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Investigation of Hardness of Electroless Ni-P-CNF Composite Coatings

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Abstract
In the current experimental work, the electroless Ni-P-CNF nano-composite plating has been deposited upon basic mild steel substrate. The activated 1.5 gpl CNF nano-particles were integrated into an acidic electroless Ni-P matrix as a second phase material and were condensed by a reducing agent named as sodium hypophosphite. After coating, as-prepared Ni-P/Ni-P-CNF EL deposition were heated at 350°C in Ar environment for one hour duration and were analysed for surface morphology and elemental composition by SEM and EDAX. A homogeneous and heavy consistent allocation of CNF nano-particles into EL Ni-P matrix is established through analysis of SEM and EDAX. The hardness (HV_{50}) is measured by micro-hardness tester. The micro-hardness of the substrate, Ni-P coated sample and Ni-P-CNF coated samples are in subsequent order as Ni-P-CNF (heated) > Ni-P-CNF (as-coated) > Ni-P (heated) > Ni-P (as-plated) > MS.

Keywords- Electroless, Composite Coating, FESEM-EDAX, Hardness, Ni-P-CNF Coatings.

1. Introduction

The electroless plating has attained extensive increased attention owing to its superior tribological and corrosion resistance properties. The electroless coating is a less complicated set-up and has controlled chemical reduction process. In this plating process, several chemical reactions take place concurrently in aqueous medium. In EL plating there is consistency in composition and depth of plating. It is also very useful as complicated part of the substrate has like prospect to coat (Brenner and Riddell, 1946, 1947; Agarwala and Agarwala, 1987, 2003). The pure metallic Ni, binary alloy Ni-P (Brenner and Riddell, 1946 and 1947; Agarwala and Agarwala, 1987, 2003), Ni-B (Brenner and Riddell, 1946; Datta et al., 1991; Srivastava et al., 1992), Co-P (Brenner and Riddell, 1947; Agarwala and Agarwala, 2003) and Co-B (Brenner and Riddell, 1947; Agarwala and Agarwala, 2003), etc., were plated effectively by electroless deposition technique and analysed for their wear and hardness resistance properties. In the previous decade, importance has been swing in the direction of co-plating of second stage particles in the EL Ni-P matrix to mutate their tribological properties for numerous industrial applications. There are a lot of number of particles, which have been included into EL Ni matrix and opportunity of co-plating of second stage (X) particles depend on application. Further, in support of, when elevated wear and hardness resistance virtues are major requisite afterwards hard particle, as, SiC, Al_2O_3, ZnO, ZrO_2, WC, TiO_2, Si_3N_4 and CNF, etc., are favoured for the co-deposition (Sharma, 2002; Apachitei et al., 2002; Huang et al., 2004; Jiaqiang et al., 2006; Sudagar et al., 2013). In addition, soft particles named as PTFE, MoS_2, BN (h), WS_2, CNT and graphite (C) provide good lubrication when incorporated into EL Ni-P matrix (Sharma, 2002; Sudagar et al., 2013). These soft/lubricating elements have capability towards stop linkage between two adjacent layers under un-lubricated circumstances.

The chemical and physical properties of CNF make it a potential material for improved technological applications in various field including catalytic support, catalyst, electrode materials, electromagnetic wave absorber, electronic applications, hydrogen storage materials, etc., (Shi et al., 2004; Raghubanshi and Dikio, 2015; Ghaemi et al., 2016). Limited studies have been carried out on Ni-P-CNF composite coatings which states that coatings exhibit increased wear and corrosion resistance (Gao et al., 2015; Alishahi et al., 2012). It has also been reported that on inclusion of CNF into Ni-P matrix improves the tribological properties (Alishahi et al., 2012; Shi et al., 2004). However, Sung-Kyu and Tae-Sung (2011) reported that the corrosion resistance of Ni-P is better than Ni-P-CNF coatings.

On considering these contradictory results it is worth mentioning to conduct the study on Ni-P-CNF composite coatings along with Ni-P alloy coating. Therefore, deposition of CNF nano-particles into the acidic EL Ni-P matter onto MS substrate with EL procedure has been conceded out. The CNFs (Sigma-Aldrich) are reinforced into EL Ni-P-matrix from outside. For application of Ni-P-CNF nano-composite coatings their characterization, micro-hardness resistance properties have been carried out.

2. Experiment

2.1 Materials and Method

In this research work, EL plating was done upon MS material and chemical composition of coupons is as under in Table 1:

Table 1. Chemical composition of mild steel sample

Elements	C	Cu	Mn	S	P	Si	Fe
Weight%	0.08	0.05	0.34	0.02	0.007	0.03	balance

The well polished and clean test coupon of MS of volume (20 mm × 20 mm × 3 mm) was used. After it the sample has sensitization through 1.0 % $SnCl_2$ and subsequently activation by 0.05 % $PdCl_2$ for 60 seconds duration. In sensitization process time, Sn ions are set down on coupon surface towards which ions of Pd were set down in activation stage headed for

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afford nucleation/catalytic location to plating procedure. The operating as well as bath parameters for coatings are given in Table 2. The all chemicals have nil contamination.

Table 2. Chemical composition and operational parameters of the (EL) electroless bath

S.No.	Salt/Compound chemical formula	Quantity in gram (g) for 100 ml)	Function of chemicals
1	Nickel Sulphate ($NiSO_4$)	3.54 g	Source of Ni^{2+} ions
2	Trisodium Citrate	4.82 g	Complexing agent, prevent uncontrolled release of Ni^{2+} ions
3	Sodium Acetate	2.21 g each	Work as basic buffer in the presence of ammonia, to maintain the pH
4	Sod. Hydroxide/ Acetic acid 10% Solution	Added drop wise	Maintain pH of the solution ~5
5	Sodium Hypophosphite	2.3 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	0.1mg	Stabilizer
8	Activated CNF	0.15 g	Work as reinforcement into the matrix
9	Bath Operating Conditions	-	pH 5; Temperature 80-82°C; constant stirring is required
10	Annealing Hotness	Up to 350 ^{0}C	Understand the consequence of heat conduct on corrosion resistance

2.2 Characterization and Hardness Techniques

Surface morphology of powder and platings in this test is examined by SEM technique. The EDAX method, for qualitative atom examination of platings was approved out using a connection with FESEM equipment. The hardness (VHN) of platings was determined with a micro-hardness tester.

3. Results and Discussion

3.1 Ni-P/Ni-P-CNF Depositions by Electroless Technique

Plating developments were carried-out for total 2 hours, at temperature (80 ± 2°C). By the side of primary, Ni-P deposit was set down for 30 minute duration (avoid every porosity in plating) as well as after that activated CNF nano-particles (~80 nm size) were bring in through fixed stirring in identical bath used for 90 minute for co-plating of CNF in the Ni-P environment are shown in Figure 1. To have any conclusion, basic EL Ni-P plating lacking CNF nano particles was also organized. Subsequent to coating, coated coupons were engaged away from the bath, wash by means of deionised water, air dried in addition to accumulated in void desiccators. The heat handling of the EL Ni-P /Ni-P-CNF platings were conceded out in Ar ambience on 350^0 C for one hour duration and photographs are depicted in Figure 2. The established fact is that, heating will cause a phase renovation from micro-crystalline to crystalline nature due to precipitation of Ni_3P, and results enhance bond of plating to base material (Sharma, 2002; Huang et al., 2004; Sudagar et al., 2013) and get better triobological properties with respect to as-plated samples.

Figure 1. Deposition of CNF nano-particles introduced into EL Ni-P matrix

(a) Ni-P as-Coated Coupon **(b) Ni-P-CNF Heated Coupon**

Figure 2. Photographs of coated coupons

3.2 Morphology of CNF Nano-Powder and EL Ni-P/ Ni-P-CNF Depositions

The SEM micrographs of as-plated and heated Ni-P and Ni-P-CNF platings in Figure 3 are shown. Subsequent to heat action, some noteworthy transform in topography of platings is experiential. The micro-structure of the Ni-P plating illustrated distinctive spherical bulbous consistent structure. While, in Ni-P-CNF platings, the CNF nano particles are in healthy form of flakes and diffused into Ni-P matrix. The estimated stoicheo-metric ratio of atomic analysis (wt. %) with EDAX is specified in Table 3. The EDAX study, in case of heat treated Ni-P-CNF depositions, suggest a decrease in concentration of Ni on addition of CNF (1.5 gpl) and an increase in concentration of P, C and Fe %. It has also been reported (Bouanani et al., 1999; Valova et al., 2001; Balaraju et al., 2003; Veeraraghavan et al., 2003; Deng et al., 2007; Hamdy et al., 2007; Neubauer et al., 2010) that atomic allocation into plating influences plating properties as well as makes an inter-diffusion deposit.

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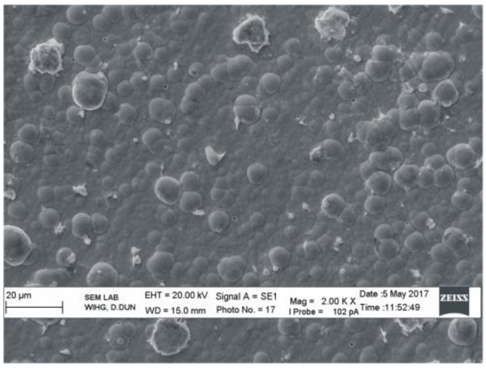
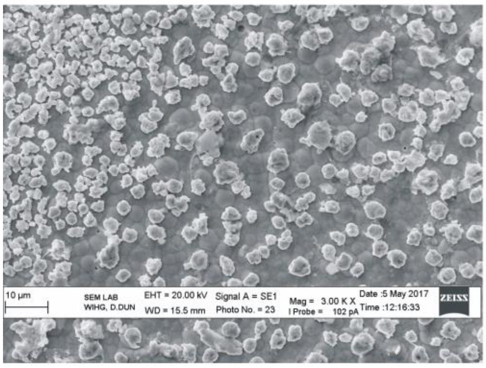
Table 3. EDAX values of EL Ni-P -CNF as-plated and heat treated samples

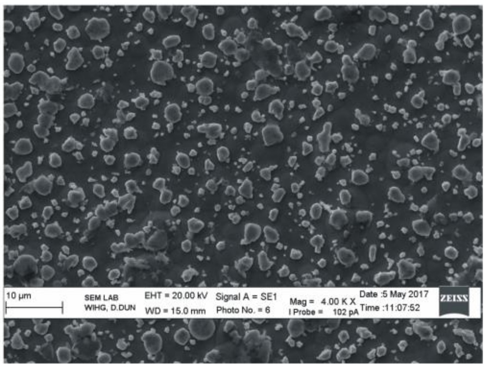
Element	Weight %	
	Ni-P-CNF (As-Coated)	Ni-P-CNF (Heated)
Ni K	82.26	79.62
P K	11.53	12.55
Fe K	2.10	3.67
C K	4.11	4.16
Total %	**100**	**100**



(a)



(b)



(c)

Figure 3. FESEM micrographs (a) Ni-P heated (b) Ni-P-CNF as-coated and (c) Ni-P-CNF heated

3.4 Hardness Study of EL Ni-P/Ni-P-CNF Platings

The micro-hardness of Ni-P and Ni-P-CNF coatings in as-coated and heated environment were resolute using micro-harness tester through residence time having 15 second under a load 50 gf. and results are depicted by Figure 4 and Table 4. The micro-hardness of the substrate, Ni-P coated sample and Ni-P-CNF coated samples are in subsequent order as Ni-P-CNF (heated) > Ni-P-CNF (as-coated) > Ni-P (heated) > Ni-P (as-plated) > MS. The result analysis of micro-hardness recommends that the adding of CNF nano-particles into the coating does add significantly to the micro-hardness of coupons. Because CNF nano-particles

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are hard metal oxide and also some inter-metallics of Ni-P, Ni-Fe, Ni-CNF (crystalline structure) etc. are formed.

Table 4. Micro-hardness values of Ni-P-CNF EL nano-composite coatings

Test Samples	Value of Micro-hardness (HV_{50})
Mild Steel (MS)	323
Ni-P as- coated coupon	434
Ni-P heated coatings	476
Ni-P-CNF (as-coated) coating	656
Ni-P-CNF (heated) coating	728

Figure 4. The photographs of micro-hardness tester

4. Conclusions

A mild black greyish and uniform nano coating of Ni-P-CNF on basic MS substrates is experiential. The FESEM-EDAX results put forward that nano-particles of CNF are consistently co-plated into an EL Ni–P matrix upon basic substrate (MS) as well as at some places extreme plating of CNF nano particles. A very good improvement in micro-hardness values for Ni-P-CNF nano-composite platings is observed at the same time as contrast to Ni-P and MS coupons.

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