared to amorphous surface) and a grain border region being elevated energy locations (b) The inter-metallics are cathodic as contrast to base Ni medium and unswerving to development of galvanic cells (ii) The P in Ni-P depositions make adsorbed deposit of hypophosphite which obstruct water with Ni and offer corrosion protection to depositions^{9-12,16}. In heated coupons decline in quantity of P (EDAX data-Table 5) is supposed to lessen prospect of creation of hypophosphite and create depositions additional susceptible to deterioration. (iii) The variation in (HEC) heat expansion coefficients of MS ($\sim 12.6 \times 10^{-6}/^\circ\text{C}$) and Ni-P ($\sim 11.1 \times 10^{-6}/^\circ\text{C}$) marks in non attachment of deposition plus consequential look of cracks/annulled. This is true by elevated porosity in heated depositions^{6-12,16-23}. The XRD facts of heated depositions demonstrate construction of Ni-P and CNF-P etc. inter-metallics. The EL Ni-P-CNF (Heated) depositions depict low corrosion resistance in compare to as-plated coupons; even though it is improved than MS and SS316L coupons. Consequently heated depositions can be recommended for application in cases where compulsion is for enhanced triobological qualities along with not so corrosive environments.

IV. Conclusions

Thus result obtained from weight loss and electrochemical corrosion tests in terms of corrosion rate, pitting potential (E_p) and passivation range for all samples in peracid solutions, degree of corrosion resistance varies as SS2205 > Ni-P-CNF (As-plated) > Ni-P-CNF (Heated) ~ SS316L > MS. A suggestion is now given about the appropriate material for handling peracid solutions. On the basis of immersion corrosion test and criterion by^{6,7}, SS316L and MS are not appropriate for peracid solutions. The use of EL Ni-P-CNF nano composite coated coupons is doubtful in view of the electrochemical measurements. Immersion and electrochemical corrosion tests show better performance of duplex SS2205 material. The application of material SS2205 is also more cost effective on the basis of its improved cost/strength ratio in addition to better corrosion resistance. The hardness and wear measurements illustrated better performance of Ni-P-CNF nano-composite coatings than some conventional/Ni-P materials.

References

- [1]. Amini B. and Webster J. - On-site peracids : Tools For Bleaching Strategies to meet the Cluster Rule, and considerations on how to select among them, Proc. Tappi Intl. Pulping Conf., Atlanta, p 371 (1994)
- [2]. Liebergott N. - Peracid Delignification and Bleaching, Proc. Tappi Intl. Pulping Conf., Atlanta, p357 (1994).
- [3]. Varjonen, O.A. and Hakkarainen, T.J., Tappi J. 78(6): 161 (1995).[7]
- [4]. Macdiarmid, J.A. and Reichert, D.L., Proc. International Symposium on Corrosion in Pulp & Paper Industry, Atlanta, p 99 (1992).
- [5]. Pehkonen, A., Salo, T., Aromaa, J. and Forsen, O. Pulp & Paper Canada 101(4):T104(2000)
- [6]. Singh, R. and Singh, A.K. Tappi J. 78(12): 111 (1995).[9]
- [7]. Singh, A.K., Gaur (54) B., Rao, N.J.; "Corrosion of mild steel in hypochlorite solution- An electrochemical and weight loss study", IJCT, Vol 1, No.7, P 225, 1994
- [8]. A. Sharma, "Corrosion Investigations in Pulping and Bleaching media", PhD. Thesis, Indian Institute of Technology Roorkee, 2006.
- [9]. K. Ravindranath and S.N. Malhotra, "Influence of aging on intergranular corrosion of a 5 % Cr 5% Ni duplex stainless steel", Corrosion-NACE, Vol. 50, pp. 316-319, 1994.
- [10]. J.N. Balaraju, T.S.N. Sankara Narayanan and S.K. Seshadri, "Electroless Ni-P composite coatings", *J. Appl. Electrochem*, vol. 33, pp. 807-816, 2009
- [11]. A. Grosjean, M. Razrazi and P. Bercot, Surf. Coat. Technol. 130 (2000) 252
- [12]. P Gadhari and P. Sahoo, 'Improvement of Corrosion Resistance of Ni-P-Al₂O₃ Composite Coating by Optimizing Process Parameters Using Potentiodynamic Polarization Test', *Portugaliae Electrochimica Acta* 32(2) (2014) pp. 137-156.
- [13]. R. Parkinson, "Properties and applications of electroless nickel", http://www.nipera.org/~Media/Files/TechnicalLiterature/PropertiesAndApplicationsOfElectrolessNickel_10081_.pdf.

- [14]. G.O. Mallory, "Products finishing magazine", reprinted courtesy Allied-Kellite Products Division (originally presented at Electroless Nickel Conference, 6-7 Nov., Cincinnati, OH, 1979).
- [15]. A. Brenner and G.E. Riddell, "Nickel coating on steel by chemical reduction," *Journal of Research of National Bureau of Standards*, vol. 37, pp. 31–34, 1946.
- [16]. W. Yating, S. Bin, L. Lei and H. Wenbin, "Artificial neural network modelling of plating rate and phosphorus content in the coatings of electroless nickel plating", *Journal of Materials Processing Technology*, vol. 205, pp. 207–213, 2008.(Cross references cited therein)
- [17]. Crowe, D.C."Stress Corrosion Cracking of Carbon Steel in Kraft Digester Liquor". Proc. of 8thIntiSympo on corrosion in pulp and paper industry, pp. 38, 1989.
- [18]. Superbatch:The most advanced cooking technology (Technical Publication of Sunds defibrator,Sweden,1993).
- [19]. Metals Handbook 9th Edition, Volm. 13 Corrosion, (ASM International, USA).
- [20]. Powder Diffraction File, Joint Committee on Powder Diffraction Standard (JCPDS file).
- [21]. A. Sharma and A.K. Singh, "Electroless Ni-P and Ni-P-Al₂O₃ Nanocomposite Coatings and Their Corrosion and Wear Resistance", *J. Mater. Eng. Perform*, Vol. 22, pp. 176-183, 2013.
- [22]. A. Wensley, "The High Cost of Corrosion", *Pulp & Paper Canada Journal*, 105 (5), 10, 2004.
- [23]. ASTM GI-10, Vol.03.02, 'Preparing, cleaning and evaluating corrosion test specimens' (1991)

IOSR Journal of Applied Physics (IOSR-JAP) is UGC approved Journal with Sl. No. 5010, Journal no. 49054.

Manoj Kumar Dhiman" Corrosivity of Peracetic Acids Against Electroless Ni-P-CNF Nanocomposite Coatings." IOSR Journal of Applied Physics (IOSR-JAP) , vol. 10, no. 5, 2018, pp. 41-46.