Investigations on Surface Behavior of Electro-Less Nickel Phosphorus Coatings with Nano Additives on Magnesium Alloy Used In Automotive Applications

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ABSTRACT

To enhance the damage and corrosion behaviour for alloys, the coating is found because of the maximum fitted technique. Mg-based alloys have a good range of business application. These alloys show a high specific strength but bad attire and corrosion resistance. A standard coating of Cu, Ni & Zn etc. provides a physical barrier against the wear and tear rate and corrosion attack of magnesium substrate. In the recent study, plating Ni-P was thru going on AZ91 composite by immersing samples into Nickel sulphate bath in the existence of surfactants. The study of the mechanism of Ni-P deposits was studied utilizing SEM. Ni-P coating was coated consistently within the existence of surfactants. Result of surfactant and Result of Nano-additives ZnO, Al_2O_3 and SiO with various quantities were examined. 0.5 g/l Nano Al_2O_3 additive-enhanced the deposition of Ni-P on AZ91 magnesium composite and hereafter the similar consequences are detected just in case of SiO accumulation. Effect of ZnO was also noticed. So is extremely clear that Ni-P coating is extremely effective to scale back the corrosion and rise the wear and tear behaviour if it's used together with Nano additive and therefore the surfactants.

Keywords

Nano-additives, Coating, surfactants, Scanning Electron Microscope

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Introduction

Amid the numerous materials existing for the automotive and aerospace industry, a Magnesium alloy overcomes a significant place. Mg alloys show lower density, higher exact strength and exceptional machinability [1, 2]. However, despite these properties, these alloys have a susceptibility to corrosion in a moist atmosphere and thus they have restricted application in the areas where high wear resistance is vital [3]. The coating is found as the utmost suitable technique to progress the wear characteristic [4]. Magnesium alloys are light in weight but their applications are restricted in engineering industries due to the poor wear & corrosion resistance. The difficult of corrosion was enhanced by the overview of pure alloys [5]. Alloying develops the overall corrosion behaviour, but no important development has been detected in galvanic corrosion [6, 7]. To solve this concern proper coating is vital [8]. The Ni-P coating is the exact operative for reduction corrosion but the task is to do the coating by the effective way. For that accumulation of Nano additives and the separate surfactants on Ni-P deposition was used and their result considered in this determination by Sun et. al. [9]. Electroless plating technique outcomes in the decrease of a well, smooth and uniform surface that gives good surface roughness properties, wear resistance and defence beside corrosion [10-12]. In recent times researchers have their attention towards Ni-P coatings which includes the effect of phosphorous content on structure and surface morphology. Ni-P coating has categorized and based on content phosphorous. Higher content of phosphorous (higher than 8 %) tells the finest corrosion properties and suggested for the environment where serious corrosion happens. Although a coating with lower phosphorus contents (lesser than 3 %) shows Deprived corrosion resistance and noble wear properties. Thus, Magnesium alloys Corrosion resistance not only depends lone on the content of phosphorous. According to Mimani et.al. [13], the corrosion behaviour of amorphous state can be focused by the grade of amorphous state, the amount of inner stress and the weight percentage of content phosphorus. Many researchers have reported the coating performance in different environments concerning the amount of phosphorus used. To additional advance, the coating completing present days scientists are through Nanoparticles along with electroless Ni-P coating. The Nanoparticles like Al_2O_3, SiO_2, TiO_2 etc. are normally further in an electrolytic bath to formulate the electroless Ni-P Nanoparticle coating. Though Nano additive advances the corrosion behaviour and wear execution of coating nevertheless still it has few tasks. The first thing is the identical distribution of Nanoparticles and the next one is the agglomeration which affects the stability of Nano elements in the solution [14]. Nano Al_2O_3 particles are used by several researchers because of high strength and good stability. These particles are relatively cheap and exhibit good hardness [15]. These particles are generally used for copper and steel substrate and slight work has been specified on Magnesium alloys. The objectives of this effort are to work the Mg AZ91D composites (Mg with 1% wt MWCNT-(1%wt) Al203) which can be used as a substrate material and the Al2O3, ZnO & SiO are used as Nano additives for checking their outcome. Tests are conducted to get the effect of Nano additives on the properties of mechanical of less electro Ni-P Coated Mg composite and their outcomes are presented and discussed in the further section.

Experimental details

A. Preparation of specimen for the test

Substrate materials selected for the coating were magnesium (Mg) composite comprising 1 wt. % of MWCNT and 1 wt. % of Al_2O_3 which was bought from Mangaluru, India. The sample as shown in Figure1 was cutting through wire EDM for Ni-P coating. Rectangular (8 mm x 26 mm x 8 mm) sample of Mg composite are first ground increasingly with SiC abrasive paper have 400 500, 600, 800, 1500 and 2000, mesh to achieve an acceptable surface uniformity. Similarly, for the corrosion test, the sample is cut to dimension (10 mm x 20 mm x 8 mm).

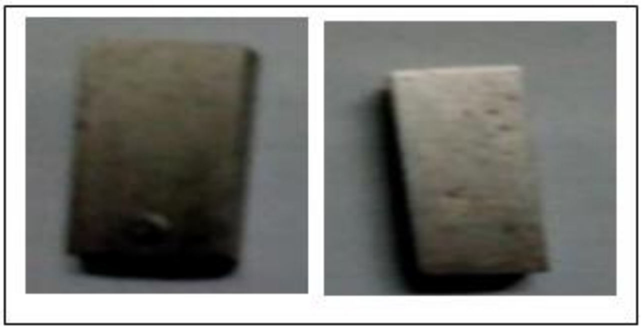


Figure1. The sample preparation for the test.

B. Pretreatment process

During the process of pre-treatment, the acetone is used for the cleaning of the substrate. Extra, alkaline cleaned with NaOH (45 g/L) is ready follows by Na_3PO_4 Trisodium orthophosphate (10 g/L) for 20 minutes; at 65^0C temperature. Subsequently, it is continued by acid treatment with chromium tri-oxide (125 g/L) and nitric acid (100 ml/L) for 40 sec. Finally, the fluoride activation is done with hydro fluoride at 10 minutes at room temperature. The procedure is followed as per the literature [16]. The setup shows in Figure 2.

Figure2. Alkaline cleaning setup.

C. Electroless nickel coating bath and operating conditions

The coating bath consists of:

(a) Nickel Sulphate (26 g/L),
(b) Sodium hypo-phosphate (30 g/L) as reducing agent,
(c) Sodium acetate (16 g/L) as stabilizer and
(d) Ammonium hydrogen difluoride (8 g/L) as the complexing agent.

The surfactant SLS (1.2g/L) is added in the solution earlier EN deposition. The stabilizer thiourea (1ppm) is added into the bath when the reaction is stable. Process parameter like Temperature, pH and effect of Surfactant concentration changes. The pH level is modified by adding NaOH pallets. The temperature and pH values are changing at 3 different levels 4 to 5, 6 to 7 and 8 to 9 and 70ºC, 85ºC and 90ºC respectively. The surfactant SLS is used and its concentration was the change from 0 to 1.2 g/L. It is observed that pH value 6-7, temperature preserved at 85°C and SLS (1.2 g/L) offers improved coating with Nano additive [17]. The composition of the coating baths and the varying percentage of Nano additives are specified in tables I and II.

Table I. Compositions of bath for electroless Ni – P coating

Particulars	Bath A	Bath B	Bath C
	Quantity(g/L)		
$NiSo_4.6H_2O$	28	28	28
Na $H_2O_2PO_2$ H_2O	33	33	33
HF (40%, v/v)	12 ml	12 ml	12 ml
$NaC_2H_3O_2$	18	18	18
NH_4HF_2	8	8	8
$NaC1_2H_{25}So_4$	1.3	1.3	1.3
Thiourea	1 ppm	1 ppm	1 ppm
Nano Al_2O_3, 40 nm	00.5-2	-	-
Nano ZnO, 50 nm	-	00.5-2	-
Nano SiO, 25 nm	-	-	00.5-2

Table II. Concentration details of the Nano additives employed

Element Line	Weight(%)	Atom(%)	Formula
O K	4.29	11.77	O
Al K	0.62	0.88	Al
P K	8.49	12.20	P
Ni K	86.60	75.15	Ni
Total	100	100	

D. Electroless coating procedure

The coating is put on for 1hr with a total bath volume of 400 ml is shown in Fig 3 and Fig 4. The Al_20_3 (40 nm size), SiO (25 nm average size) and ZnO (50 nm size) nanoparticle are added to the appropriate solutions (Table1) to study the comparisons of tribological properties. Ultra sonication method was applied to minimalize the agglomeration of the Al_20_3, SiO and ZnO which was applied for 15 mins. The magnetic moving at a constant speed of 100 rpm was performing for 60 minutes for electroless deposition [18]. The pH levels are altered by adding NaOH pallet. Image of the coated sample is shown in Figure5.

Figure3. Experimental set up used for EN deposition. Figure4. Bath preparation for the test.

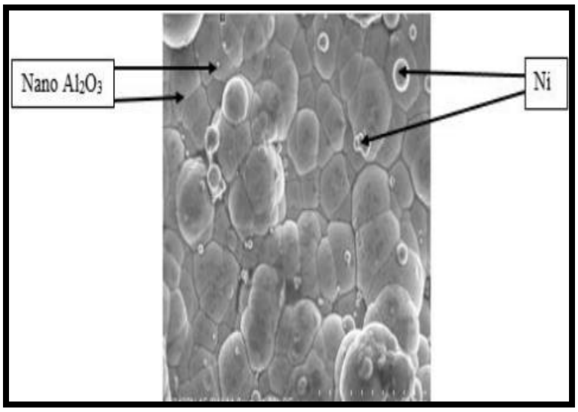
Figure5. Coated samples used for the test

E. Scanning of electron microscopy

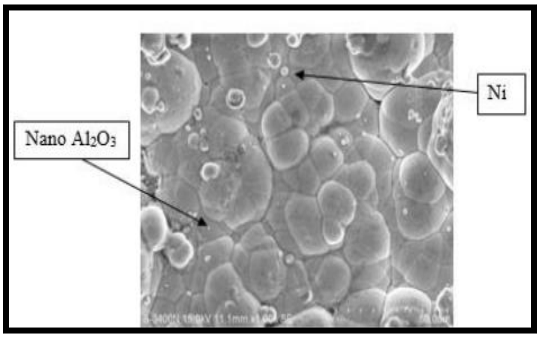
SEM was utilized for the surface topography. The study has given the details about the texture, crystalline structure, orientation and the sample of chemical composition.

Results and discussion

A. Result of Al_2O_3 difference The SEM image of deposit taken at an unlike Al_2O_3 percentage of bath solutions for magnesium composite substrate are shown in Figure6. Figure6 (a) to (d) show the EDAX image represent the existence of Nano Al_2O_3 particle. It is further observed from beyond mentioned EDX image, the Al_2O_3 particle is similarly spread in EN deposit and this is taken in a high percentage of Nano additive related to a low percentage. Hereafter, it is noticed that the accumulation of changing percentage of Al_2O_3 Nano additive, increases coating uniformity (shown in Figure6). The introduction of the SLS (sodium lauryl sulphate) anionic surfactant into the coating bath results into de-agglomeration of Nano-alumina particles as shown in Figure6 (d). The morphology of different coatings deposited from the bath solution of different % Al_2O_3 is investigated. Maximum consistency in the microstructure was found in coatings taken at 2% Al_2O_3 Nano additives, (Figure6 (d)). The non-constant of the surface due to the different % Ni in the coating.



A



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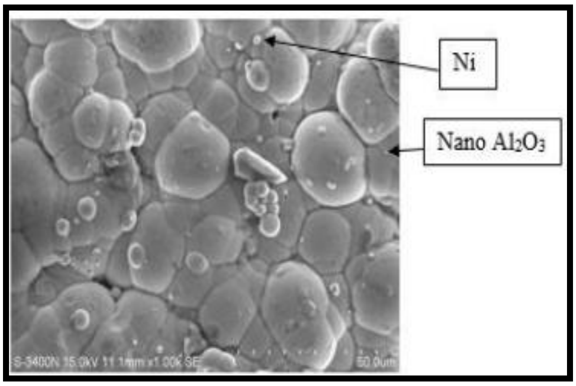

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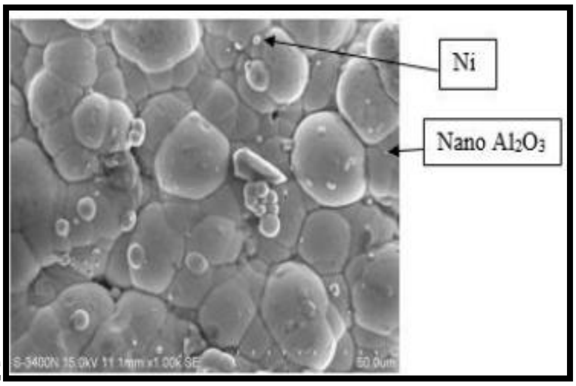
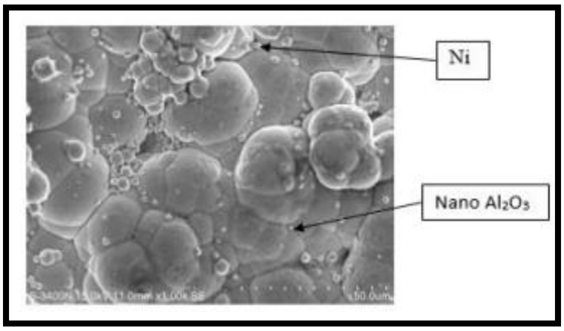


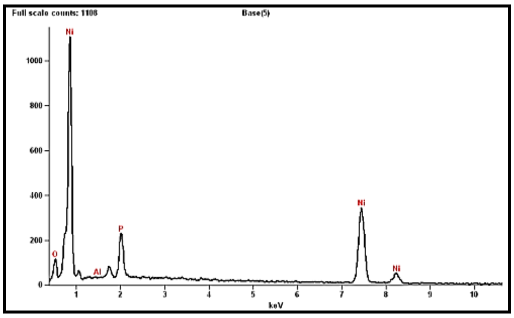


D

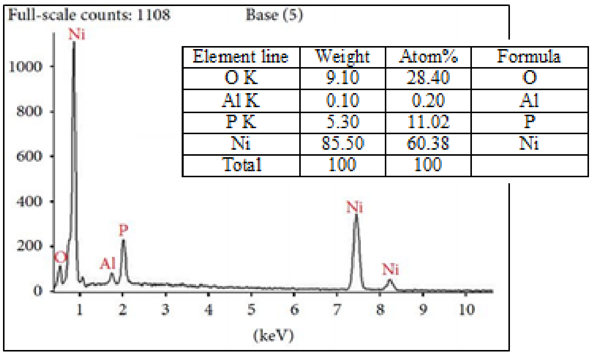
Figure6. SEM micrograph (1000X) of electro less Ni-P coating on magnesium (Mg) composite reinforced with multiwall carbon nanotube (MWCNT) at varying % of Al_2O_3 (a) 0.1% (b) 0.5% (c) 1% (d) 2%, with surfactant (SLS)

B. Elemental analysis–EDAX

The Mg composite with an increasing percentage of Al_2O_3 of EDAX Pattern of nickel electroless Nano additive shown in Figure7.The presence of nickel in varying percentage is seen as sharp peaks within the all the EDAX spectrum, while the spectra of Al_2O_3 Nanocoatings shown in Figure7 (a, b, c, d) indicate typical peaks of Al and Oxide in ascending proportion indicate the consistency adherent and porosity free surface with an increased percentage of Al_2O_3 Nano additive on the Substrate.

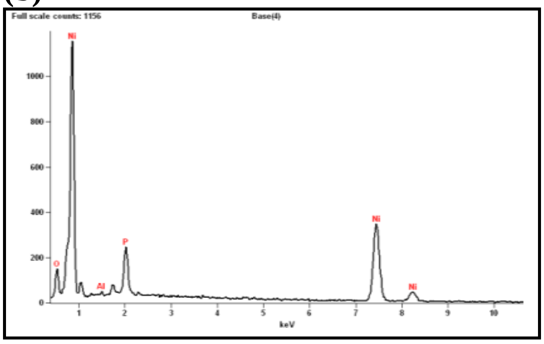


(a)



Element line	Weight	Atom%	Formula
O K	9.10	28.40	O
Al K	0.10	0.20	Al
P K	5.30	11.02	P
Ni	85.50	60.38	Ni
Total	100	100	

(b)



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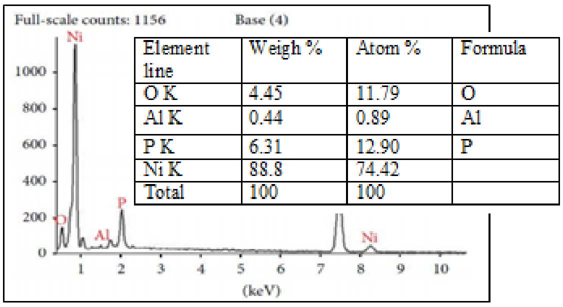


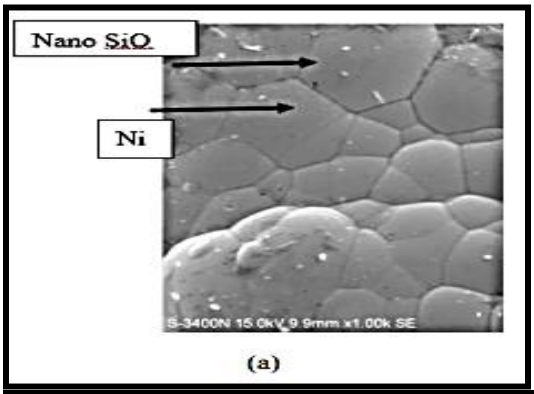
Element line	Weigh %	Atom %	Formula
O K	4.45	11.79	O
Al K	0.44	0.89	Al
P K	6.31	12.90	P
Ni K	88.8	74.42	
Total	100	100	

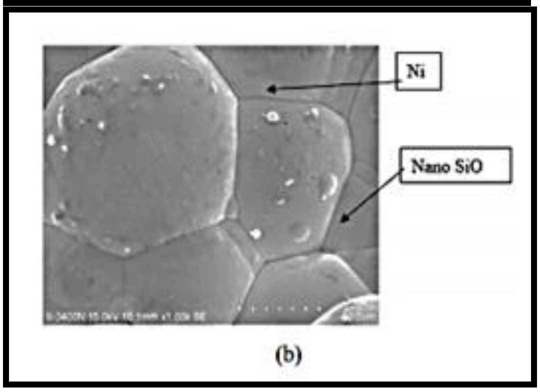
(d)

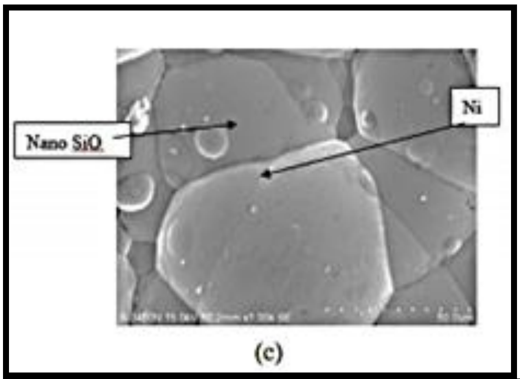
Figure7. EDAX spectrum showing presence of Ni-P coated on magnesium (Mg) composite reinforced with multiwall carbon nanotube (MWCNT) at varying % of Al_2O_3 (a) 0.1% (b) 0.5% (c) 1% (d) 2%, with surfactant (SLS).

C. Effect of SiO variation

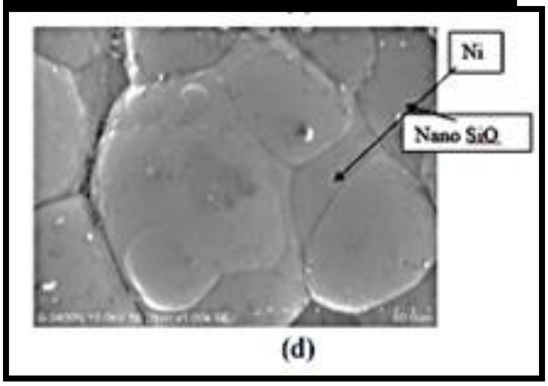
Different percentage of SiC Nano additives display quiet different surface morphologies (shown in figure 8). The morphology of coating is a deposit from the bath solution of various % SiO is investigated. Figure8 (a) to (d) shows the uniform distribution of SiO particles within the coating. The nickel particles deposited on the surface substrate expedite the method and decreases the contacts angle which eventually results in the superior wettability on the substrate. The coating thus produced would always have an honest bonding to the substrate. The agglomeration of Nanoparticle is prohibited using anionic SLS- (sodium lauryl sulphate surfactant). By comparing the addition of Nano additive with one another, a compressed and defect-free composite coating is obtained with 2% SiO amount. It implies that with increase SiO web page, uniformity increases.







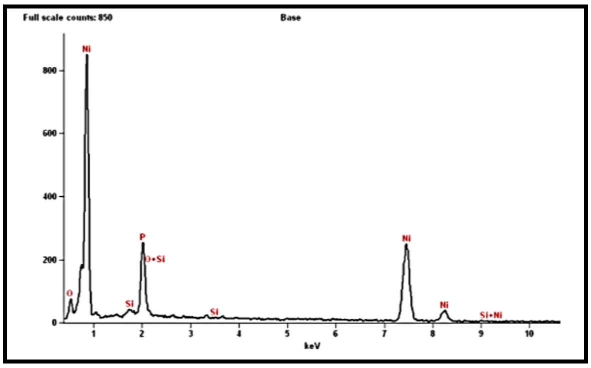
(c)



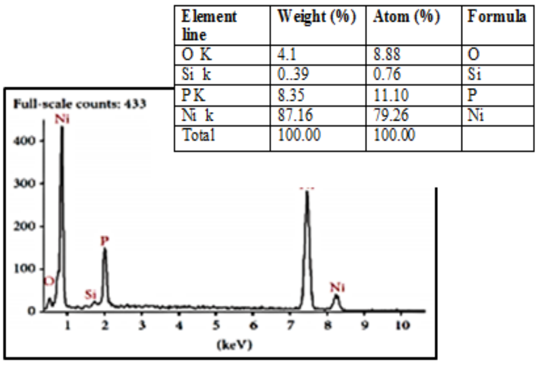
(d)

D. Elemental analysis of mg composite – EDAX

The EDAX pattern of the electroless nickel coated Mg composite with an increased percentage of SiO Nano additive are shows in Fig.9. An element analysis made on the surface (Fig.9 (a)-(d)) indicates that Ni, P, Si and O elements exist in the coating. The presence of nickel in varying percentage is seen as sharp peaks in the all the EDAX spectrum, while the spectra of SiC Nanocoatings shown in Figure9 (a),(b),(c),(d) indicates typical Si and O in ascending proportions contributing to the uniformity, adherent and porosity free smooth surface on the Substrate.

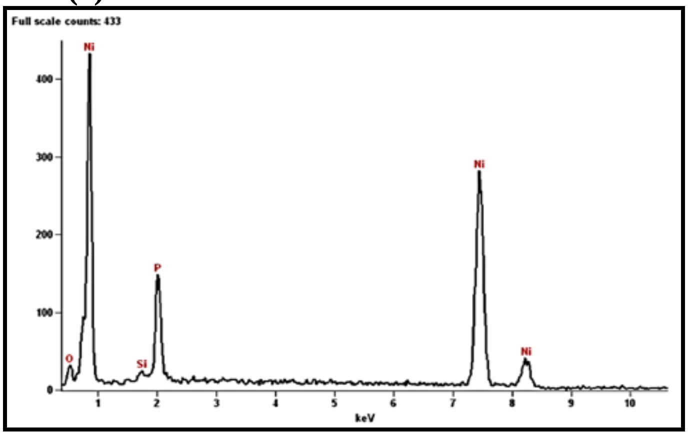


(a)
Base (2)

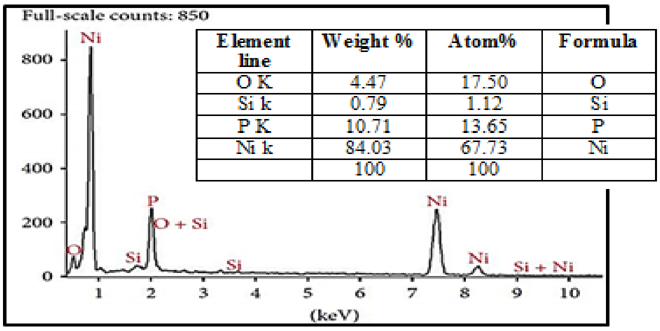


Element line	Weight (%)	Atom (%)	Formula
O K	4.1	8.88	O
Si k	0..39	0.76	Si
PK	8.35	11.10	P
Ni k	87.16	79.26	Ni
Total	100.00	100.00	

(b)
Base(2)



(c)
Base



Element line	Weight %	Atom%	Formula
O K	4.47	17.50	O
Si k	0.79	1.12	Si
P K	10.71	13.65	P
Ni k	84.03	67.73	Ni
	100	100	

(d)

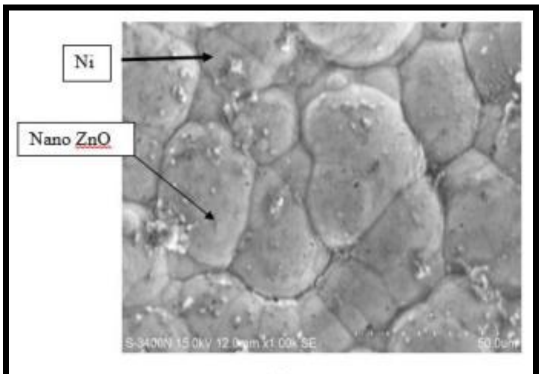
Fig9. EDAX spectrum showing presence of Ni-P coated on magnesium (Mg) composite reinforced with multiwall carbon nanotube (MWCNT) at varying % of SiO (a) 0.1% (b) 0.5% (c) 1% (d) 2%, with surfactant (SLS).

E. Effect of ZnO variation

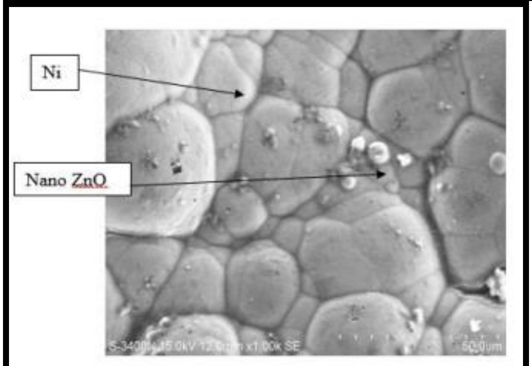
Fig.10. (a), (b), (c) and (d) is showing the incorporation of higher % of ZnO Nano-particles in the coating has resulted in a rougher surface ((Ra value =1.26), of for composite coatings in comparison to low % of ZnO. It is similarly seen that the surge in the amount of the ZnO Nano-particles in the Ni-P matrix happened to attain an

additional uneven surface (Fig. 10- b and c). Since the rougher morphology might be a proof for the existence of the ZnO Nano-particle at the surface, it has observed the rise in nanoparticles concentration in the bath tends to increasing volumes of Nano-particles incorporation in the coating.

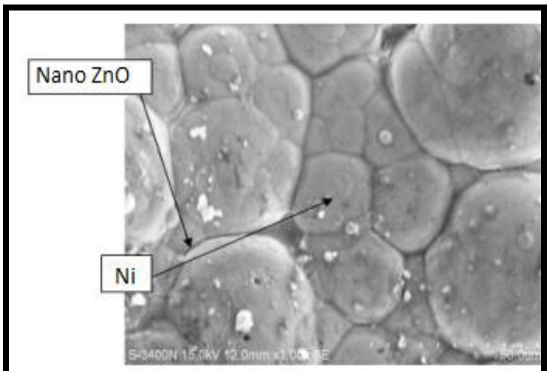
F. Elemental analysis of mg composite - EDAX



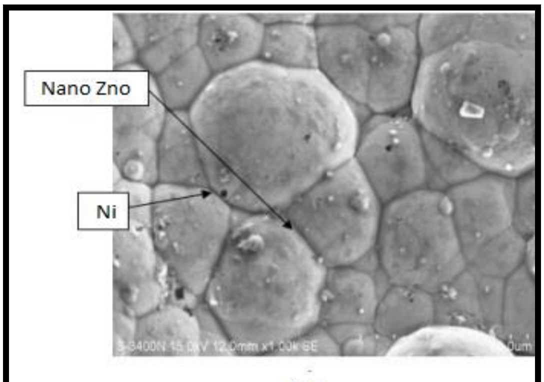
(a)



(b)



(d)



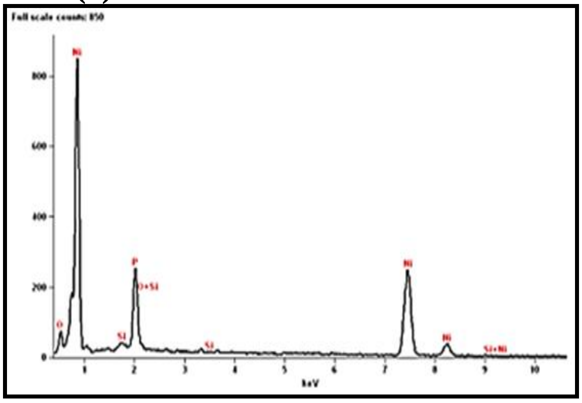
(c)

Fig10. SEM micrograph (1000X) of electro less Ni-P coating on magnesium (Mg) composite reinforced with multiwall carbon nanotube (MWCNT) at varying % of ZnO (a) 0.1% (b) 0.5% (c) 1% (d) 2%, with surfactant (SLS).

F. Elemental analysis of mg composite - EDAX

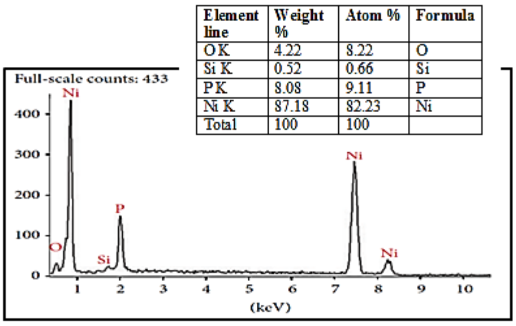
The EDAX patterns of the electroless nickel coated Mg composite with increasing percentages of ZnO Nano additives shown in Figure11 a component analysis made on the surface (see Figure 11 (a)-(d)) indicates that Ni, P, Zn and O elements exist within the coating. it's shown that Nanoparticles incorporation within the Ni-P matrix's affects the structure of the EN coating and also the EDAX spectrum of both low and high % of ZnO shows the presence of ZnO and increased P content. The increase in P content due to the addition of surfactants in EN bath. Surfactant promotes P content within the coating as reported in Elansezhian et al (2008). While the spectra of Nano ZnO coating shown in Fig11-(b) & (d) indicates typical Zn (1.67 to 3.05 Wt.%) in ascending proportion to finish up within the formation of the rougher surface because of high agglomeration of ZnO particles. Excess ZnO Nanoparticle in amorphous phase could increase the resistance of corrosion of EN coated composites. Hereafter, Variation in corrosion resistance of EN coating as part of ZnO with surfactant (SLS) in EN bath is the study and also the effects are analyzed within the next section

Base (7)



(a)

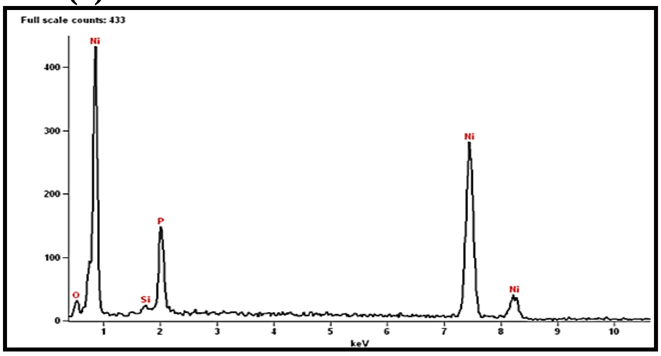
Base(8)



Element line	Weight %	Atom %	Formula
O K	4.22	8.22	O
Si K	0.52	0.66	Si
P K	8.08	9.11	P
Ni K	87.18	82.23	Ni
Total	100	100	

(b)

Base(8)



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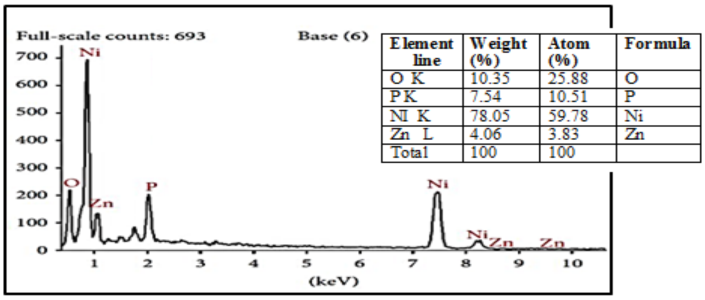

Element line	Weight (%)	Atom (%)	Formula
O K	10.35	25.88	O
P K	7.54	10.51	P
Ni K	78.05	59.78	Ni
Zn L	4.06	3.83	Zn
Total	100	100	

(d)

Fig11. EDAX spectrum showing presence of Ni-P coated on magnesium (Mg) composite reinforced with multiwall carbon nanotube (MWCNT) at varying % of ZnO (a) 0.1% (b) 0.5% (c) 1% (d) 2%, with surfactant (SLS).

G. SEM Ni-P images of Coated Mg composite without surfactant and Nano additive

The SEM micrographs in Figure12 show the non-consistency deposition of Ni particles on the substrate. Deprived of the existence of anionic surfactant SLS-sodium lauryl sulphate, the agglomerations of Nanoparticle are visible. It is decided that the surface of morphology EN coated Mg composite substrate lacking Nano additive and surfactant have lower surface texture when related with coatings with 2% Nano additives.

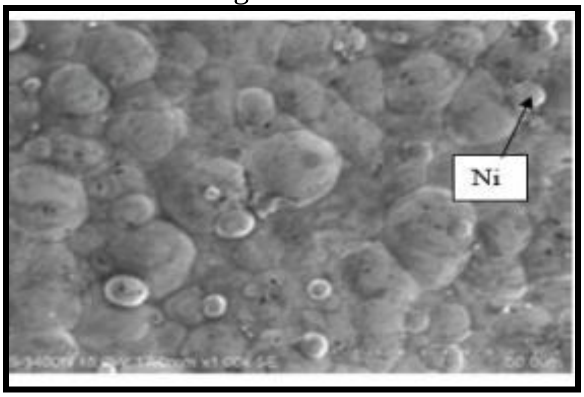

Figure12. (1000×) SEM micrograph of EN coated Mg composite without surfactant and Nano additives.

Conclusion

On AZ91 magnesium the Electroless Ni-p Electroless coating is carried successfully overall progress has found with surfactant accumulation through enhanced distribution was reached with a minimum amount of SLS and surfactant. The process of pretreatment benefits in avoiding galvanic corrosion and it plays a very significant role. Thus entire Ni-p coatings initially pretreated earlier applying on mg substrate. The coatings Electroless Ni-P was successfully carried out on AZ91 magnesium the pretreatment helps to avoid galvanic corrosion with a minimum amount of SLS & surfactant better distribution was attained it plays a significant role. With the addition of surfactant, a general improvement has been obtained consequently, pre-treated all Ni-P coating applied on magnesium substrate earlier. Expedite the electroless reaction Nano additive acted as catalyst Nano-additives enabled the better distribution of Ni-P coating. The surface tension between the eventually abridged the chances of cluster and particles by Surfactants lessen on AZ91 magnesium substrate (Al_2O_3, SiO, and ZnO) compare to others the SiO provides most uniform particle distributions. It was found that ZnO and Al_2O_3 were capable of also equally to do the same. The wider reaction generated by Nano additive site on magnesium and the serve substrate purpose is uniform coating distribution on substrate. It is concluded that along with surfactants the Nano-additives addition helps the distribution and deposition of coating for industrial applications which surges usefulness of coating.

References

[1] Yamashita, Z. Horita, and T. G. Langdon, "Improving the mechanical properties of magnesium and a magnesium alloy through severe plastic deformation," Materials Science and Engineering: A, vol. 300, pp. 142-147, 2001.

[2] A. Singh and S. P. Harimkar, "Laser surface engineering of magnesium alloys: a review," Jom, vol. 64, pp. 716-733, 2012.

[3] W. Kasprzak, F. Czerwinski, M. Niewczas, and D. Chen, "Correlating hardness retention and phase transformations of Al and Mg cast alloys for aerospace applications," Journal of Materials Engineering and Performance, vol. 24, pp. 1365-1378, 2015.

[4] L. Cisar, Y. Yoshida, S. Kamado, Y. Kojima, and F. Watanabe, "Development of High Strength and Ductile Magnesium Alloys for Automobile Applications," Materials Science Forum, vol. 419-422, pp. 249-254, 2003.

[5] J. Tan and M. Tan, "Dynamic continuous recrystallization characteristics in two-stage deformation of Mg–3Al–1Zn alloy sheet," Materials Science and Engineering: A, vol. 339, pp. 124-132, 2003.

[6] P. J. Blau and M. Walukas, "Sliding friction and wear of magnesium alloy AZ91D produced by two different methods," Tribology International, vol. 33, pp. 573-579, 2000.

[7] J. K. Pancrecious, S. B. Ulaeto, R. Ramya, T. P. D. Rajan, and B. C. Pai, "Metallic composite coatings by electroless technique – a critical review," International Materials Reviews, pp. 1-25, 2018.

[8] S. Xu, S. Kamado, N. Matsumoto, T. Honma, and Y. Kojima, "Recrystallization mechanism of as-cast AZ91 magnesium alloy during hot compressive deformation," Materials Science and Engineering: A, vol. 527, pp. 52-60, 2009.

[9] Y.-h. Sun, R.-c. Wang, C.-q. Peng, Y. Feng, and M. Yang, "Corrosion behaviour and surface treatment of superlight Mg–Li alloys," Transactions of Nonferrous Metals Society of China, vol. 27, pp. 1455-1475, 2017/07/01/ 2017.

[10] C. K. Lee, "Corrosion and wear-corrosion resistance properties of electroless Ni–P coatings on GFRP composite in wind turbine blades," Surface and Coatings Technology, vol. 202, pp. 4868-4874, 2008/06/25/ 2008.

[11] M. Sribalaji, P. Arunkumar, K. S. Babu, and A. K. Keshri, "Crystallization mechanism and corrosion property of electroless nickel-phosphorus coating during intermediate temperature oxidation," Applied Surface Science, vol. 355, pp. 112-120, 2015/11/15/ 2015.

[12] A. Araghi and M. H. Paydar, "Wear and corrosion characteristics of electroless Ni–W–P–B4C and Ni–P–B4C coatings," Tribology - Materials, Surfaces & Interfaces, vol. 8, pp. 146-153, 2014/09/01 2014.

[13] T. Mimani and S. M. Mayanna, "The effect of microstructure on the Surface and Coatings Technology, vol. 79, pp. 246-251, 1996/02/01/ 1996.

[14] X. L. Ge, D. Wei, C. J. Wang, B. Zeng, and Z. C. Chen, "A study on wear resistance of the Ni-P-SiC coating of Magnesium Alloy," in Applied Mechanics and Materials, 2011, pp. 1078-1083.

[15] Y. Choi, C. Lee, Y. Hwang, M. Park, J. Lee, C. Choi, et al., "Tribological behaviour of copper nanoparticles as additives in the oil," Current Applied Physics, vol. 9, pp. e124-e127, 2009/03/01/ 2009.

[16] M. Saeedi Heydari, H. R. Baharvandi, and S. R. Allahkaram, "Electroless nickel-boron coating on B4C-Nano TiB2 composite powders," International Journal of Refractory Metals and Hard Materials, vol. 76, pp. 58-71, 2018/11/01/ 2018.

[17] M. Gholizadeh-Gheshlaghi, D. Seifzadeh, P. Shoghi, and A. Habibi-Yangjeh, "Electroless Ni-P/nano-WO3 coating and its mechanical and corrosion protection properties," Journal of Alloys and Compounds, vol. 769, pp. 149-160, 2018/11/15/ 2018.

[18] L. Bonin, V. Vitry, and F. Delaunois, "The tin stabilization effect on the microstructure, corrosion and wear resistance of electroless NiB coatings," Surface and Coatings Technology, vol. 357, pp. 53-363, 2019/01/15/ 2019