Research Journal of Physical Sciences ISSN 2320–4796
Vol. **5(1),** 6-9, February **(2017)** *Res. J. Physical Sci.*

Investigation of corrosion, hardness and wear resistant of electroless Ni-P/ Ni-P-ZrO_2 nano-composite coatings

Devanshu Mudgal[1*], Sulaxna Sharma[2], Vakul Bansal[3] and Awanish Sharma[1]
[1]Graphic Era Hill and Deemed University, Dehradun, India
[2]THDC Institute of Hydropower Engineering and Technology Tehri, India
[3]J.V. Jain (PG) College, Saharanpur, India
dev.vats3@gmail.com

Available online at: www.isca.in, www.isca.me
Received 29th November 2016, revised 4th January 2017, accepted 30th January 2017

Abstract

In current research investigation, Ni-P/ Ni-P-ZrO_2 nano-composite depositions was developed by electroless deposition method on mild steel substrate in an acidic bath with sodium hypophosphite used as reducing agent. The second phase, ZrO_2 nano-particles having content 5 gram per liter were add to the electroless bath for co-deposition along with Ni-P matrix. The heat treatment of as-deposited Ni-P/Ni-P-ZrO_2 coatings was carried out at 360 ^oC in Argon atmosphere for 1hour duration. The depositions were analyzed for surface morphology, elemental composition and phase analysis by FESEM, EDAX and XRD analysis. The corrosion resistance behavior of depositions was studied in 3.5% NaCl solution by long term immersion corrosion experiment. From FESEM and EDAX data it has been observed that ZrO_2 nano-particles are embedded uniformly in the as-plated and heat treated coatings. From the long term immersion test it has been observed that the corrosion resistant behavior of as-coated and heat treated Ni-P-ZrO_2 coatings is better as compared to plain Ni-P coatings. The hardness and wear resistance of Ni-P-ZrO_2 nano-composite coating has also been found enhanced in comparison to MS/Ni-P electroless depositions.

Keywords: Acidic electroless, Ni-P/Ni-P-ZrO_2, Nano-coatings, Corrosion, Wear and hardness resistance.

Introduction

Electroless (EL) plating method has accomplished ample broadens interest due to its superior corrosion and tribological properties with a reduction of complicated set-up. EL deposition is enforced chemical dwindling method where plentiful chemical consequence takes place concurrently in avoid of work out of electric charge. In electroless plating procedure there is consistency in work and thickness of plating as well as long-winded fraction of substrate has an indistinguishable vision to deposition[1-3]. In electroless coating procedure, uncontaminated metallic Ni, binary alloy Ni-P[1-3] along with Ni-B[1-4] and Co-B[1-3] in addition ternary alloy Ni–P–B [3,5], Ni–W–P[5] and Ni–Co–P[5,6], etc were deposited effectively and their mechanical behavior explored widely. In the most recent decade, significance is dangle towards co-deposition of subsequently phase particles into EL Ni-P matrix having innumerable industrial application. Composite coatings have also been studied widely[1-3, 7-20] by incorporation of second phase particles e.g., SiC, SiO_2, TiO_2, ZnO, Al_2O_3, and Si_3N_4, etc., in to Ni-P matrix and studied for their triobological properties. Furthermore, particles as MoS_2, WS_2, PTFE, BN (h), CNF, carbon nano-tubes and graphite (C) make available high-quality lubrication when included into electroless Ni-P matrix[7-20]. These soft/lubricating particles include the potential to discontinue connection between two exteriors underneath un-lubricated surroundings. In perseverance our preceding research work[16,20], due to antibacterial disorder plus suitability under insensitive indulgence situation of ZnO nano-particles, in present investigation synthesized ZrO_2 nano-particles are deposited into the electroless Ni-P matrix on mild steel substrate. For panorama significance of Ni-P-ZrO_2 nano-composite deposition like, characterization, wear and micro-hardness resistance as well as corrosion resistance properties have been carried out in present investigation.

Methodology

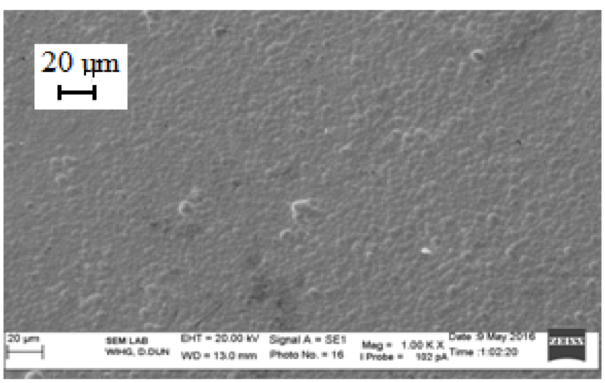
Electroless deposition of Ni-P/Ni-P-ZrO_2 was carried out on mild steel base coupon. The mild steel base coupon having dimension (20 mm × 20 mm × 4 mm) was selected for depositions. The chemical composition of mid steel material is given in earlier studies [20,21]. The electroless bath parameters for coatings are in accordance of earlier studies[16,17, 20,21].

Characterization of Ni-P/Ni-P-ZrO_2 Coatings: The synthesized ZrO_2 fine particles, Ni-P as well as Ni-P-ZrO_2 depositions were analyzed by XRD technique. The outer surface/inner surface morphology was inspected by FESEM/EDAX and SEM techniques. Corrosion behavior of Ni-P/Ni-P-ZrO_2 depositions was investigated by long-term immersion experiment of six month duration in 3.5 % NaCl solution. Weight loss was measured by the formula given in Sharma N. et al[21]. The exposed coupons were analyzed for crevice and pitting corrosion attacks using metallurgical microscope (Make: Reichert Jung, USA. The hardness and wear resistance of the depositions was calculated by micro-hardness and pin-on-disc equipments.

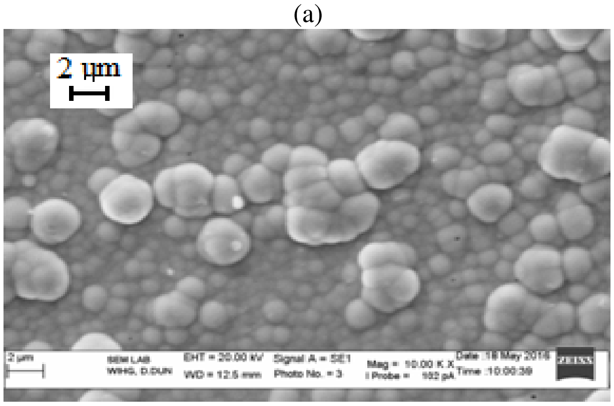
Results and discussion

Plating of Ni-P/Ni-P-ZrO_2 by electroless method: For Ni-P / Ni-P-ZrO_2 deposition on mild steel substrate, electroless deposition procedure was used in acidic bath the details of the procedure are mentioned in previous studies[17,20,21]. The behavior of the coatings was determined in as-plated and heat treated conditions. For heat treatment the as-coated coupons were heated in Ar atmosphere for 1 hour duration at 360^0C.

XRD/FE-SEM-EDAX analyses of fine particles of ZrO2, Ni-P and Ni-P-ZrO_2 coatings: XRD spectra of as-plated electroless Ni-P deposits are measured by diffraction Ni (111) along with Fe peak. The corresponding spectra of as-plated Ni-P-ZrO_2 depositions reveal diminutive peaks of ZrO_2 particles. The heating at 360°C for 1hour, reveals crystallization of Ni-P medium i.e., Ni, Ni_3P in addition to ZrO_2 stage (JCPDS00-024 to 1164, 01 to 078-0047). FESEM micrographs of heat treated Ni-P and Ni-P-ZrO_2 are shown in Figure-1. The microstructure of Ni-P-ZrO_2 coating demonstrates the characteristic globular homogeneous phase. The EDAX analysis of heat treated Ni-P-ZrO_2 is shown in Figure-2 and elemental analyses of all depositions carried out are given in Table-1.

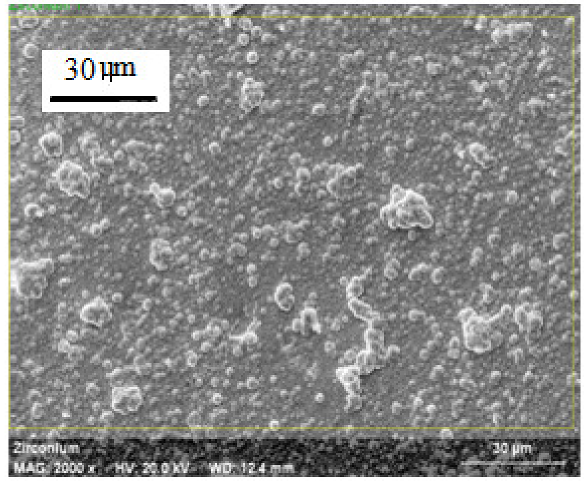


(a)

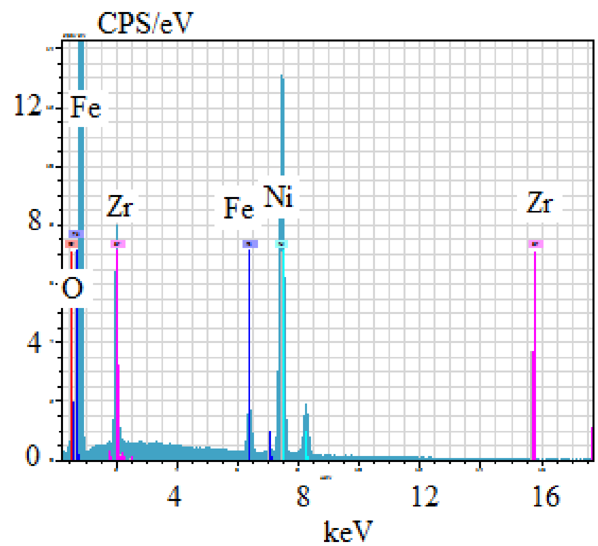


(b)

Figure-1: FE-SEM Micrograph of heat treated (a) Ni-P and (b) Ni-P-ZrO_2 coatings.



(a)



(b)

Figure-2: EDAX analysis of heat treated Ni-P-ZrO_2 (a) FE-SEM micrograph and (b) elemental analysis.

Table-1: EDAX analysis of Ni-P and Ni-P-ZrO_2 coatings

Elements	Elemental Wt%		
	Ni-P as-plated	*Ni-P-ZrO_2 as-plated*	*Ni-P-ZrO_2 Heat treated*
O K	3.10	3.32	2.88
Zr K	-	2.16	2.14
P K	11.76	11.74	11.52
Ni K	81.35	80.21	79.76
Fe K	3.79	2.57	3.70
Total	100	100	100

Hardness and wear resistance of Ni-P/Ni-P-ZrO_2 coatings: Micro-hardness (VHN) of Ni-P in addition Ni-P-ZrO_2 nano-composite depositions in 'as plated' and heat treated conditions was determined by means of micro-harness equipment with the residence of 15 sec below 50 g of weight. Hardness of substrate, Ni-P plated coupon plus Ni-P-ZrO_2 plated coupons are into following order Ni-P-ZrO_2 (HT) > Ni-P-ZrO_2 (as-plated) > Ni-P > MS (Table-2). The grades of micro-hardness propose addition of ZrO_2 nano-particles into Ni-P electroless plating donate significantly to micro-hardness of Ni-P coupon.

Table-2: Micro-hardness values of Ni-P, Ni-P-ZrO_2 EL nano-composite coatings

Samples	Micro-hardness (HV_{50})
MS	347
Ni-P $_{\text{as-plated}}$	454
Ni-P-ZrO_2 $_{\text{as-plated}}$	631
Ni-P-ZrO_2 $_{\text{Heated}}$	689

The wear test was performed under non-lubricated condition, temperature 38°C with relative humidity of 68% in a pin-on disc arrangement by a coated pin of dimension 6 mm x 30 mm. The pin was sliding with linear sliding speed of 0.2 meter per second. The radius of bath was 25 mm at 30 N loads on steel disk.

The wear loss was calculated by measuring weight loss owing to friction of sample for sliding space of 500 m (Table-3). The grades of wear resistance propose addition of ZrO_2 nano-particles into Ni-P electroless plating contribute significantly to wear resistance of Ni-P coupon.

Corrosion Resistance Investigation of Ni-P/Ni-P-ZrO_2 coatings: The amount of corrosion attack for all tested base coupons has been listed in Table-4, and it is observed that mild steel coupon experienced maximum (16.76 mpy) rate of uniform corrosion followed by Ni-P $_{\text{Plated}}$ (0.49 mpy), Ni-P-ZrO_2 $_{\text{heated}}$ (0.20 mpy) and Ni-P-ZrO_2 $_{\text{Plated}}$ (0.15 mpy). In standard NaCl test solution, the better resistance against uniform corrosion shown by Ni-P-ZrO_2 $_{\text{Plated}}$ coupon may be because it has an amorphous configuration (SEM, XRD analysis).

In other expressions, it does not produce inter-granular limitations which can operate as cathodic and anodic sites and will augment uniform corrosion rate. In the electroless nano-composite coated materials, Ni-P-ZrO_2 $_{\text{heated}}$ (19 µm) shows slight higher pitting corrosion attack than Ni-P-ZrO_2 $_{\text{as-plated}}$ (15 µm).

The more pitting attack of Ni-P-ZrO_2 $_{\text{heated}}$ than Ni-P-ZrO_2 $_{\text{as-plated}}$ can be because of the transform of amorphous structure to the crystalline structure after heat treatment. This can be observed by SEM/XRD microstructures too. It is fine known that crystallinity generates grain boundaries in addition next phases which may be the strong position for corrosion attack.

Table-3: Wear Loss values of Ni-P, Ni-P-ZrO_2 EL nano-composite coatings

Samples	Weight loss (in mg) at total sliding distance 500 m, 30N applied load
MS	15.83
Ni-P $_{\text{as-plated}}$	5.65
Ni-P-ZrO_2 $_{\text{as-plated}}$	4.45
Ni-P-ZrO_2 $_{\text{Heated}}$	3.62

Table-4: Corrosion attack on coupons exposed in 3.5 % wt. NaCl solution

Grade of Material	Corrosion Rate (mils per year, mpy)	Localized Corrosion Maximum Pit Depth (mm)	Crevice Corrosion Maximum Pit Depth (mm)
MS	16.76	0.020	0.049
Ni-P $_{\text{Plated}}$	0.49	0.023	0.025
Ni-P-ZrO_2 $_{\text{as-plated}}$	0.15	0.015	0.023
Ni-P-ZrO_2 $_{\text{heated}}$	0.20	0.019	0.029

In all the corroded coupons, mild steel reveals the highest crevice type attack (49 µm) followed by Ni-P-ZrO_2 $_{\text{heated}}$ (29 µm), Ni-P $_{\text{Plated}}$ (25 µm) and Ni-P-ZrO_2 $_{\text{as-plated}}$ (23 µm). The depth of attack under crevice is slightly higher in comparison to pitting attack on an open surface on all coupons. The crevice type attack can be due to the higher concentration of oxidized chemical (NaCl) under crevice former than open surface.

Conclusion

A glittering grayish along with constant nano-composite deposition of Ni-P-ZrO_2 on mild steel base coupon is observed. The coated substrate was heat treated at 360^0C to attain crystalline nature of deposition. The electroless Ni-P-ZrO_2 depositions demonstrate high-quality performance on mild steel coupons. FESEM-EDAX study revealed that in Ni-P-ZrO_2 coating, ZrO_2 particles are constantly co-plated into EL Ni–P matrix on the outer surface. As a consequence an improvement in micro-hardness and wear resistance for Ni-P-ZrO_2 depositions has been observed. In 3.5 wt. % NaCl, solution, resistance against corrosion of EL Ni–P plating is improved by incorporation of ZrO_2 nano-particles.

Acknowledgment

The authors recognize VC and Prof. Sanjay Sharma, Graphic Era Hill (ME Department) also Deemed University for providing different labs and experimental assistance into the completion of this experimental research work.

References

1. Agarwala R.C. and Agarwala V. (2003). Electroless alloy/composite coatings: A review. *Sadhana*, 28(3-4), 475-493.

2. Balaraju J.N., Narayanan T.S.N. and Seshadri S.K.S. (2003). Electroless Ni–P composite coatings. *J. Appl. Electrochem*., 33(9), 807–816.

3. Sudagar J., Lian J. and Sha W. (2013). Electroless nickel, alloy, composite and nano coatings–A critical review. *J. Alloy. Compds.*, 571, 183-204.

4. Datta P.K., Bedingfield P.B., Lewis D.B., and Wells P.B. (1991). Structure and phase changes accompanying treatment of electroless Ni–B alloy coating. *Conf. Proc. 2nd Int. Electroless Nickel Conference*, 139-153.

5. Balaraju J.N., and Rajam K.S. (2005). Electroless Deposition of Ni-Cu-P, Ni-W-P and Ni-W-Cu-P Alloys. *J.* Surf. Coat. Technol., 195(2), 154-161.

6. Kim D.H., Aoki K. and Takano O. Soft magnetic films by electroless Ni-Co-P plating. *J. Electrochem Soc*., 142(11), 3763-3767.

7. Apachitei I., Tichelaar F.D., Duszczyk J. and Katgerman L. (2002). The effect of heat treatment on the structure and abrasive wear resistance of autocatalytic NiP and NiP–SiC coatings. *Surf. Coat. Technol*., 149(2), 263-278.

8. Huang Y.S., Zeng X.T., Hu X.F. and Liu F.M. (2004). Corrosion resistance properties of electroless nickel composite coatings *Electrochem. Acta.*, 49(25), 4313–4319.

9. Dong D., Chen X.H., Xiao W.T., Yang G.B. and Zhang P.Y. (2009). Preparation and properties of electroless Ni-P-SiO_2 composite coatings. *Appl. Surf. Sci.*, 255(15), 7051-7055.

10. Chen W., Gao W. and He Y. (2010). A novel electroless plating of Ni-P-TiO_2 nano composite coatings. *Surf. Coat. Tech.*, 204(15), 2493–2498.

11. Moonir S.M., Saatchi A. and Hedjazi J. (1997). Tribological Behaviour of Electroless NiP-MoS_2 Composite Coatings. *Zeitschrift für Metallkunde,* 88(6), 498-501.

12. Ger M.D. and Hwang B.J. (2002). Effect of Surfactants on Codeposition of PTFE Particles with Electroless Ni-P Coating *J. Mater. Chem. Phy.*, 76(1), 38-45.

13. Chen W.X., Tu J.P., Xu Z.D., Tenne R., Rosenstveig R., Chen W.L., and Ganand H.Y. (2002). Wear and friction of Ni-P electroless composite coating including inorganic fullerene WS_2 nanoparticles. *Adv. Eng. Mater.,* 4(9), 686-690.

14. León O.A., Staia M.H. and Hintermann H.E. (2003). High-temperature wear of an electroless Ni-P-BN(h) composite coating. *Surf. Coat. Tech.*, 163–164, 578-584.

15. Feldstein N., Mallory G.O., and Hajdu J.B. (1990). Electroless Plating: Fundamentals and Applications. American Electroplaters and Surface Finishers Society, Orlando, Florida,(Eds.), William Andrew, 269.

16. Sharma S., Saini C.K. and Sharma S. (2014). To Develop The Electroless Ni-P-ZnO Coating On Glass Substrate By Electroless Technique. *J. Mater. Environ. Sci.*, vol. 5(5), 1667-1670.

17. Sharma Sarika, Sharma Sulaxna, Agarwala Pooja, Garg Rajnish and Gopinath P. (2012). A study on Ni-P and Ni–P–ZnO composite coatings developed by electroless technique. *Adv. Mat. Res.*, 585, 512-516.

18. Zoikis-Karathanasis A., Pavlatou E.A. and Spyrellis N. (2009). The effect of heat treatment on the structure and hardness of pulse electrodeposited NiP–WC composite coatings. *Electrochim. Acta*., 54(9), 2563–2570.

19. Zielinska K., Stankiewicz A. and Szczygiel I. (2012). Electroless deposition of Ni–P–nano-ZrO_2 composite coatings in the presence of various types of surfactants. *J. Colloid. Interf. Sci*., 377(1), 362-367.

20. Saini C.K. (2015). Development of Electroless Ni-P-ZnO Nano-composite Coatings. Thesis GEU.

21. Sharma N., Sharma S., Sharma K., Kalra G.S., Sharma A. (2016). Corrosion and Hardness Study of Electroless Ni-P-ZnO Nano-composite Coatings. *J. Graphic Era Univ*., 5, 45-51.