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Hardness Resistance Investigations on Novel Electroless Ni-P-X ($X=Al_2O_3$ -ZrO_2) Nano-composite Coating

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Abstract: *The Ni-P-X EL nano-composite coatings are obtained by the immersion of the substrate material (Mild Steel, MS AISI1040) into electroless bath solution having second phase alumina and zirconia particles respectively. Microstructure and constituent composition of as-plated and heat treated specimens were analyzed by SEM and EDAX techniques and for electrochemical testing, as-plated and heat treated cylindrical samples were employed. The SEM results indicated the supplement of Al_2O_3 and ZrO_2 nano-particles separately into an EL Ni-P matrix and were confirmed through EDAX analysis. When the coated specimens were heated at 380°C for 1 hour in argon atmosphere, nano-particles turned out to be closely packed which suggest an improvement in hardness resistance of EL nano-composite coatings.*

Keywords*: Electroless coating, EDAX, hardness, SEM, XRD*

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I. Introduction

In all the process industries it is experienced that corrosion and wear phenomenon results thrashing of plant competency and sporadically a shutdown of all industrial plants. The industries such as mining, mineral processing, petro-chemical and chemical processing, pulp and paper production, textile, automobile and energy production are badly affected due to corrosion and wear phenomenon both. In copious applications, it has been observed that surface properties of plant materials such as hardness, corrosion and wear and abrasion resistance can be efficiently enhanced by techniques like carburizing, laser hardening, nitriding, flame hardening, internal oxidation, chemical and physical vapor deposition etc. The above mentioned techniques also look more economical options rather than improving the bulk properties of plant materials. Currently, metal deposition processes (eletro- and electroless depositions) are getting munificent attention due to their amazing advantages such as simplicity, uniformity of deposits, low cost, high deposition rate and well-brought-up wear and corrosion resistance properties. In recent times, electroless (EL) coatings have put on extensive popularity in petrochemicals, automobiles, space, nuclear, textile and paper, computer, opto-electronics, food casing, printing and in scientific domain, owing to its capability to produce hard, wear and friction resistant, antibacterial and corrosion resistant surfaces [1-4]. Electroless (EL) coating is an auto-catalytic procedure in which reduction of metallic ions and coating deposition can be conceded elsewhere through oxidation of reducing agent. The substrate develops a potential when it is dished in electroless bath, which hold a resource of metallic ions, reducing driving force, complexing agent, stabilizer, additives and drenched agents etc. due to the developed potential, both positive and negative ions are attracted towards the substrate surface and release their energy through charge transfer process [5-13]. The review papers [13-27] confer chromate, fluoride, phosphate, stannate, rare earth metals on Mg and its alloys by electroplating and electroless procedures. Therefore, the current study covenants with the synthesis and assessment of hardness resistance behavior of Ni-P-Al_2O_3 (NiPA) and Ni-P-ZrO_2 (NiPZr) EL nano-composite coatings. The surface morphology and compositions of Ni-P-Al_2O_3 (NiPA) and Ni-P-ZrO_2 (NiPZr) EL nano-composite coatings (as-plated and heat treated) are considered with the help of SEM, EDAX and XRD studies [28-35].

II. Material And Methods

2.1. Mild steel material

In contemporary study mild steel (MS, AISI 1040) having proportions 20 mm × 20 mm × 4 mm (flat coupons) and proportions 10 mm × 11 mm (cylindrical coupons) is selected as substrate material for NiPA and NiPZr EL nano-composite coatings. For substrate sample preparation, shaping, parting, milling and surface grinding course of action are adopted. After above processes, substrate surface is mechanically cleaned by

distilled water and a pickling action is lay down with dilute (50 %) HCl for diminutive time to get rid of any surface rust pursue by rinsed with distilled water and methanol cleaning. The glowing polished, cleaned sample was then immersed in 1% aqueous solution of $SnCl_2$ (2-3 drops of 1M HCl was added to dissolve $SnCl_2$) for 40 seconds to activate the substrate face. The substrate sample was subsequently washed by resources of distilled water and air dried. Soon after the substrate sample is erect active by dipping it into a mild hot palladium chloride solution (55 °C, $PdCl_2$) followed by distilled water washing and air dry. Now the well activated substrate sample is dipped into EL bath solution retain at 85 °C and nano composite coating is conceded out of a time of two to three hours.

2.2. Electroless coating bath unit

It consist a magnetic stirrer (Remi make) with heater and temperature ranges launch 0 to 100 °C with stirrer rate 0 to 400 rpm. A fixed stand is provided for holding and supporting the substrate sample and thermometer. A glass beaker (250 ml volume) roofed with electroless bath (200 ml volume) is positioned on to the heating plate. The stirrer rate and bath temperature are put with help out of speed setting and temperature sensing grip. The purpose of magnetic agitator is to maintain nano-composite particles in suspension keep away from of agglomeration in underneath of glass beaker. Bath composition and working conditions for EL NiPA and NiPZr nano-composite coatings are selected after copious experiments and apposite range of parameters are prepared.

Coating thickness is calculated by means of formula

$$\text{Coating thickness (t in µm)} = \frac{W \times 10^4}{D \times A}$$

Here W plunk for weight gain (g), D is the density of deposits (7.75 g/cm^3 for deposits) and A is surface area of deposition (cm^2). The deposition rate (µm/h) was measured as thickness of coating set down per unit time of deposition [35]. In the current work, coating thickness is established in variety of 19 to 25 µm. When coating is over, coated coupons are washed by distilled water and dried in air. To make out the conclusion of annealing on corrosion resistance of EL nano-composite coatings, coated coupons are annealed in furnace for 1 hr period at temperature (380 °C) according to an orthogonal display. Consequent to annealing, coated coupons are cooled to room temperature.

2.3 Characterization techniques used for surface coatings

The microstructure and constituent composition of as-plated and heat treated specimens were calculated 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 ($t = 0.9\lambda / B \cos\theta_B$) where parameter λ is Cu K_α wavelength (λ=1.54 A^0), B is broadening of full width at half maximum and θ_B is the Bragg's angle by the intense Ni (111) peak (after removal of instrumental broadening cause [17, 18-23].

III. Results And Discussion

3.1 Characterization of coatings

From the SEM with EDAX micrographs (Fig. 1) of NiPA and NiPZr EL nano-composite coated (as-plated) coupons it can be concluded that the SEM micrograph of as-plated coupons predicted the supplement of Al_2O_3 and ZrO_2 nano-particles separately into an EL Ni-P matrix which is confirmed by EDAX analysis given in Table 1. This makes improvements in metallic polished surfaces. Also the steady distributions of Al_2O_3 and ZrO_2 nano-particles in their entity class (NiPA and NiPZr) on the coated surface are observed with very little porosity. When the EL nano-composite coated coupons are heated at 380 ^{0}C for one hour under Argon atmosphere, the globules of nickel and phosphorus with well-established Al_2O_3 (in NiPA) and ZrO_2 (in NiPZr) nano-particles turn out to be more close packed.

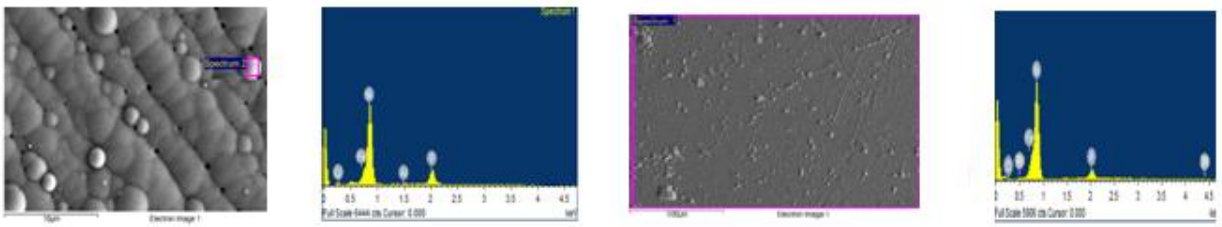

Figure 1: SEM/EDAX of heat treated (a) NiPA and (b) NiPZr coatings

Table 1: EDAX analysis of NiPA and NiPZr coatings

Elements	Weight %			
	NiPA		NiPZr	
	As-plated	Heat treated	As-plated	Heat treated
O K	3.12	2.86	3.02	2.58
Al K	1.54	1.21	-	-
Zr K	-	-	2.21	2.1
P K	11.74	10.87	11.87	11.46
Ni K	81.43	79.64	80.93	79.88
Fe K	2.17	5.42	1.97	3.98
Total	100	100	100	100

The EDAX analysis (Table 1) recognized that EL nano-composite coatings (NiPA and NiPZr) under as-plated conditions consisting of 5 gpl of Al_2O_3 nano-particles have 81.43 wt% of nickel, 11.74 wt% of phosphorus, 3.12 wt% of oxygen, 2.17 wt% Fe and 1.54 wt% of aluminium while 5 gpl ZrO_2 nano-particles, have 80.93 wt% of nickel, 11.87 wt% of phosphorus, 3.02 wt% of oxygen, 1.97 wt% of Fe and 2.21 wt% of zirconium. In NiPZr EL nano-composite coatings phosphorous and second phase nano-particle content is slightly higher than the other case and thus exhibiting the higher fineness and density of the surface structure. The heat treated EL nano-composite coatings (NiPA and NiPZr) have 79.64 wt% of nickel, 10.87 wt% of phosphorus, 2.86 wt% of oxygen, 5.42 wt% Fe and 1.21 wt% of aluminium for NiPA while for NiPZr, have 79.88 wt% of nickel, 11.46 wt% of phosphorus, 2.58 wt% of oxygen, 3.98 wt% of Fe and 2.10 wt% of zirconium. The SEM/EDAX images (Fig.1) of heat treated EL (NiPA and NiPZr) nano-composite plating illustrate happening of several globules on to the base surface. It is also noticeable from the EDAX analysis that quantity of coating element Ni, P, O, Al and Zr decreases on heating while that of Fe increases. This result can be possible because of diffusion of coating element towards interface of coating and substrate surface and increased corrosion in heat treated case [2, 7, 47]. However, less amount of Fe for NiPZr (heat treated) EL nano-composite coating in comparison to NiPA (heat treated) coatings suggests less diffusion of second phase ZrO_2 nano-particles, which make easy to prevent the corrosion phenomenon. The XRD diffraction plots of EL NiPZr nano-composite coatings under as-plated condition suggests that phase is roughly amorphous (more amorphous less crystalline) in character as a single wide peak is available at the diffraction angle of 44.5^0 (Ni) and other very low peak is available at angle of 28.2^0 (ZrO_2). It can be possible because of co-deposition of ZrO_2 nano-particles with high distribution and in very less amount into the Ni-P EL matrix. On the other hand, amorphous phase of NiPZr coating (after heat treatment at 380 °C for one hour duration) gets transformed into roughly crystalline (more crystalline less amorphous) phase and other peaks of Ni and P are noticed at differentdiffractionangles. [21-43,47].

3.2 Investigation of hardness resistance

The hardness of as-plated and heated (380 ^{0}C) EL NiPA and NiPZr nano-composite specimens is determined by micro hardness tester machine having a Vickers diamond indenter. For hardness testing, plated coupons are selected of dimensions 30 mm x 30 mm x 4 mm with 50 g load for 10 seconds settle time as well as indentation speed 50µm/sec. The average of five results is taken as hardness value (Table2). The hardness test results substantiate that micro-hardness of NiPAZr depositions is maximum and NiPA is least. The heat healing improved micro-hardness extensively due to precipitation of hard Ni_3P particles in all coupons. The better hardness acquired for heat treated depositions is as dispersion escalation of hard phase as well as precipitation rise of Ni-P alloy. It is exemplify that micro-hardness of all heated depositions depends on three character (i) level of merging of particles (ii) heating temperature (iii) consistent distribution with lesser quantity of agglomeration of nano-particles [25-48

Table 2: Micro-hardness values of NiPA and NiPZr EL nano-composite coatings

Samples	Micro-hardness (HV_{50})
MS	353
NiPA (as-plated)	467
NiPA (Heated)	553
NiPZr (as-plated)	498
NiPZr (Heated)	605

Conclusion

The XRD/SEM examinations illustrate that nano-composite coating is done successfully on base material and as-plated depositions have amorphous nature; while heated materials demonstrate decline in amorphous nature and enrichment in crystallization nature. These transformations propose to elevated hardness in EL deposited heated coupons. The micro-hardness of NiPZr depositions is the maximum and for NiPA is least. The heat healing improved micro-hardness extensively due to precipitation of hard Ni_3P particles in all coupons. Thus these depositions may accredit good and cost effective option for easy-going corrosive environment, with superior hardness properties.

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