Effect of Electroless Ni-P Coatings Containing Nano Additives on Surface Topography of Magnesium Alloy

Motilal Lakavat, Pankaj Kumar Sharma, Mukesh Saxena, Parag Diwan

Abstract*: *In order to improve the wear and corrosion behavior for the alloys, coating is found as the most suitable method. Mg base alloys have a wide range of industrial application. These alloys shows a high specific strength but poor wear and corrosion resistance. An ordinary coating of Cu, Ni & Zn etc. provide a physical barrier against the wear rate and corrosion attack of magnesium substrate. In the present investigation, Ni-P plating was done on AZ91 composite by immersing samples into Nickel sulphate bath in presence of surfactants. The mechanism of Ni-P deposits was studied by using SEM. Ni-P coating was coated uniformly in the presence of surfactants. Effect of surfactant and Effect of Nano-additives Al_2O_3, ZnO, and SiO with different quantities were studied. 0.5 g/l Nano Al_2O_3 additive enhanced the deposition of Ni-P on AZ91 magnesium composite and the same results have been observed in case of SiO addition. Influence of ZnO was also observed. So is very clear that Ni-P coating is very effective to reduce the corrosion and increase the wear behaviour if it is used along with Nano additive and the surfactants.

Index Terms*: Coating, *Nano-additives, Scanning Electron Microscope, surfactants.

I. INTRODUCTION

Amongst the various materials available for the aerospace and automotive industry, Magnesium alloys conquers an important place. Mg alloys shows low density, high specific strength and exceptional machinability [1, 2]. However, despite of these properties these alloys have susceptibility to corrosion in moist environment and therefore they have limited application in the areas where high wear resistance is required [3]. Coating is found as the most suitable method to improve the wear characteristics. [4]. Magnesium alloys are very light in weight but their applications are limited in engineering industries because of the poor wear & corrosion resistance. The problem of corrosion was improved by the introduction of pure alloys [5]. Alloying improves the general corrosion behaviour, but no significant improvement has been observed in galvanic corrosion [6, 7]. To solve this issue proper coating is required [8]. The Ni-P coating is very effective to reduce corrosion but the challenge is to do the coating by effective way. For that addition of Nano additives and the different surfactants on Ni-P deposition was used and their effect was studied in this effort by Sun *et. al.* [9].

Electroless plating technique results in the reduction of a fine, uniform and smooth surface that provides good surface roughness properties, wear resistance and protection against corrosion [10-12]. Recently researchers have paid their attention towards Ni-P coatings which includes the effect of phosphorous content on structure and surface morphology. Ni-P coating have been classified on the basis of the phosphorous content. High phosphorous content (more than 8 %) reveals best corrosion properties and recommended for the environment where severe corrosion occurs. Whereas coatings with low phosphorus content (less than 3 %) shows poor corrosion resistance and good wear properties. Therefore, Corrosion resistance of Mg alloys not depends only on the phosphorous content. According to Mimani *et. al*. [13], corrosion behaviour can be directed by degree of amorphous state, the amount of internal stress and the weight percentage of phosphorus content. Many researchers have reported the coating performance in different environments with respect to the amount of phosphorus used.

To further improve the coating performance now a day's researchers are using Nano particles along with electroless Ni-P coating. The Nano particles like Al_2O_3, SiO_2, TiO_2 etc. are generally added in electrolytic bath to formulate the electro less Ni-P Nano particle coating. Although Nano additive improves the corrosion behavior and wear performance of coating but still it has few challenges. First thing is the uniform distribution of Nano particles and another one is the agglomeration which effects the stability of Nano particles in the solution [14].

Nano Al_2O_3 particles are used by many researchers because of their high strength and good stability. These particles are relatively cheap and exhibits good hardness [15] These particles are mostly used for copper and steel substrate and few work has been reported on Magnesium alloys.

The objective of this work is to utilize the MgAZ91D composite (Mg with 1%wt MWCNT-(1%wt) Al_20_3) which has been used as a substrate material and the Al_2O_3, ZnO & SiO are used as Nano additives for checking their effect. Tests are conducted to get the influence of Nano additives on the mechanical properties of electro less Ni-P Coated Mg composite and their results are presented and discussed in the further sections.

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II. EXPERIMENTAL DETAILS

A. *Preparation of specimen for the test*

Substrate material chosen for the coating was magnesium (Mg) composite containing 1 wt. % of MWCNT and 1 wt. % of Al_2O_3 which was purchased from Bangalore, India. The sample as shown in Fig 1 was cut by wire EDM for Ni-P coating. Rectangular (8 mm x 26 mm x 8 mm) samples of Mg composite are first ground progressively with SiC abrasive papers having 300, 400, 800, 1000, 1500 and 2000, mesh to achieve an acceptable surface uniformity. Similarly, for the corrosion test, sample is cut to dimension (10 mm x 20 mm x 8 mm).

Fig 1. Sample prepared for the test.

B. Pretreatment process

During the pre-treatment process, the acetone is used for the cleaning of the substrate. Further, alkaline cleaning with sodium hydro-oxide (45 g/L) is done followed by Tri-sodium orthophosphate (10 g/L) for 20 min; at 65 ^{0}C 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 for 10 min at room temperature. The procedure is followed as per the literature [16]. The setup is shown in Fig 2.

Fig 2. Alkaline cleanig setup.

C. Electroless nickel coating bath and operating conditions

The coating bath consists of:
(i) Nickel Sulphate (26 g/L),
(ii) Sodium hypo-phosphate (30 g/L) as reducing agent,
(iii) Sodium acetate (16 g/L) as stabilizer and
(iv) Ammonium hydrogen difluoride (8 g/L) as the complexing agent.

The surfactant SLS (1.2g/L) is added into solution before EN deposition. The stabilizer thiourea (1ppm) is added into the bath when the reaction is stable. Process parameters such as pH, Temperature and effect of Surfactant concentrations are varied. The pH level is adjusted by addition of sodium hydroxide pallets. The pH and temperature values are varied at 3 different levels 4-5, 6-7, 8-9 and 70ºC, 85ºC and 90ºC respectively. The surfactant SLS is used and its concentration was varied from 0 to 1.2 g/L. It is noticed that pH value 6-7, temperature maintained at 85°C and SLS (1.2 g/L) provides better coatings with Nano additives [17]. The composition of the coating baths and the varying percentage of Nano additives is tabulated in table 1 and 2.

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

Particulars	Bath A	Bath B	Bath C
	Quantity(g/L)		
$NiSo_4.6H_2O$	26	26	26
Na $H_2O_2PO_{2.}$ H_2O	30	30	30
HF (40%, v/v)	12 ml	12 ml	12 ml
$NaC_2H_3O_2$	16	16	16
NH_4HF_2	8	8	8
$NaC1_2H_{25}So_4$	1.2	1.2	1.2
Thiourea	1 ppm	1 ppm	1 ppm
Nano Al_2O_3, 40 nm	0.5-2	-	-
Nano ZnO, 50 nm	-	0.5-2	-
Nano SiO, 25 nm	-	-	0.5-2

Table II. Concentration details of the Nano additives employed

Al_2O_3	SiO	ZnO
0.1%	0.1%	0.1%
0.5%	0.5%	0.5%
1%	1%	1%
2%	2%	2%

D. *Electroless coating procedure*

The coating is applied for 1hr with total bath volume of 400 ml as shown in Figure 3 and Figure 4. The Al_20_3 (with size of 40 nm), SiO (with average size of 25 nm) and ZnO (with size of 50 nm) nanoparticles are added to the appropriate solutions (Table 1) to study the comparisons of tribological properties. Ultra sonication technique was applied to minimize the agglomeration of the $Al_20_{3,}$ SiO and ZnO which was applied for 15 min. The magnetic stirring at a constant speed of 100 rpm was performed for 60 min for electro less deposition [18]. The pH level is adjusted by addition of sodium hydroxide pallets. Image of the coated samples are shown in Fig 5.

Fig 3. Experimental set up used for EN deposition.

Fig 4. Bath preparation for the test.

Fig 5. Coated samples used for the test

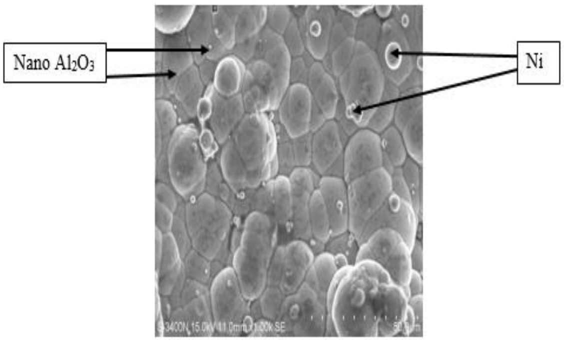
E. Scanning electron microscopy

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

III. RESULTS AND DISCUSSION

A. Effect of Al_2O_3 variation

The SEM images of deposits obtained at different Al_2O_3 percentage of bath solution for magnesium composite substrate are shown in Figure 6. Figures 6 (a) to (d) shows the EDAX images represents the presence of Nano Al2O3 particles. It is further observed from above mentioned EDX images, the Al_2O_3 particles are homogeneously dispersed in EN deposit and this is obtained in higher percentage of Nano additives compared to lower percentages. Hence, it is observed that the addition of varying percentages of Al_2O_3 Nano additives, increases coating uniformity (as shown in Figures 6). The introduction of the anionic surfactant sodium lauryl sulphate (SLS) into the coating bath results in to de-agglomeration of Nano-alumina particles as shown in Fig. 6 (d). The morphology of different coatings deposited from bath solution of different % Al_2O_3 is investigated. Most uniformity in the microstructure was found in coating obtained at 2% Al_2O_3 Nano additives, (Figure 6 (d)). The non-uniformity of the surface could be due to the different % Ni in coating.



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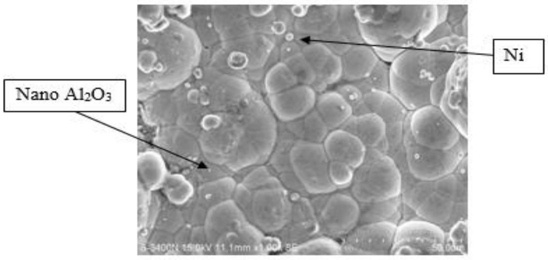

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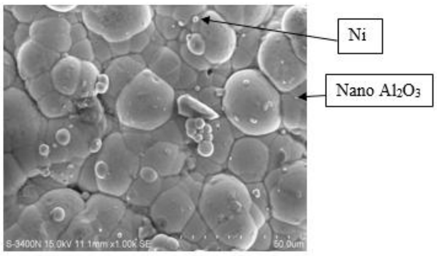

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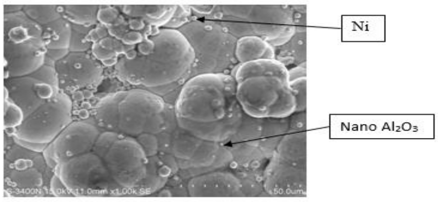


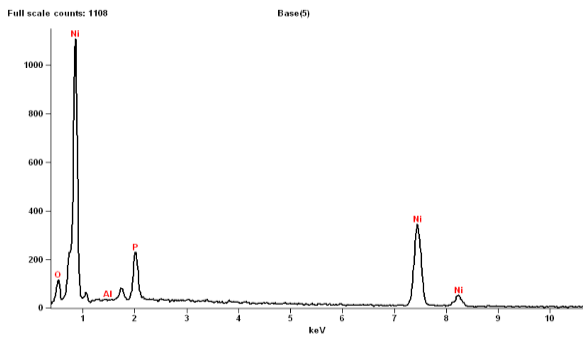
(d)

Fig 6. 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 EDAX patterns of the electro less nickel coated Mg composite with increasing percentage of Al_2O_3 Nano additives are shown in Fig.7.

The presence of nickel in varying percentage is seen as sharp peaks in the all the EDAX spectrum, while the spectra of Al_2O_3 Nano coatings shown in Fig 7. (a), (b), (c), and (d) indicates typical peak of Al and Oxide in ascending proportions indicating the uniformity, adherent and porosity free surface with increasing percentage of Al_2O_3 Nano additives on the Substrate.



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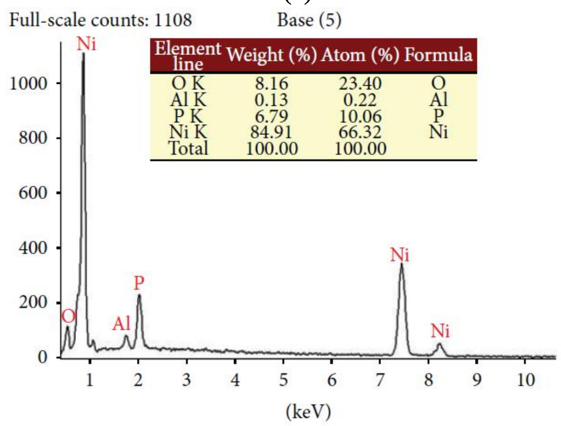

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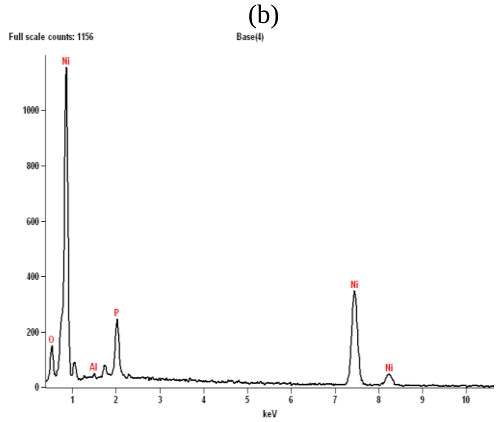

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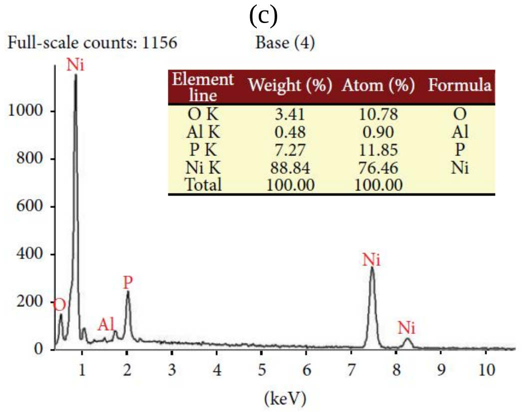


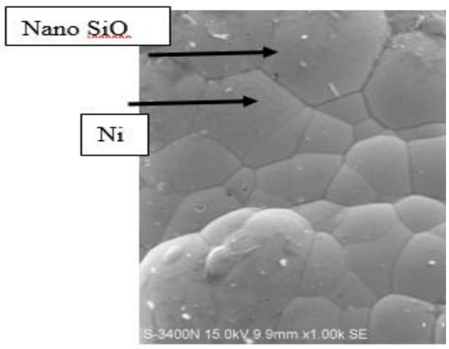
(d)

Fig 7. 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 Fig. 8).The morphology of coatings deposited from bath solution of different % SiO is investigated. Fig.8 (a) to (d), shows the uniform distribution of SiO particles within the coating. The nickel particles deposited on the substrate surface expedite the process and reduces the contact angle which eventually leads to the superior wettability on the substrate. The coating thus produced would always have a good bonding to the substrate. The agglomeration of Nano particles is prevented by using anionic surfactant sodium lauryl sulphate (SLS).

By comparing addition of Nano additive with each other, a compressed and defect-free composite coating is obtained with 2% SiO amount. It means that with increase SiO % content, uniformity increases.



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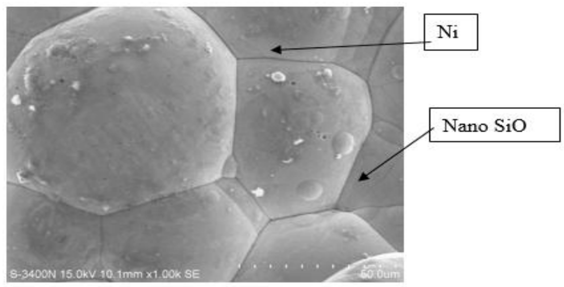

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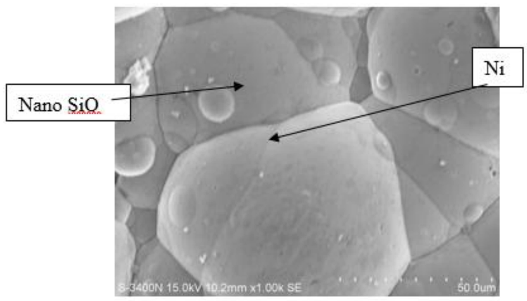

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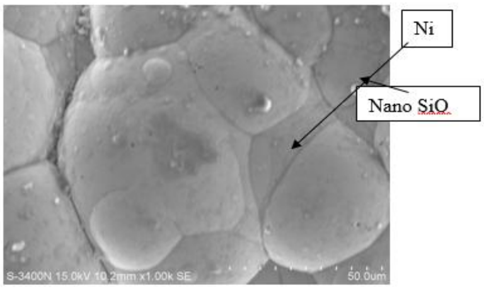
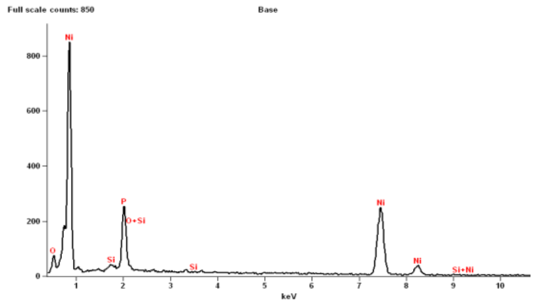


(d)

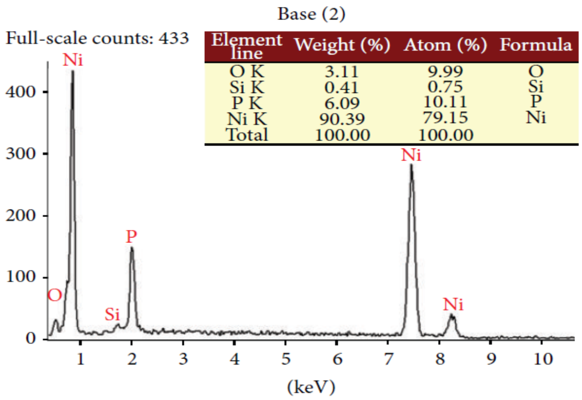
Fig 8. SEM micrograph (1000X) of electro less Ni-P coating on magnesium (Mg) composite reinforced with multiwall carbon nanotube (MWCNT) at varying % of SiO (a) 0.1% (b) 0.5% (c) 1% (d)2%, with surfactant (SLS).

D. *Elemental analysis of mg composite - EDAX*

The EDAX patterns of the electro less nickel coated Mg composite with increasing percentages of SiO Nano additives are shown 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 Nano coatings shown in Fig 9-(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.

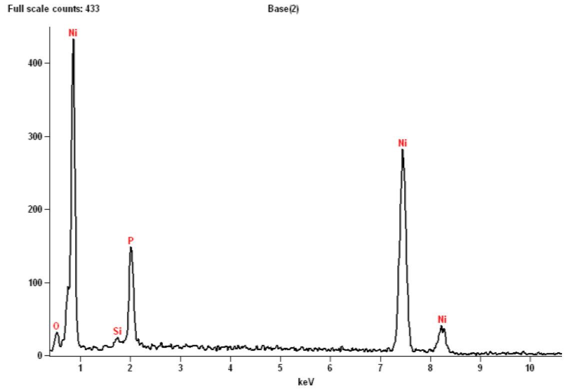


(a)



Element line	Weight (%)	Atom (%)	Formula
O K	3.11	9.99	O
Si K	0.41	0.75	Si
P K	6.09	10.11	P
Ni K	90.39	79.15	Ni
Total	100.00	100.00	

(b)



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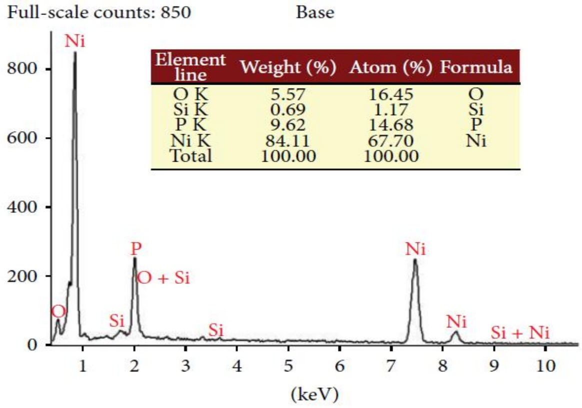


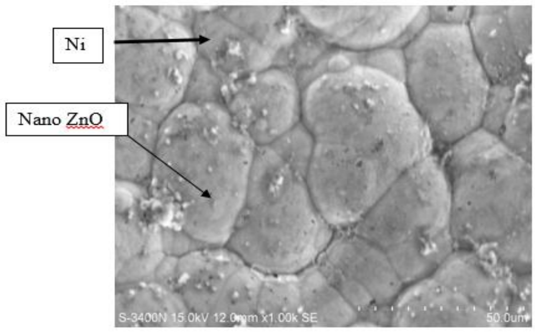
Element line	Weight (%)	Atom (%)	Formula
O K	5.57	16.45	O
Si K	0.69	1.17	Si
P K	9.62	14.68	P
Ni K	84.11	67.70	Ni
Total	100.00	100.00	

(d)

Fig 9. 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), shows the incorporation of higher % of ZnO Nano-particles in the coating has resulted in a rougher surface ((R_a value =1.26), of for composite coatings in comparison to low % of ZnO. It is also seen that the increase in the amount of the ZnO Nano-particles in the Ni-P matrix has caused to obtain a more uneven surface (Fig. 10- b and c). Since the rougher morphology could be a proof for the presence of the ZnO Nano-particles at the surface, it is observed that with increase in nanoparticles concentration in the bath tend to an increasing amount of Nano-particles incorporation in the coating.



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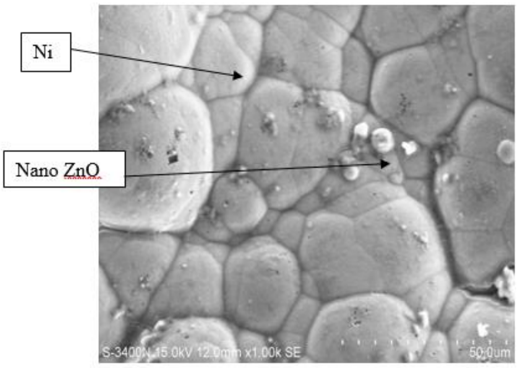

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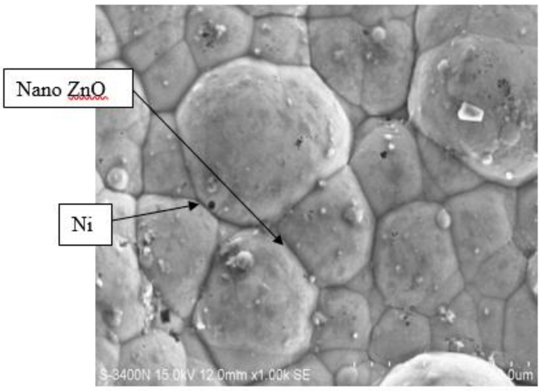

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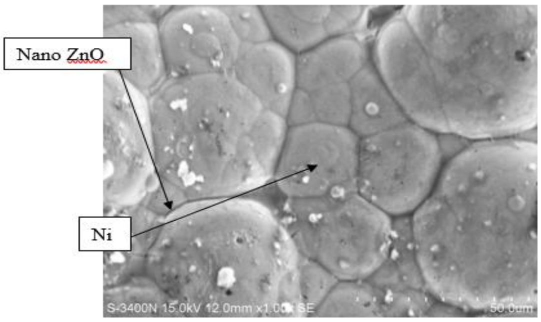
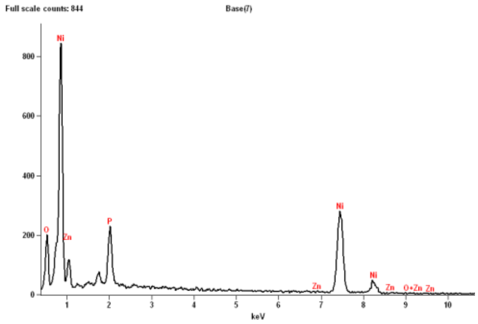


(d)

Fig 10. 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 electro less nickel coated Mg composite with increasing percentages of ZnO Nano additives are shown in Fig.11. An element analysis made on the surface (see Fig 11 (a)-(d)) indicates that Ni, P, Zn and O elements exist in the coating. It is shown that Nano particles incorporation in the Ni-P matrix has been effective on the structure of the EN coating and the EDAX spectrum of the both low and high % of ZnO shows presence of ZnO and increased P content. The increase in P content may be due to addition of surfactant in the EN bath. Surfactant promotes P content in the coating as reported in Elansezhian et al (2008). While the spectra of ZnO Nano coatings shown in Fig 11-(b) & (d) indicates typical Zn (1.67 to 3.05 Wt.%) in ascending proportion to end up in the formation of rougher surface due to high agglomeration of ZnO particles. Excess ZnO Nano particle in amorphous phase could increase the corrosion resistance of the EN coated composite. Hence, Variation in corrosion resistance of EN coatings as a function of ZnO with surfactant (SLS) in EN bath is studied and the results are analysed in the next section.



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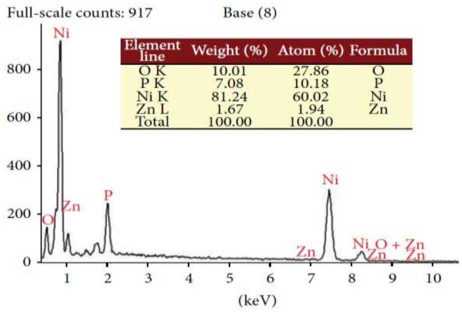

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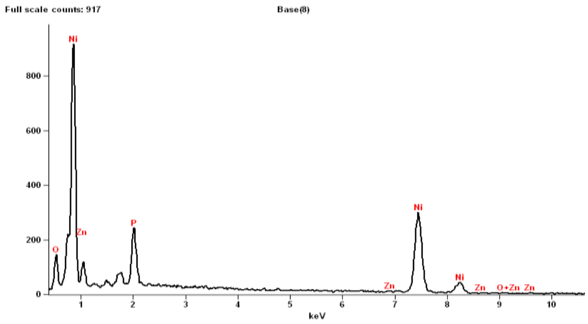

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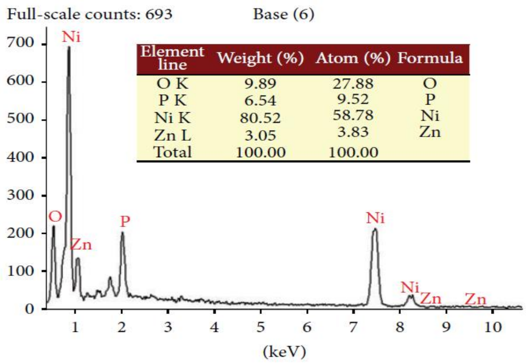

(d)

Fig 11. 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 images of Ni-P Coated Mg composite without surfactant and Nano additives

The SEM micrograph in Figure 12 clearly shows the non-uniform deposition of nickel particles on the substrate. Without the presence of anionic surfactant sodium lauryl sulphate (SLS), the agglomeration of Nano particles are clearly seen. It is concluded that the surface morphology of EN coated Mg composite substrate without Nano additives and surfactant possess inferior surface texture when compared with coatings with 2% Nano additives.

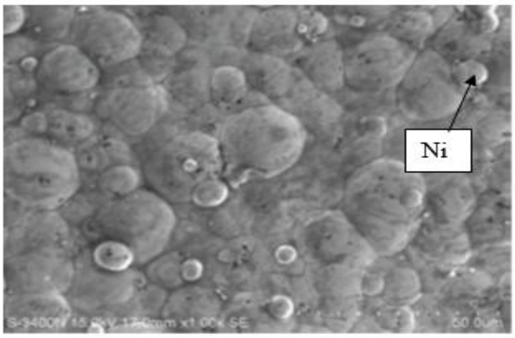

Fig 12. SEM micrograph (1000×) of EN coated Mg composite without surfactant and Nano additives.

IV. CONCLUSION

The Electro less Ni-P coating was successfully carried out on AZ91 magnesium. A general improvement has been obtained with surfactant addition. Though, better distribution was attained with minimum amount of surfactant & SLS. Pre-treatment process help in avoiding galvanic corrosion and play very important role. Therefore, all Ni-P coatings pre-treated initially before applying on magnesium substrate. Surfactants lessen the surface tension between the particles & eventually abridged the chances of cluster. Nano-additives (Al2O3, SiO, and ZnO) enabled the better distribution of Ni-P coating on AZ91 magnesium substrate. Nano additive acted as catalyst and expedite the electro less reaction. SiO provides the most uniform particle distributions as compare to others. It was found that Al_2O_3 and ZnO were also equally capable to do the same. Nano-additives generate wider reaction sites on the agnesium substrate and serve the purpose of uniform distribution of coating on the substrate. It was observed and concluded that the addition of Nano-additives along with surfactants provides the proper distribution and deposition of coating which surges the usefulness of the coating for industrial applications.

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