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INFLUENCE OF NANO Al_2O_3 ON Ni–P/Ni-B ELECTROLESS DUPLEX COATING

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ABSTRACT

In this paper, the experimental process on electroless Ni-P/Ni-B-Al_2O_3(nano) composite coatings and influence of non-ionic surfactant were investigated. The coating thickness was improved by adding the polyethylene glycol hexadecyl ether (non-ionic surfactant) on electroless Ni-P bath. The purpose of using non-ionic surfactant is to improve the coating thickness on low carbon steel. Coating thickness was calculated by using weight analysis method. Surface morphology was studied using SEM analysis.

Keywords: duplex coating, non-ionic surfactant, nano Al_2O_3.

INTRODUCTION

A metal form may have been produced by machining, casting, forging, and other methods. These processes produce different surfaces, and one (or more) subsequent operation is generally required to produce a desired surface. This is what is called "surface coating of metals". Coatings are used on most metal products today, either for protective or for both protective and decorative purposes. In general, coatings or finishes are used for the purpose of decoration, surface [1]. The covering should be uniform and free from runs, checks or peelings. The one of most popular surface coating technique is electro plating.

Electroplating is a process that uses electric current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. Electroplating is primarily used to change the surface properties of an object e.g. wear resistance, corrosion protection, lubricity, aesthetic qualities, etc. In electroless process, metal deposition is driven by the catalytic oxidation of the reductant on the substrate surface [3].

Electroless coating is autocatalytic process, the first Ni-P coating is obtained by Brenner and Riddell in 1946. Over the year, the electroless coating is developed due there high hardness, corrosion resistance, wears resistance etc. The electroplating need external sources of electricity, essential parameter used in plating are cathode, anode, electrolyte and direct current (low voltage). But in electroless process no need of any direct current. Due to the chemical reaction coating process is occurring. In electroless coating have more advantage; the deposition rate is uniformly in catalytic surface. Ferrous, non-ferrous and metallic, non-metallic can be coated on electroless process [2]. A major drawback of EN coating is poor nickel recovery from the bath, post treatment processes to recover the nickel from spent bath. Nickel recovery efficiency is only about 35% after adding the surfactant. Due to these reasons product cost is increased. Efforts based on additives which influence the chemical process and surfactant to improve the coating efficiency have been made by several researchers.

One possible alternate approach for improving the both nickel recovery and coating efficiency of EN coating process might be the additive of some suitable surfactant in the electrolyte bath [4]. Surfactant (Surface active agent) is an additive to reduce the surface tension into the electrolyte bath. There are 4 types of surfactant i. anionic, ii. cationic, iii. zwitterionic, iv. non-ionic.

SURFACTANTS

Surfactants are a large group of surface active substances with a great number of (cleaning) applications. Most surfactants have degreasing or wash active abilities [5]. They reduce the surface tension of the water so it can wet the fibres and surfaces, they loosen and encapsulate the dirt and in that way ensure that the soiling will not re-deposit on the surfaces.

Surfactants have a hydrophobic (water repellent) part and a hydrophilic (water loving) part. The hydrophobic part consists of an uncharged carbohydrate group that can be straight, branched, cyclic or aromatic. Depend on the nature of the hydrophilic part the surfactants are classified as an-ionic, non-ionic, cat-ionic or amphoteric and zwitterionic [6].

A surfactant with a non-charged hydrophilic part, e.g. ethoxylate, is non-ionic. These substances are well suited for cleaning purposes and are not sensitive to water hardness. They have a wide application within cleaning detergents and include groups like fatty alcohol polyglycosides, alcohol ethoxylates etc.

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Table-1. Non-ionic surfactant properties (Polyethylene glycol hexadecyl ether).

Related categories	**Biochemical And Reagents, culture, detergents, detergents A To M, detergents by applications.**
Description	Non-ionic
Aggregation Number	70
Cmc	0.016 g/l
Melting Point	~38 °C
Transition Temperature	cloud point >100 °C
Hlb	16

Table-2. Aluminum oxide Al_2O_3 properties.

Related categories	**Aluminum, ceramics, biomaterials, materials science.**
Description	gamma phase
Form	Nano powder
Particle Size	<50 nm (TEM)
Surface Area	>40 m^2/g (BET)

EXPERIMENTAL DETAILS

Nickel (II) chloride (or just nickel chloride), is the chemical compound $NiCl_2$. The anhydrous salt is yellow, but the more familiar hydrate $NiCl_2{\cdot}6H_2O$ is green. In general nickel (II) chloride, in various forms, is the most important source of nickel for chemical synthesis. The nickel chlorides are deliquescent, absorbing moisture from the air to form a solution. Nickel salts are carcinogenic.

Sodium hypophosphite ($NaPO_2H_2$, also known as sodium phosphate) is the sodium salt of hypo phosphorous acid and is often encountered as the monohydrate, $NaPO_2H_2{\cdot}H_2O$. It is a solid at room temperature, appearing as odorless white crystals. It is soluble in water, and easily absorbs moisture from the air. Sodium hypophosphite should be kept in a cool, dry place, isolated from oxidizing materials. It decomposes when heated and produces toxic phosphine gas, causing irritation to the respiratory tract [9].

Trisodium citrate has the chemical formula of $Na_3C_6H_5O_7$. It is sometimes referred to simply as sodium citrate, though sodium citrate can refer to any of the three sodium salts of citric acid. It possesses a saline, mildly tart flavour [10]. For this reason, citrates of certain alkaline and alkaline earth metals (e.g. sodium and calcium citrates) are commonly known as "sour salt" (occasionally citric acid is erroneously termed sour salt).

Ammonia solution, also known as ammonium hydroxide, ammonia water, ammoniac liquor, ammonia liquor, aqua ammonia, aqueous ammonia, or simply ammonia, is a solution of ammonia in water. It can be denoted by the symbols NH_3 (aq). Although the name ammonium hydroxide suggests an alkali with composition $[NH_4^+]$ $[OH^-]$, it is actually impossible to isolate samples of NH_4OH.

Ammonium chloride, an inorganic compound with the formula NH_4Cl, is a white crystalline salt, highly soluble in water. Solutions of ammonium chloride are mildly acidic. Sal is a name of the natural, mineralogical form of ammonium chloride. The mineral is commonly formed on burning coal dumps, due to condensation of coal-derived gases. It is also found around some types of volcanic vents. It is used as a flavoring agent in some types of liquor ice. It is the product from the reaction of hydrochloric and ammonia.

Proper preparation of the substrate to be plated is vital for quality results. Poor surface preparation can cause lack of adhesion, deposit porosity, roughness, on-uniform coatings and/or dark deposits [11].

A properly prepared substrate is one whereby surface contamination is removed, which leaves a clean, nominally oxide-free surface. Typical surface contaminants that must be removed prior to plating.

Depending on the type of impurities present, different pretreatments are needed. Pretreatment choice should be the best available for the specific substrate and should be closely monitored. Cleaners and pickling solutions should be changed at predetermined intervals to eliminate the possibility of ineffective cleaners and descalers, which will cause poor adhesion, streaky deposits, or blistering.

The quality of the substrate itself also must be checked carefully as a potential problem source. Often plating problems resulting from inferior substrates are wrongfully diagnosed as pretreatment or bath chemistry problems; for example, intermetallic compounds at aluminium substrate surfaces can manifest themselves as nodules or pits in the final plate [12].

Annealing, in metallurgy and materials science, is a heat treatment that alters the physical and sometimes chemical properties of a material to increase its ductility and to make it more workable. It involves heating a material to above its glass transition temperature, maintaining a suitable temperature, and then cooling. Annealing can induce ductility, soften material, relieve internal stresses, refine the structure by making it homogeneous, and improve cold working properties [10].

In the cases of copper, steel, silver, and brass, this process is performed by heating the material (generally until glowing) for a while and then slowly letting it cool to room temperature in still air. Copper, silver and brass can be cooled slowly in air, or quickly by quenching in water, unlike ferrous metals, such as steel, which must be cooled slowly to anneal. In this fashion, the metal is softened and prepared for further work-such as shaping, stamping, or forming.

Annealing temperature: 800°c
Cooling method: Furnace cooling up to 2 or 3 days
Dimensions of samples (after machining):

Outer diameter : 24mm
Thickness : 7mm

Pretreatment of sample

Acetone cleaning

Acetone cleaning is to remove the unwanted matter like (oil, dust particles) present in the substrate, and then clean in Distilled water.

Ethanol cleaning

Ethanol is commonly referred to simply as alcohol or spirits; ethanol is also called ethyl alcohol, ethanol cleaning is used to remove the pigment, tine dust particles present in the substrate, and then clean in Distilled water.

The final pretreatment is sulphuric acid cleaning. The substrate is immersed in sulphuric acid at 3 minutes for remover unwanted particles. A pickling treatment is given to the substrate with dilute (50%) sulphuric acid for short duration to remove any surface layer formed like rust followed by rinsing with distilled water.

During chemical reaction nickel sulphate supplies the nickel ions in the solution, while sodium hypophosphite reduces the nickel ions from their positive valence state to zero valence state. But as the reaction between nickel sulphate and sodium hypophosphite is quite fast and intense, instant decomposition of the bath is inevitable. Hence, complexing agents (tri sodium citrate and sodium acetate) are required to slowdown the reaction into a feasible form [12]. Complexing agents form metastable complexes with nickel ions and release them slowly for the reaction. But even after the addition of complexing agents, there remains a possibility of solution breakdown. Hence, a stabilizer (Lead acetate) is needed so that the solution remains stable for the duration of the coating. To increase the wettability and surface charge of Al_2O_3 particles non-ionic surfactant is used [9]. The surfactant lowers the surface tension of liquid, hence easier spreading of the particles, and reduces the interfacial tension between the solid and liquid surfaces.

Table-3. Nickel phosphorous and Nickel boron compositions and their conditions.

S. No	Chemicals used and conditions	Nickel phosphorous (Ni-P)	Nickel boron (Ni-B)
1	Nickel chloride	30 gl^{-1}	30 gl^{-1}
2	Sodium hypo phosphate	25 gl^{-1}	-
3	Thallium acetate	-	14 mgl^{-1}
4	Ammonium chloride	50 gl^{-1}	-
5	Sodium borohydride	-	90 gl^{-1}
6	Tri sodium citrate	40 gl^{-1}	-
7	Liquid ammonia	Maintaining pH level	-
8	Ethylene di amine	-	0.8 gl^{-1}
9	Non-ionic surfactant	0.016 g	0.016g
10	Al2O3(nano) powder	0%,2%,4%,6%,8%	0%,2%,4%,6%,8 %
11	PH	8	14
12	Temperature	80-90^{o}C	80-90^{o}C

RESULTS AND DISCUSSION

HARDNESS TEST

The Vickers test can be used for all metals and has one of the widest scales among hardness tests. The unit of hardness given by the test is known as the Vickers Pyramid Number (HV) or Diamond Pyramid Hardness (DPH) [8]. The hardness number can be converted into units of Pascal's, but should not be confused with pressure, which also has units of Pascal's. The hardness number is determined by the load over the surface area of the indentation and not the area normal to the force, and is therefore not pressure [9]. It was decided that the indenter shape should be capable of producing geometrically similar impressions, irrespective of size the impression should have well-defined points of measurement and the indentor should have high resistance to self-deformation.

The micro vickers hardness testing machine has a load range of 10 grams to 1 kg load with a least count of 0.01 mm and a diamond indentor cone angle of 136^0.

Table-4. Micro-hardness test values.

Sample ID	**Sample-1** (without nano)	**Sample-2** (with 0.02g nano)	**Sample-3** (with 0.04g nano)	**Sample-4** (with 0.06g nano)	**Sample-5** (with 0.08g nano)
1	336.9	743.8	641.7	475.4	396.7
2	777.9	538.3	1161	422.1	404.5
3	512.5	550.1	454.5	729.8	426.2
Average	542.43	610.73	752.4	542.43	409.13

MICROHARDNESS INDENTATION

Micro-hardness indentation image of Ni-P/Ni-B-Al_2O_3 composite electroless coating is taken by Micro Vickers Hardness Tester, the sample 3 image are given below:

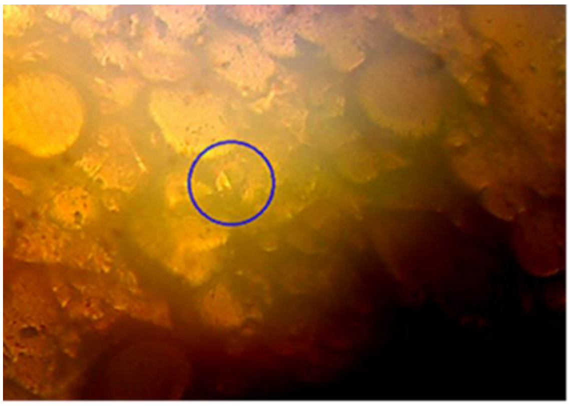

Figure-1. Micro-hardness indentation of sample C.

Deposition rate

Deposition rate was determined using weight gain method

$$R = \frac{w1-w2}{\rho at}$$

where, w_1 - Initial weight (g), w_2 - Final weight (g), ρ- density of nickel (μm/hrs), a - area of substrate (mm^2), t - time taken for coating (hrs).

Table-5. Deposition rate.

	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
Coating duration on Ni-P & Ni-B (hrs)	2	2	2	2	2
Al_2O_3	-	0.02	0.04	0.06	0.08
Non-ionic surfactant (g/ltr)	0.016	0.016	0.016	0.016	0.016
Weight gain (g)	0.50	0.52	0.64	0.57	0.54
Coating thickness (μm)	36.68	38.14	46.95	41.81	39.61
Deposition rate (μm/hr)	18.34	19.07	23.47	20.90	19.8

SEM ANALYSIS

The specimen is bombarded by a convergent electron beam, which is scanned across the surface. This electron beam generates a number of different types of signals, which are emitted from the area of the specimen where the electron beam is impinging.

SURFACE MORPHOLOGY

Microstructure of Ni-P/Ni-B and Al_2O_3 composite electroless coating is taken by using Scanning Electron Microscope and results for different composition with a magnification of 5xs to 300,000xs is given below,

The sample A is microstructure of Ni-P/Ni-B electroless duplex coating which looks like a bubble like structure. The nickel is present in the form of spherical shape. The sample B is microstructure of Ni-P/Ni-B-Al_2O_3 electroless coating, looks like a flaky structure, and the concentration of alumina is 4%. The nickel is present in the form of spherical shape and alumina is present in the form of small white dot. In sample B the amount of nickel deposition is high and Al_2O_3 present in particular area only. The sample C is microstructure of Ni-P/Ni-B-Al_2O_3

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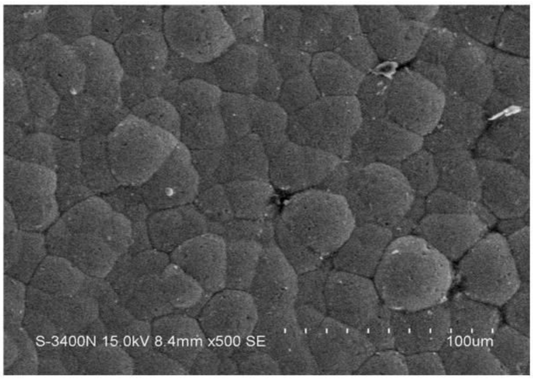
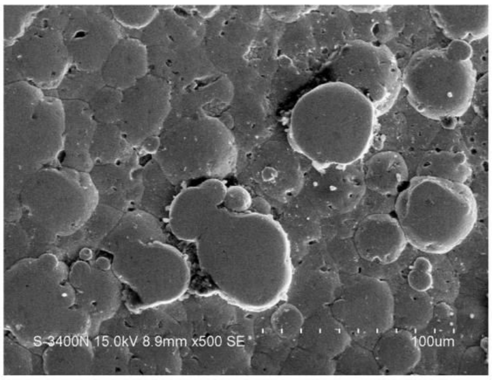
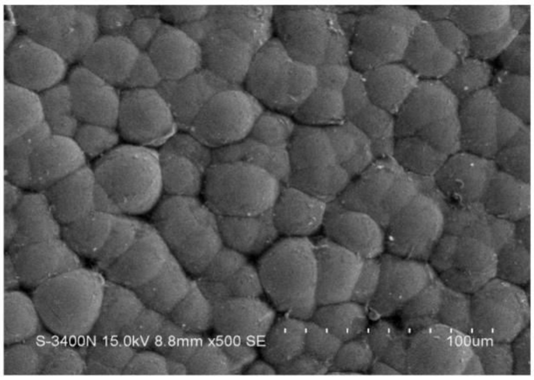
electroless duplex coating, results closely bonding with each other, and the concentration of alumina is 6%. The nickel is present in the form of spherical shape and alumina is present in the form of small white dot.



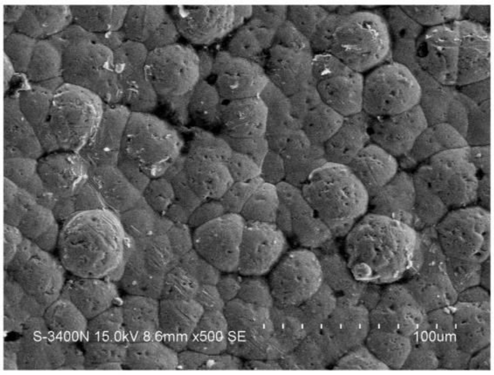
Ni-P/Ni-B Al_2O_3 coating with 2% of alumina



Ni-P/Ni-B Al_2O_3 coating with 4% of alumina



Ni-P/Ni-B Al_2O_3 coating with 6% of alumina



Ni-P/Ni-B Al_2O_3 coating with 8% of alumina

Figure-2. Surface morphologies of Ni-P/Ni-B-Al_2O_3(nano) electroless duplex coating.

In sample C the nickel and Al_2O_3 deposition is high, and the smooth surface is obtained. The sample D is microstructure of Ni-P/Ni-B-Al_2O_3 electroless duplex coating, and the concentration of alumina is 8%. The nickel is present in the form of spherical shape and the presence of alumina is in the form of small white dot. In sample D the nickel deposition is higher than sample A, B and C and the nano Al_2O_3 recovery is very poor.

ADHESION PROPERTIES

Essentially, cohesion and adhesion are the "stickiness" that water molecules have for each other and for other substances [6]. The water drop is composed of water molecules that like to stick together, an example of the property of cohesion and adhesion is

Cohesion: Water is attracted to water
Adhesion: Water is attracted to other substances

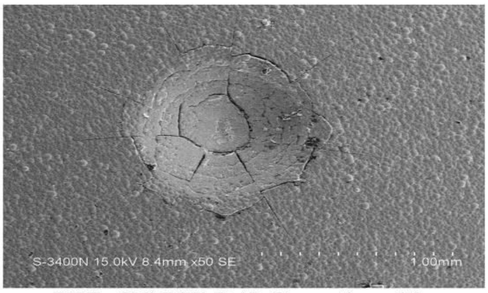
ROCKWELL INDENTATION SEM IMAGE

SEM image of Ni-P/Ni-B-Al_2O_3 composite electroless coating is taken by Scanning Electron Microscope and result for different composition is given below, in sample A, more cracks are developed and the crack propagation is higher in manner. In sample B, few cracks only developed and deep crack propagation is occur. In sample C, more cracks are developed and the crack propagation is not higher than sample A, B and D.
In sample D, more cracks are developed and the big crack propagation was occurred.

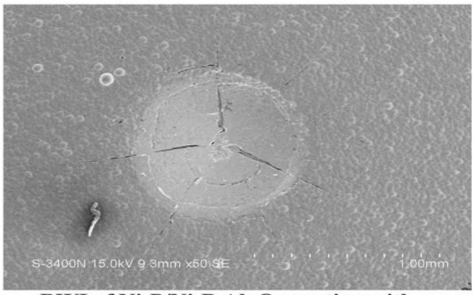
CONCLUSIONS

In this work, electroless Ni-P/Ni-B-Al_2O_3 coating has been deposited on mild steel substrates to understand the influence of Al_2O_3 with particular reference to improve the wear and corrosion resistance. Based on the experimental results and analysis, the following discussion has been drawn.

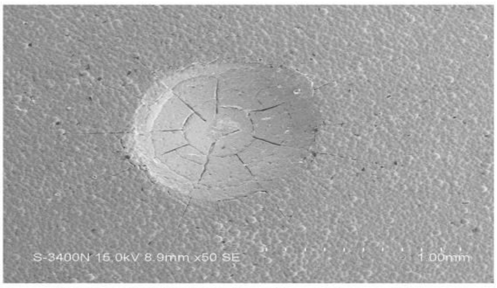
- The optimum Al_2O_3 concentration was 4% for second phase particle which gives maximum coating efficiency and better surface finish. Maximum amount of nickel particles are recovered from the electrolyte and coated only on the substrate. It leading to increased coating thickness.
- Non-ionic surfactant completely reduces the interfacial bonding between Ni and H_2 particles on result of reduction of surface tension.



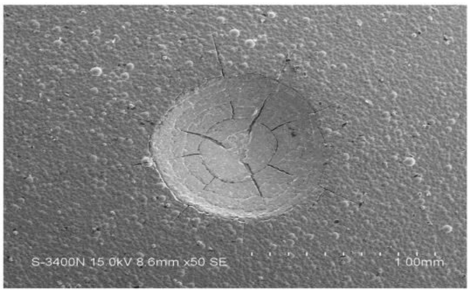
RWI of Ni-P/Ni-B Al_2O_3 coating with concentration of 2% of alumina in SEM



RWI of Ni-P/Ni-B Al_2O_3 coating with concentration of 4% of alumina in SEM



RWI of Ni-P/Ni-B Al_2O_3 coating with concentration of 6% of alumina in SEM



RWI of Ni-P/Ni-B Al_2O_3 coating with concentration of 8% of alumina in SEM

Figure-3. Rockwell Indentation of Ni-P/Ni-B-Al_2O_3 (nano) electroless duplex coating.

- The addition of Al_2O_3 promotes the deposition rate to 23.47 μm/hr. There will be possible to improve the interfacial adhesion of coating and coating thickness of electroless Ni-P/Ni-B-Al_2O_3 coatings with this surfactant.
- Al_2O_3 (nano) particle deposit on the surface of mild steel has been better compared with the Ni-P/Ni-B coating, observed from microstructure using SEM.

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