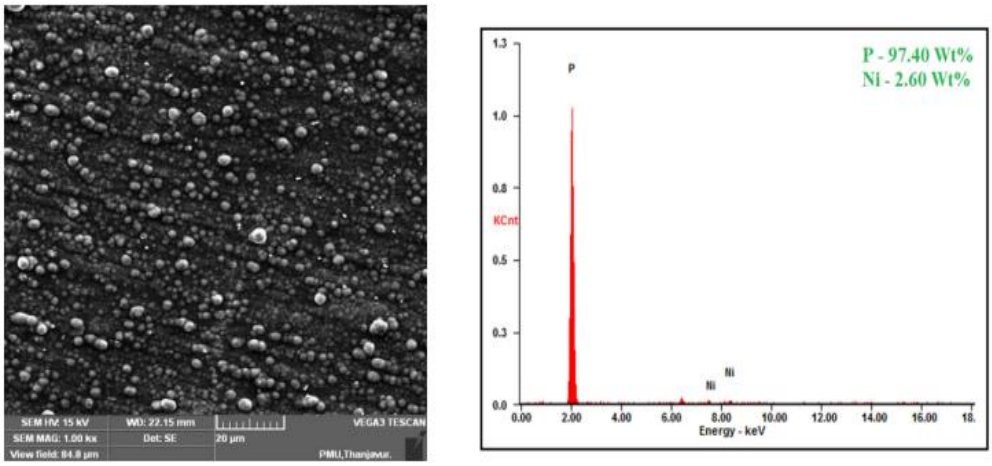


Figure. 3.1 SEM and EDAX image of ENi-B coatings without zincating

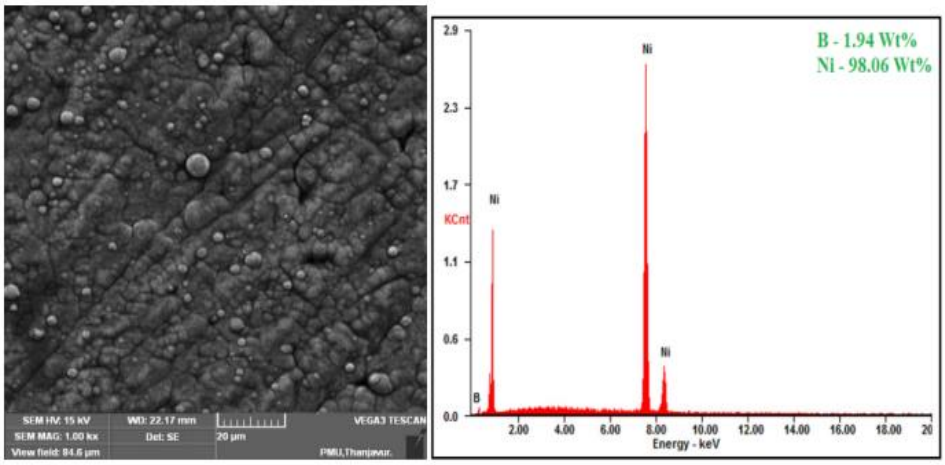


Figure. 3.2 SEM and EDAX image of ENi-B coatings with zincating



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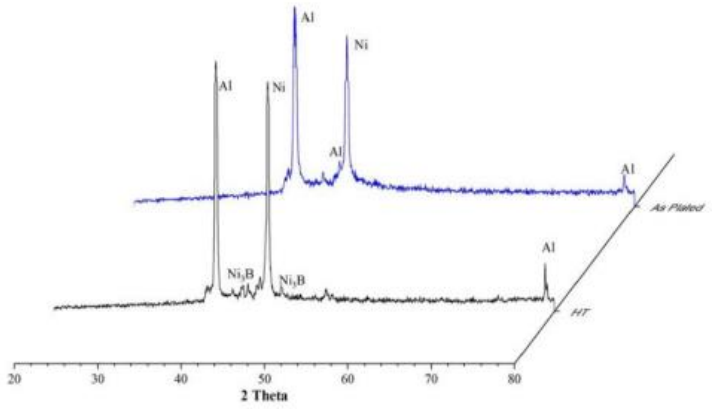


Figure. 3.3 XRD of ENi-B deposit in the as plated condition and heat treatment (HT) at 400 °C for 1 h

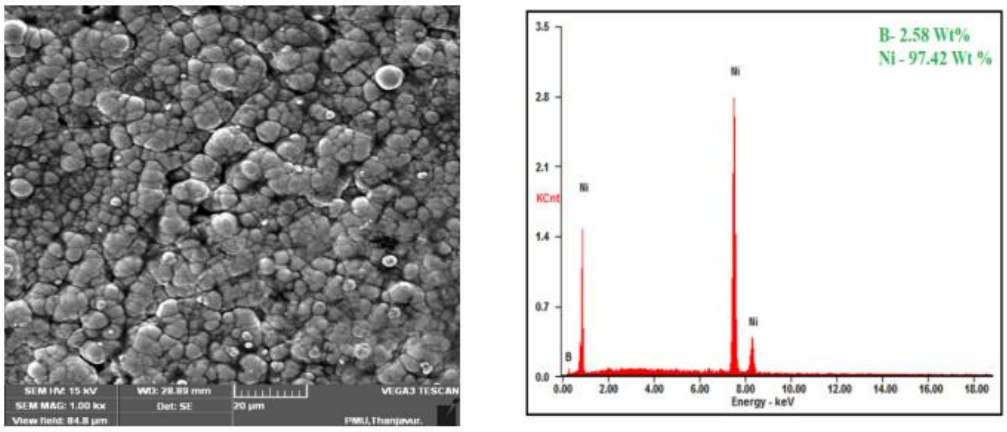


Figure 3.4. SEM image and EDX image of ENi-B coatings with SDS

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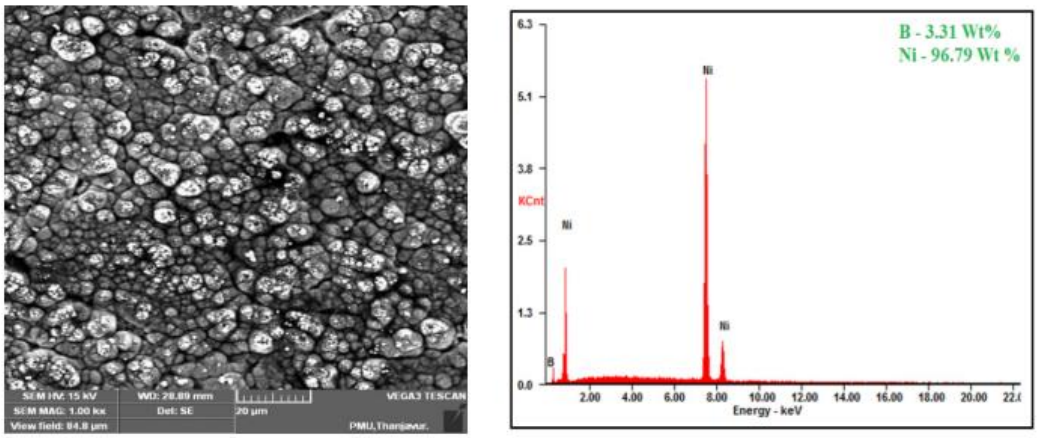
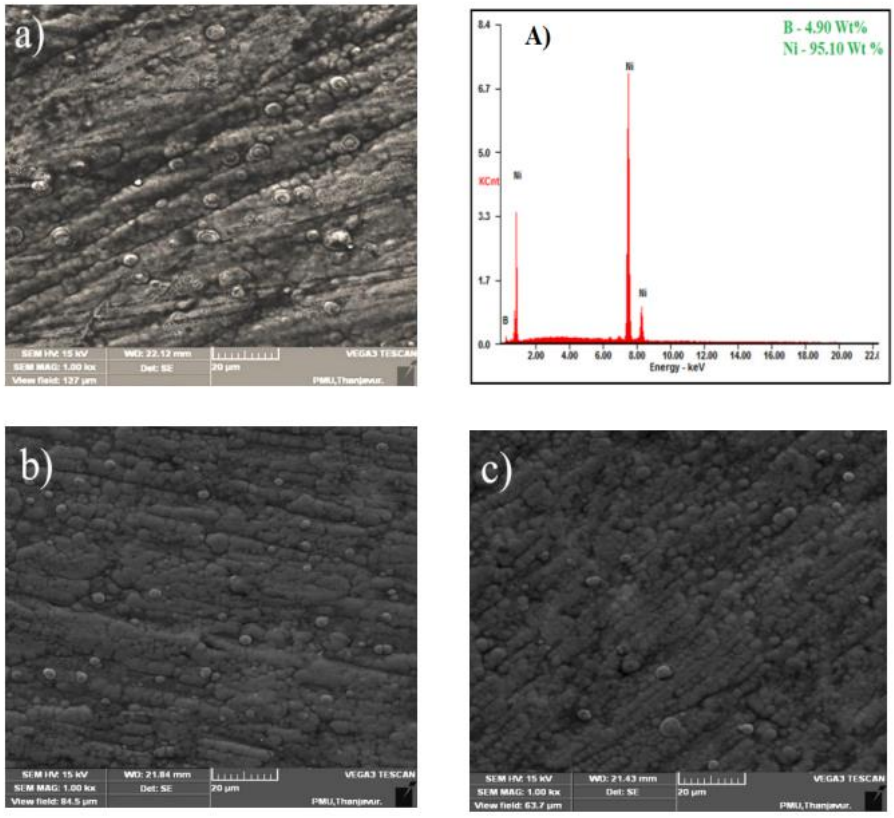


Figure 3.5. SEM image and EDX image of ENi-B coatings with CTAB



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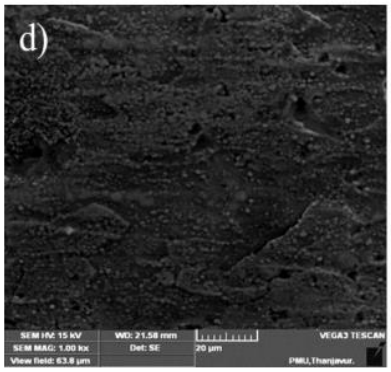


Figure 3.6 (a) SEM image (A) EDX image of ENi-B coatings with amphoteric 0.1 mM; SEM images of (c) with amphoteric 0.2 mM; (c) with amphoteric 0.3 mM; and (d) with amphoteric 0.4 m

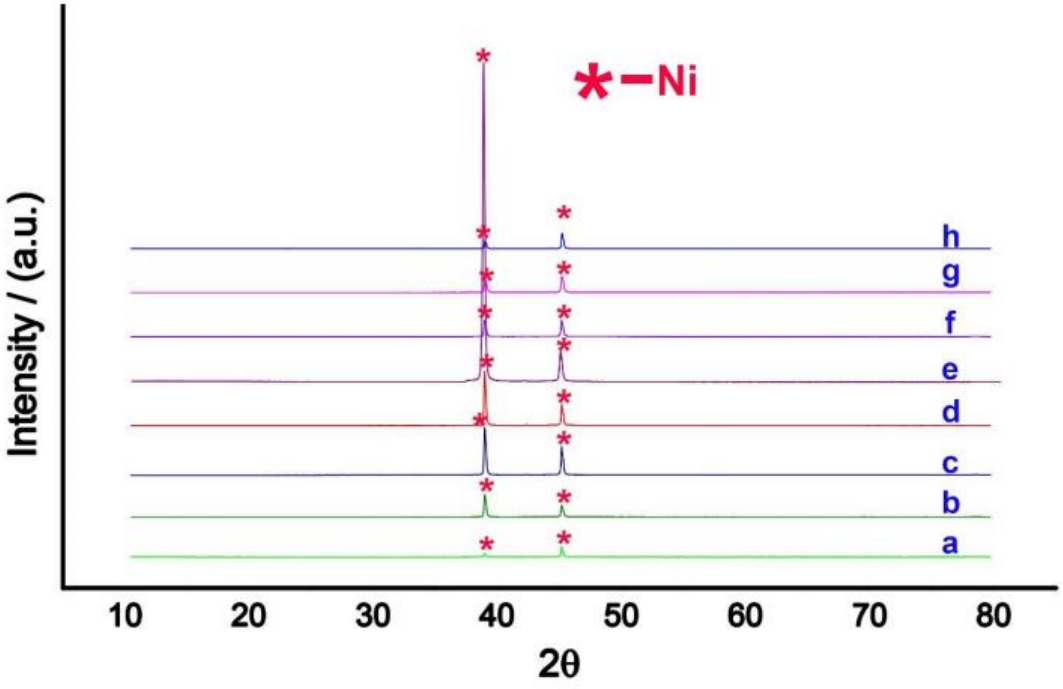


Figure 3.7 XRD patterns of ENi-B coatings: (a) without zincating; (b) with zincating& without surfactant; (c) with SDS; (d) with CTAB; (e) with Amphoteric 0.1mM; (f) with Amphoteric 0.2mM; (g) with Amphoteric 0.3mM; (h) with Amphoteric 0.4mM



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FORM 2

THE PATENTS ACT, 1970

(39 of 1970)

&

THE PATENTS RULES, 2003

COMPLETE SPECIFICATION

(See section 10 and rule 13)

1. TITLE OF THE INVENTION

A METHOD OF ELECTROLESS PLATING USING AN ECO-FRIENDLY STABILIZER

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3. PREAMBLE TO THEDESCRIPTION

The following specification particularly describes the invention and the manner in which it is to be performed.

FIELD OF INVENTION:

The present invention relates to a method of developing a novel electrolyte bath for electroless plating using an eco-friendly stabilizer. More particularly, the present invention is directed toward the electroless nickel-boron (ENi-B) plating.

BACKGROUND OF INVENTION:

It is important to mention here that the method of electroless plating is conventionally known. More particularly, the method of electroless nickel-boron (ENi-B) plating is also known as an alternative to hard chrome deposits. To formulate the electrolyte bath for the electroless nickel-boron coatings, heavy metals such as lead and thallium were used as stabilizers. But, the usage of heavy metals is restricted to a greater extent in the coating process due to their higher toxicity levels. Therefore, there is a need to use an eco-friendly compound for bath stability.

Mukhopadhyay et al. (2018) deposited electroless Ni–B–W coatings on AISI 1040 steel specimen with sodium borohydride as the reducing agent and lead nitrate as a stabilizer. Improvement in the wear rate and coefficient of friction (COF) was observed at 300 ºC and 500 ºC, especially for the heat-treated coatings.

ENi-B coatings were developed by Jaime Taha-Tijerina et al. (2019) on tool steel using sodium citrate, 2-mercaptobenzothiazole (2MBT), and dimethylamine borane (DMAB). The tribological evaluations revealed a reduction in the specific wear rate of the substrate.

Box Behnken Design (BBD) was used by Sarkar et al. (2019) to optimize 3 factors, concentration of cobalt sulphate, concentration of sodium hypophosphite, and bath temperature were used to maximize the hardness value. 1921 HV_{10g} was achieved at 15 g/L of cobalt sulphate, 25 g/L of sodium hypophosphite, and bath temperature of 85 °C.

Surfactants were added by Sudagar et al. (2012) in electroless coatings to produce a smooth surface finish. An average roughness value of 1.412 μm for CTAB and 1.789 μm for SLS were obtained, which are less than the value (2.98 μm) without surfactant addition.

Zwitterionic surfactant was added by Muraliraja et al. (2018) to enhance the deposition rate of composite coating and assisted in distributing the nanoparticle effectively. No decomposition of electrolyte was observed during the coating process. Hence electroless plating industries could make use of Zwitterionic surfactant when the composite coatings are prepared.

ENi-B coatings with Sodium borohydride as the reducing agent and lead nitrate as stabilizers were developed by Tima et al. (2021). The effect of plasma nitriding (PN) temperature on the microstructural properties and wear behaviour of ENi-B coatings were investigated. The results showed that the PN replaces the primary superficial cracks and nodular structure of the ENi-B coatings with a dense and granular structure.

OBJECTIVES OF THE INVENTION:

The primary objective of the present invention is to devise a method of electroless nickel-boron (ENi-B) plating and develop an electrolyte bath with an eco-friendly stabilizer for its stability and to produce, evaluate and characterize the nickel-boron deposits with and without surfactants, and with different types of pre-treatments, prior to the nickel-boron deposition.

Another objective of the present invention is to produce ENi-B deposits on Al 7075 alloy substrate in the absence of heavy metals as a stabilizer by using the autocatalytic (electroless) method.

Yet another objective of the present invention is to optimize the process parameters of the ENi-B coatings without the addition of surfactant for maximum microhardness and minimum average surface roughness (R_a) using modelling techniques like Plackett–Burman design (PBD), Response surface methodology-based Box-Behnken design (RSM-BBD), Backpropagation artificial neural network (BPNN) and optimization techniques like Simulated annealing (SA), Genetic algorithm (GA), and Intuitive search technique.

Yet another objective of the present invention is to study the influence of different types of surfactants on microhardness, average surface roughness, and corrosion resistance of the ENi-B deposits and to explore the effect of amphoteric surfactant concentration on the surface properties of ENi-B deposits.

Yet another objective of the present invention is to study the effect of heat treatment on the microhardness of the deposits.

Yet another objective of the present invention is to study the wear behaviour of ENi-B deposits under different pre-treated conditions.

Yet another objective of the present invention is to study the different properties by using SEM, XRD, EDAX, AFM and potentiodynamic polarization test.

Other objectives and advantages of the present invention will become apparent from the following description.

SUMMARY OF INVENTION:

The present invention relates to a method of electroless plating using an eco-friendly stabilizer, which comprises the following steps: i) preparing an aqueous solution for electroless nickel-boron coatings which comprises of the source of nickel ion, reducing agent, stabilizer, complexing agent, with and without amphoteric surfactant. ii) placing a disc substrate of 7075-T6 aluminium alloy with a composition of Si 0.4, Fe 0.5, Cu 2.0, Mn 0.3, Mg 2.9, Cr 0.28, Zn 6.1, Ti 0.2, and rest Al in weight percentage having a size of diameter 25 mm × thickness 5 mm, in the said aqueous solution. iii) preparing the deposition of the said electroless nickel-boron coatings after double zincating pre-treatment for 90 min without the said aqueous solution replenishment in a non-agitated freshly prepared electrolyte bath.

BRIEF DESCRIPTION OF DRAWINGS:

The present invention will be better understood after reading the following detailed description of the presently preferred aspects thereof with reference to the appended drawings, in which the features, other aspects, and advantages of certain exemplary embodiments of the invention will be more apparent from the accompanying drawings in which:

Figure 3.1 illustrates SEM and EDAX image of ENi-B coatings without zincating;

Figure 3.2 illustrates SEM and EDAX image of ENi-B coatings with zincating;

Figure 3.3 illustrates XRD of ENi-B deposit in the as plated condition and heat treatment (HT) at 400 °C for 1 h;

Figure 3.4 illustrates SEM image and EDX image of ENi-B coatings with SDS;

Figure 3.5 illustrates SEM image and EDX image of ENi-B coatings with CTAB;

Figure 3.6 illustrates (a) SEM image (A) EDX image of ENi-B coatings with amphoteric 0.1 mM; SEM images of (c) with amphoteric 0.2 mM; (c) with amphoteric 0.3 mM; and (d) with amphoteric 0.4 m;

Figure 3.7 illustrates XRD patterns of ENi-B coatings: (a) without zincating; (b) with zincating& without surfactant; (c) with SDS; (d) with CTAB; (e) with Amphoteric 0.1mM; (f) with Amphoteric 0.2mM; (g) with Amphoteric 0.3mM; (h) with Amphoteric 0.4mM;

DETAILED DESCRIPTION OF DRAWINGS:

The following description describes various features and functions of the disclosed devise and methods with reference to the accompanying figures. In the figures, similar symbols identify similar components, unless context dictates otherwise. The illustrative aspects described herein are not meant to be limiting. It may be readily understood that certain aspects of the disclosed system, method, and apparatus can be arranged and combined in a wide variety of different configurations, all of which are contemplated herein.

These and other features and advantages of the present invention may be incorporated into certain embodiments of the invention and will become more fully apparent from the following description and claims or may be learned by the practice of the invention as set forth hereinafter.

Accordingly, those of ordinary skill in the art will recognize that various changes and modifications of the embodiments described herein can be made without departing from the scope of the invention. In addition, descriptions of well-known functions and constructions are omitted for clarity and conciseness.

The terms and words used in the following description and claims are not limited to the bibliographical meanings, but, are merely used to enable a clear and consistent understanding of the invention. Accordingly, it should be apparent to those skilled in the subject that the following description of exemplary embodiments of the present invention are provided for illustration purposes only and not for the purpose of limiting the invention.

It is to be understood that the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise.

It should be emphasized that the term “comprises/comprising” when used in this specification is taken to specify the presence of stated features, integers, steps, or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

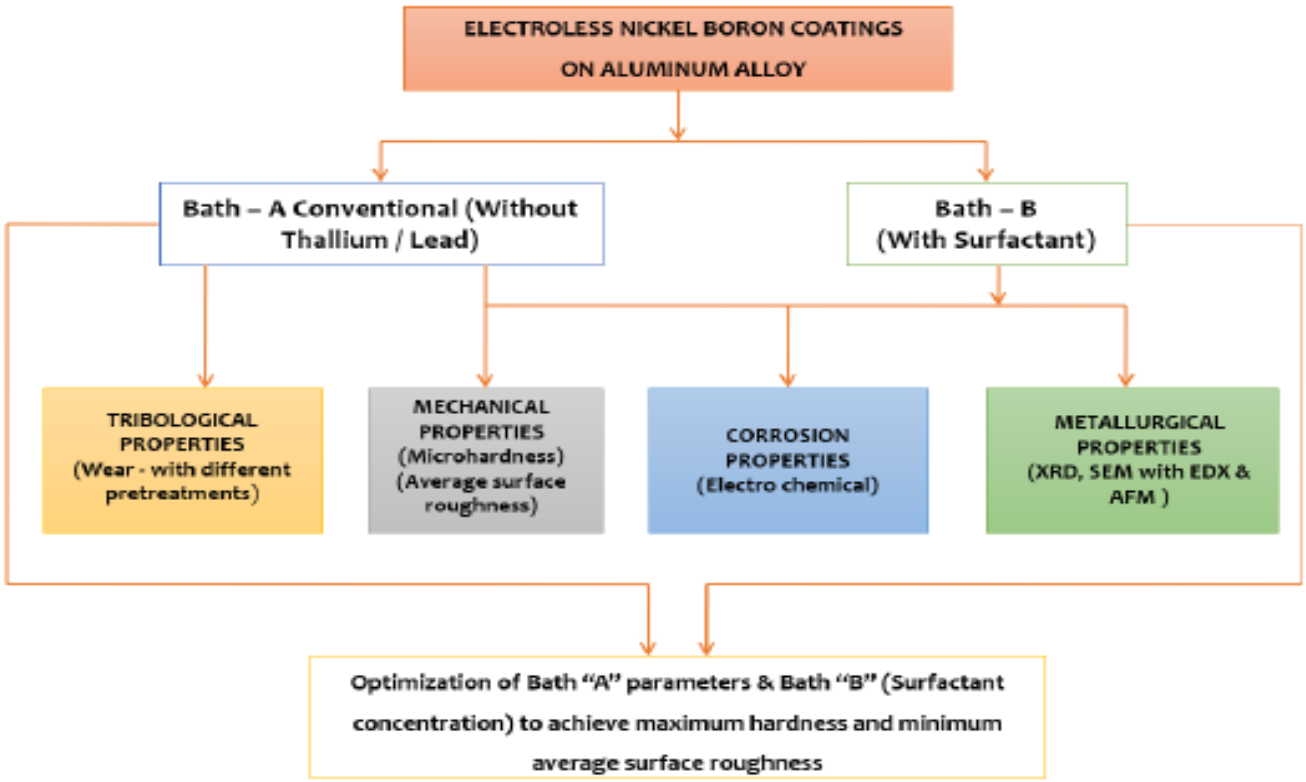
In accordance with the present invention, instead of using heavy metals such as lead and thallium as stabilizers and formulating the electrolyte bath in the ENi-B coating process, the present invention is using the eco-friendly compound trisodium citrate as a stabilizer for bath stability and 3- (N, N-Dimethylmyristylammonio) propanesulphonate as amphoteric surfactant.

In particular, the method of electroless plating using an eco-friendly stabilizer, which comprises the following steps: i) preparing an aqueous solution for electroless nickel-boron coatings which comprises of the source of nickel ion, reducing agent, stabilizer, complexing agent, with and without amphoteric surfactant. ii) placing a disc substrate of 7075-T6 aluminium alloy with a composition of Si 0.4, Fe 0.5, Cu 2.0, Mn 0.3, Mg 2.9, Cr 0.28, Zn 6.1, Ti 0.2, and rest Al in weight percentage having a size of diameter 25 mm × thickness 5 mm, in the said aqueous solution. iii) preparing the deposition of the said electroless nickel-boron coatings after double zincating pre-treatment for 90 min without the said aqueous solution replenishment in a non-agitated freshly prepared electrolyte bath.

Electroless nickel-boron (ENi-B) plating, in accordance with the present invention, refers to the electroless nickel-boron (ENi-B) plating using an eco-friendly stabilizer.

RESULTS AND DISCUSSION:

Work Plan:



3.1 Development of Heavy Metals Free Electroless Nickel-Boron Coatings with and Without Zincating Pre-Treatment:

A novel electroless bath was developed in this study with eco-friendly trisodium citrate as a stabilizer. Zincating is the pre-treatment process used for aluminium alloys to remove the oxide layer before the nickel deposition. Because, electroless nickel baths with borohydride are very corrosive due to their high alkalinity, pH>13. Double zincating with intermediate deposition of nickel was carried out to protect the substrate from corrosion.

The coating thickness achieved was 14 µm. The Vickers hardness of ENi-B coating was 589 HV in the as-plated condition which is higher than the uncoated substrate (212 HV). The coatings were subjected to heat treatment for 1 h at 400 °C and a hardness of 750 HV was achieved. The surface hardness was thus increased by 178% and 254% after ENi-B coating and heat treatment respectively. The average surface roughness (R_a) value of 0.256 µm was obtained in the as plated condition.

3.2 Optimization of Process Parameters for Minimum Average Surface Roughness (R_a):

A two-level, fractional factorial screening design, Plackett–Burman design (PBD), was used to identify the significant process parameters influencing the average surface roughness and hardness of the ENi-B coatings. The factors affecting coating formation on the substrate in the electroless bath are concentrations of the metal ion source, reducing agent, stabilizer, complexing agent, pH, bath temperature, and plating time, and the levels were selected from the literature. The experiments were performed according to the PBD matrix and the difference, mean square and total percentage contribution (TPC) of each factor were calculated. The factors were ranked based on their TPC. A factor with the highest TPC was ranked 1 and so on. From the PBD analysis, it was evident that to achieve a minimum average surface roughness and maximum microhardness, the three most influencing factors are (i) Stabilizer concentration; (ii) Nickel ion concentration; and (iii) Reducing agent concentration. While varying these factors at three levels, other factors were maintained at a constant level of either low or high.

Metal ion source concentration (25-35 g/L), reducing agent concentration (0.6-1.0 g/L) and stabilizer concentration (20-40 g/L) were the independent factors and average surface roughness (R_a) and microhardness (HV) were a response (dependent factor). 15 trials were performed to optimize the factors in Box-Behnken design (BBD). According to the regression analysis of the experimental design, all the linear and quadratic terms have negative and positive values, respectively, that tend to improve the surface finish. ANOVA for the quadratic response surface model demonstrates that the model is significant, as is evident from the high Fisher's F-test value (2498.87) with a low p-value (<0.0001). A high value of the coefficient of determination (R2 = 0.9984) showed that the model was successful in predicting local optimum values for average surface roughness.

The optimal settings for metal ion source concentration, reducing agent concentration and stabilizer concentration were obtained at 29.66 g/L, 0.78 g/L, and 29.25 g/L respectively from BBD.

According to the GA, the optimal conditions for minimum Ra of 0.2515μm were 29.66 g/L metal ion concentration, 0.7855 g/L reducing agent concentration and 29.24 g/L stabilizer concentration. For minimum R_a of 0.2519 μm, according to SA, the optimal conditions were 29.67 g/L metal ion concentration, 0.799 g/L reducing agent concentration and 29.072 g/L stabilizer concentration. The optimal values obtained by the GA & were validated by

conducting experiments in triplicate. Good conformity between the predicted and the experimental R_a proved the effectiveness of the GA & SA in the R_a optimization.

A network with too many neurons, however, may allow for too much freedom for the weights to adjust and, hence, invariably learn the noises that are present in the dataset. Hence ten neurons were selected in this study for the hidden layer. Based on the fitting criteria, the Levenberg-Marquardt (LM)- a trained network of 3-10-1 architecture with a sigmoid function for hidden layer was used in predicting R_a. The coefficient of correlation (R) indicates the goodness of fit between the experimental and predicted responses given by the artificial neural network (ANN) model. In this case, the values of R for training, testing and validation were 0.99914, 1 and 1 respectively. Since the R values for all the models are nearly equal to 1, it indicates the significance of the model. Thus, good, sufficient, higher values of coefficient (R) of the ANN predicted and experimental responses for minimum R_a suggest that the newly created ANN has the ability to predict the minimum average surface roughness.

Furthermore, the optimum values are refined for better average surface roughness using the intuitive search intelligence technique. Hence the results obtained in the genetic algorithm are taken for intuitive search. The same conditions are substituted in the regression equation and average surface roughness of 0.252018 μm is obtained which is closer to optimum values obtained in the other two algorithm methods. The experimentation is carried out using the same input conditions and the finalization of average surface roughness using intuitive Search intelligence of 0.252 μm was obtained.

Table: 3.1 Comparison of results obtained using RSM, SA, GA, and Intuitive search:

Optimization Techniques	Nickel Chloride (g/L)	Sodium borohydride (g/L)	Trisodium citrate (g/L)	Average surface roughness (μm)
RSM	29.6633	0.784285	29.2514	0.252019
SA	29.698	0.799	29.072	0.251947
GA	29.66	0.7855	29.24	0.251482
Intuitive search	29.667	0.784	29.301	0.252018
Experimental	29.667	0.784	29.301	0.252

3.3 Optimization of Process Parameters for Maximum Microhardness (HV):

The procedure adopted for the PBD, BBD, ANN, SA, and GA in modelling and optimization of microhardness is the same as the procedure adopted in the optimization of R_a. For the developed model, coefficients obtained for the linear terms are positive and the coefficients of quadratic terms are negative, which implies that the objective function is to maximize. The variance for the model, model terms, and residual was analyzed through analysis of variance (ANOVA). F and p-values of 61.70 and 0.0001 reveal that the developed model by BBD is significant. The optimal settings for metal ion source concentration, reducing agent concentration, and stabilizer concentration were obtained at 29.8596 g/L, 0.770 g/L, and 30.92 g/L respectively from BBD to achieve the maximum HV of 591.6 with the desirability of 0.991.

The values of R in BPNN for training, testing, and validation were 0.99396, 1, and 1 respectively. The R values for all the models are nearly equal to 1, which indicates the significance of the model.

The developed model is used as a fitness function in SA and GA to predict the global optimum value. For maximum HV of 591.65, according to the GA, the optimal conditions were 29.86 g/L metal ion concentration, 0.77 g/L reducing agent concentration, and 30.91 g/L stabilizer concentration, and according to SA, the optimal conditions were 29.88 g/L metal ion concentration, 0.769 g/L reducing agent concentration, and 30.75 g/L stabilizer concentration respectively. The optimum values obtained from RSM-BBD, SA, and GA (Table 3.2) were validated by performing experiments in triplicate. The variation between the values is 10%, which is within the permissible limit.

Table: 3.2 Comparison of results obtained using RSM, SA, and GA:

Optimization Techniques	Nickel Chloride (g/L)	Sodium borohydride (g/L)	Trisodium citrate (g/L)	Microhardness (HV)
RSM	29.8596	0.770	30.9211	592□45.92
SA	29.88	0.769	30.75	592□44.76
GA	29.86	0.77	30.91	592□42.37
Intuitive Search	29.87	0.77	30.92	592□42.36

3.4 Surface Morphology and XRD Studies:

In the samples coated without zincating as a pre-treatment, only a negligible amount of nickel and a major portion of phosphorus were quantized through EDX spectrum (Figure 3.1). For the samples coated with zincating (Figure 3.2) as pre-treatment, only the nickel (Ni) and boron (B) elements are present. The ENi–B deposit was obtained without any heavy metal-based stabilizer, which exhibits a typical cauliflower-like structure as in the case of regular ENi-B baths.

In the as-plated condition, the coating exhibited a quasi-amorphous structure along with a nanocrystalline structure of nickel seen as a sharp peak at around $2\theta = 44.5°$. The peaks at around $2\theta = 38.5$ and 80° confirm the aluminium substrate. Upon heat treatment, it was observed that the coatings undergo phase transformation to fully crystalline with Ni and Ni3B (Figure 3.3).

3.5 Addition of different types of surfactants:

Surfactants help in the development of pit-free coatings with the expulsion of H2 bubbles, protecting the surface coating, as well as the substrate. Thus, in the present work different types of surfactants such as sodium dodecyl sulfate (SDS) as anionic, cetyltrimethylammonium bromide (CTAB) as cationic, and 3-(N, N-Dimethylmyristylammonio) propanesulfonate (3-DMAPS) as an amphoteric surfactant were added individually in the electrolyte bath to study the influence on the properties of ENi-B coatings.

A unique concentration of SDS, CTAB, and different concentrations of 3-NNDMPS was added into the bath. In general, it has been observed that the coating thickness, microhardness, and average surface roughness of the ENi-B coated layers improved significantly and the observations are summarized below.

The coating thickness obtained in the absence of surfactant is 14 μm. With the addition of surfactant SDS, CTAB, and amphoteric at 0.1 mM, the coating thickness increased to 18, 20, and 23 μm respectively. When the amphoteric surfactant concentration increased to 0.2mM, 0.3mM, and 0.4mM the coating thickness reduces. The maximum coating thickness was achieved at 0.1 mM of amphoteric surfactant.

Similarly, with the addition of surfactant SDS, CTAB, and amphoteric at 0.1 mM, the microhardness of the deposit increased to 680, 710, and 848 HV respectively. Further increases in the concentration of amphoteric surfactant reduce the microhardness.

The maximum microhardness was achieved at 0.1 mM of amphoteric surfactant. In the as plated condition, the microhardness was 590 HV, which is increased to 743 HV after being subjected to heat treatment at 400 ºC for 1 hr. The samples coated with the addition of different surfactants also showed a significant improvement in the microhardness after being subjected to heat treatment.

The average surface roughness (R_a) obtained in the absence of surfactant is 0.256 μm. With the addition of surfactant CTAB, SDS, and amphoteric at 0.1 mM, the R_a reduces to 0.22, 0.198, and 0.174 μm respectively. When the amphoteric surfactant concentration increased to 0.2mM, 0.3mM, and 0.4mM the R_a value also increases. The minimum R_a was achieved at 0.1 mM of amphoteric surfactant.

3.6 Surface Morphology, EDX and XRD Studies:

The SEM images of the deposits with unique concentrations of SDS, CTAB, (Figures 3.4 and 3.5) and different concentrations of amphoteric surfactant are presented in Figure 3.6 (a-d). The morphology of the deposits changed after the addition of different types of surfactants. With the addition of different types of surfactants, a different structure is observed and a unique morphology is formed which is observed in all types of surfactants. The amount of deposition is increased in the presence of surfactants. Evidence for this is provided by the SEM and EDX images.

The XRD patterns (Figure 3.7) of ENi-B coatings obtained from the surfactant-free bath and with different types of surfactants were characterized using X-ray diffraction obtained. In all the cases the peaks as seen from the pattern at 2θ is equal to 39.5° and 44.5° which represents nickel, confirming the deposition of nickel in the form of crystalline on the substrate except the substrate coated without zincating as the pre-treatment. The intensity of the peak is increased for the substrate coated with the addition of surfactants.

3.7 Optimization of Surfactant Concentration for Average Surface Roughness & Microhardness to Predict the Critical Micelle Concentration (CMC):

Surfactants are used in the electroless deposition process in order to reduce the surface tension between the solid particles and the electrolyte bath. The surfactants exhibit an interfacial activity and change the surface tension of the electrolyte used in the coating process. The most important factor in the application of surfactants is the CMC. The surfactant changes the surface tension strongly before the CMC value, but the surface tension remains constant or declines, once the CMC is reached. Hence it is essential to optimize the concentration of surfactant while using in the electroless bath.

3.7.1 For Average Surface Roughness (R_a):

Mathematical models relating the concentration of amphoteric surfactant (0–0.162 g/L) as an independent variable and R_a as a dependent variable are developed using univariate regression analysis (Linear, quadratic, power, and exponential models) and backpropagation neural network (BPNN) algorithm. The number of neurons in the hidden layer is optimized to achieve minimum mean square error (MSE). The coefficient of determination (R^2) is used to evaluate the goodness of fit between the models, and the BPNN model is found to be the best fit ($R^2 > 0.98$). The minimum R_a of 0.171 ± 0.001 μm was achieved at the CMC of 0.049 g/L (0.135 mM) from the genetic algorithm (GA) using the validated models developed by quadratic regression analysis and BPNN as fitness functions.

3.7.2 For Microhardness (HV):

Similarly, as in the optimization of surfactant concentration for R_a, mathematical models are developed using regression and artificial neural network (ANN) techniques to relate the concentration of amphoteric surfactant (0-0.162 g/L) as an independent variable and microhardness as a dependent variable. The number of neurons in the hidden layer is optimized to achieve minimum mean square error (MSE). Then, the developed model was used to optimize microhardness at CMC using a genetic algorithm (GA). The goodness of fit of the models was evaluated using the coefficient of determination (R^2). The ANN model was found to be the best fit with $R^2 = 0.99$. The maximum microhardness of 852 HV was achieved at the CMC of 0.064 g/L, from the GA using the validated model as a fitness function.

3.8 Effect of Different Pre-treatment on The Wear Properties of Electroless Ni-B Coatings:

The adhesion of coating significantly depends on the pre-treatment. For any quality coatings pre-treatment is required. Zincate (Zn), Nickel (Ni) strike, absorbed hypophosphite layer (AHL) and Palladium strike (PD) are the different types of pre-treatments were given to the substrate prior to the ENi-B coating and their corresponding wear properties were examined in the as plated and heat-treated conditions by a pin on disc wear test method as per ASTM G99 standard.

The uncoated specimen experienced a wear loss of ~ 30μm for 0.25 Kg load due to fairly soft (hardness 212 HV) in comparison with the counter surface. It was observed that there is negative wear loss for the ENi-B coated samples as compared with uncoated samples.

The AHL pre-treatment develops a uniform Ni adsorbed layer and provides a good interfacial bond between ENi-B deposits and aluminium alloy with improved wear resistance ~ -70 μm and a less average coefficient of friction 0.009 after heat treatment at 400°C for 1 Hr.

It is also noted that in the process of the pre-treatment of the specimens the wear resistance is found in the following sequential order AHL – PD – Ni2 – ZN and Ni1 with AHL being the lowest wear loss and the Ni1 being the highest wear loss. The obtained average coefficient of friction (μ_{av}) for all the different pre-treatments is given in Table 3.3.

Table 3.3. Friction co-efficient of ENi-B deposits in as plated and heat-treated

Pre-treatments	Average coefficient of friction (μ_{av})	
	As plated	Heat-treated
Nickel Strike	0.175	0.143
Zincating	0.172	0.140
Palladium strike	0.089	0.015
Absorbed hypophosphate layer	0.079	0.009

3.9 Potentiodynamic Polarization Test:

The corrosion resistance of the bare, ENi-B coatings without surfactant and with amphoteric surfactant at its CMC was investigated by potentiodynamic polarization tests in 3.5 wt% NaCl. The corrosion parameters (Table 3.4) indicate that the ENi-B coatings without surfactant assured excellent protection of aluminium alloy against corrosion.

Table 3.4. Corrosion data obtained from potentiodynamic polarization Test

Material	E_{cor} (mV)	I_{cor}(mA/cm^2)	Corrosion rate (mm/year)
Aluminium (bare)	-918.32	0.0959717	1.162
ENi-B (without surfactant)	-426.86	0.0009321	0.0112873
ENi-B (with amphoteric)	-459.09	0.0016911	0.0201792

CONCLUSION:

The effect of bath additives such as trisodium citrate and ethylenediamine, different pre-treatments, as well as the addition of surfactants to the electroless bath, on coating thickness, mechanical and metallurgical properties, and other characteristics of coatings produced has been studied extensively under specific coating conditions, and the results have been presented and analyzed. In general, it has been observed that the coating thickness, microhardness, average surface roughness, and wear resistance of the ENi-B coated layers improved significantly. Based on the present investigations, the following specific conclusions have been drawn:

- Trisodium citrate is used as a stabilizer in the place of heavy metals such as lead and thallium in the development of ENi-B coatings. During the usage of trisodium citrate with ethylenediamine as an additive, no bath decomposition was observed in the entire coating process even when the different types of surfactants were used.

- The developed coatings exhibit a cauliflower-type structure in comparison to the traditional ENi-B coatings. After the addition of anionic, cationic, and amphoteric surfactants different types of surface morphology was observed.

- The crystallinity of the deposits varied with the weight percentage of boron and nickel content in the deposit. Boron weight percentage increased after adding the surfactant in the bath. In the as-plated condition, the coating exhibited a quasi-amorphous structure along with a nanocrystalline structure of nickel. The inclusion of the surfactant improves the quasi-amorphous nickel structure with a nano-crystalline structure. Upon heat treatment, it was observed that the coatings undergo phase transformation to fully crystalline with Ni and Ni_3B.

- The obtained coating thickness is 14 μm and is slightly lower than that observed in the referred literature. The reason being (1) the absence of heavy metals (2) bath replenishment. After adding the surfactants to the electroless bath the coating thickness of the substrate increased from SDS 14 to 18 μm (28.5 % improvement), CTAB 14- 20 μm (43 % improvement). and Amphoteric at 0.1 mM 14 to 23 μm (64 % improvement).

- In the as plated condition, the hardness of ENi-B coating is 589 HV which is higher than the uncoated substrate (212 HV). The coatings were subjected to heat treatment

for 1 h at 400 °C and a hardness of 750 HV was achieved. The surface hardness was thus increased by 178 % and 254% after ENi-B coating and heat treatment, respectively. The addition of surfactants also improved the microhardness (HV) of the coatings.

- ENi-B coating has R_a of 0.256 μm when it is in the plated condition. When surfactants are mixed into the bath, the Ra was reduced further. At 0.1 mM of amphoteric surfactant addition, the average surface roughness of the deposit was reduced to 0.174 μm.

- The wear properties of the coatings were studied under different pre-treatments. Among the different pre-treatments used, the absorbed hypophosphate layer provides less wear loss in microns during the pin-on-disc test method.

- ENi-B deposits with no surfactant have better corrosion resistance than those with surfactant and bare aluminium 7075 alloy. Corrosion resistance is reduced when amphoteric surfactant molecules are present.

- PBD studies revealed that the nickel ion source, reducing agent, and stabilizer concentrations were considered significant variables for the maximum HV and minimum Ra. These three factors were optimized by BBD followed by GA and SA. The achieved minimum average surface roughness and maximum microhardness of the ENi-B coatings were 0.2520.004 μm and 592 HV respectively.

- Regression and ANN models were developed to determine the surfactant's critical micelle concentration (CMC). An empirical relationship was created to estimate the minimum average surface roughness (R_a) and maximum microhardness (HV) of the coatings at the CMC of the surfactant.

- The genetic algorithm (GA) utilizing the validated models yielded a minimum R_a of 0.171± 0.001 μm at a CMC of 0.049 g/L (0.135 mM) and 852 HV at a CMC of 0.064 g/L.

We Claim:

1. A method of electroless plating using an eco-friendly stabilizer, comprising the steps of:

i) preparing an aqueous solution for electroless nickel-boron coatings which comprises of the source of nickel ion, reducing agent, stabilizer, complexing agent, with and without amphoteric surfactant.

ii) placing a disc substrate of 7075-T6 aluminium alloy with a composition of Si 0.4, Fe 0.5, Cu 2.0, Mn 0.3, Mg 2.9, Cr 0.28, Zn 6.1, Ti 0.2, and rest Al in weight percentage having a size of diameter 25 mm × thickness 5 mm, in the said aqueous solution.

iii) preparing the deposition of the said electroless nickel-boron coatings after double zincating pre-treatment for 90 min without the said aqueous solution replenishment in a non-agitated freshly prepared electrolyte bath.

2. The method of electroless plating using eco-friendly stabilizer as claimed in claim 1, wherein the said source of nickel ions used in electroless nickel-boron aqueous solution is nickel chloride.
3. The method of electroless plating using eco-friendly stabilizer as claimed in claim 1, wherein the said reducing agent used in electroless nickel-boron aqueous solution is sodium borohydride.
4. The method of electroless plating using eco-friendly stabilizer as claimed in claim 1, wherein the said stabilizer used in electroless nickel-boron aqueous solution is trisodium citrate.
5. The method of electroless plating using eco-friendly stabilizer as claimed in claim 1, wherein the said complexing agent used in electroless nickel-boron aqueous solution is ethylenediamine.
6. The method of electroless plating using eco-friendly stabilizer as claimed in claim 1, wherein the said amphoteric surfactant used in electroless nickel-boron aqueous solution, to remove H2 bubbles, is 3- (N, N-dimethylmyristylammonio) propanesulphonate.

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ABSTRACT

A METHOD OF ELECTROLESS PLATING USING AN ECOFRIENDLY STABILIZER

The present invention relates to a method of electroless plating using an eco-friendly stabilizer, which comprises the following steps: i) preparing an aqueous solution for electroless nickel-boron coatings which comprises of the source of nickel ion, reducing agent, stabilizer, complexing agent, with and without amphoteric surfactant. ii) placing a disc substrate of 7075-T6 aluminium alloy with a composition of Si 0.4, Fe 0.5, Cu 2.0, Mn 0.3, Mg 2.9, Cr 0.28, Zn 6.1, Ti 0.2, and rest Al in weight percentage having a size of diameter 25 mm × thickness 5 mm, in the said aqueous solution. iii) preparing the deposition of the said electroless nickel-boron coatings after double zincating pre-treatment for 90 min without the said aqueous solution replenishment in a non-agitated freshly prepared electrolyte bath.