

EFFECT OF SURFACTANTS ON THE ELECTRODEPOSITED NICKEL COMPOSITE COATINGS

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Abstract - There are wide ranges of applications in recent years for nickel composite coatings deposited by electrodeposition process. These nickel composite coatings have their outstanding applications in industries. There are parameters affecting the electrodeposition process. The surfactants are used in the electrodeposition process in order to enhance the properties of the coatings. The study is on different surfactants used in the composite baths with their properties. There are discussions on the different surfactants used in the electrodeposition process using nickel composite bath. The characterization tests done to check the properties of the coating using different surfactants are studied.

Index Terms— — Nickel composite coatings ; Electrodeposition.

I. INTRODUCTION

A coating can be defined as a process which is applied on the surface of the substrate or object to improve the surface properties and to protect the parts. The total corrosion and wear cost on industrial equipments each year is so high that it is incalculable. Worldwide estimated indication of corrosion and wear costs industrial firms a staggering \$2.2 trillion annually [1].

Due to this reason only the coatings are used, many techniques are used in the coating process like electrodeposition/electroplating, electro less plating, hot dipping, conversion plating, thermal spraying, physical vapor deposition and chemical vapor deposition. Among all above techniques, electro deposition is a versatile low temperature process which is used to fabricate functional coatings in a single step without going any

secondary treatment. The nickel matrix prepared by electrodeposition has minimum porosity and high density and has been widely studied.

Electrodeposition is a process of surface engineering which is used to protect materials from corrosion and wear. Electrodeposition is the application of metallic coatings to conductive surfaces or metallic by electrochemical processes. Electrodeposition is a process of coating or depositing on a cathode by immersing both anode and cathode into an electrolytic bath connected to an external power supply [2].

The demand for the metal matrix composites is reaching new heights in defense and aerospace applications in order to cope with the severe environmental and stress encountered during operations. Since nickel is a tough and strong metal which is resistant to abrasion erosion and corrosion process hence it is widely used [3].

It was discovered by Michael Faraday in the 1830's and it has contributed for the development and application in many industrial areas. Faraday's laws express the relationship between the quantity of electricity passed through an electrolyte and the chemical nature and mass, in terms of chemical equivalents, of substrate dissolved or deposited at the electrodes.

Faraday's first law of electrolysis states that the masses (m) of deposited or dissolved substances are proportional to the quantity of electricity (q) passed through. The electrolyte. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb.

The second law states that the masses of different substances dissolved or deposited as a result of the passage of the same quantity of electricity through the electrolyte are proportional to the chemical equivalents (A) of the substances. The equivalent weight of a substance is equal to its molar mass divided by the change in oxidation state it undergoes upon electrolysis. It follows from the second law that the same quantity of electricity, called the faraday constant F, is required for the deposition of the substances of the same gram-equivalent weight of different substances.

Mathematically, faraday's laws may be written as one equation

$$m = (Q/F) (M/z)$$

Where,

m- Mass

Q- Total electric charge passed through the substance

M- Molar mass of the substance

z- Valency number of ions

F- Faraday constant (96485 C mol⁻¹)

According to faraday's first law the constants are F, z and M, and when Q value is greater than "m" value will also be greater. But in second law the constants are F, z, and Q, when M/z value is greater than "m" value will also be greater. Where M/z is the equivalent weight.

$$m = (It/F) (M/z)$$

Where

n = m/M where n indicates the number of moles (liberated)

t = Total time (constant time)

Deviations from laws are observed in certain cases; such deviations may be associated with electrochemical side reactions that are taken into an example, the liberation of gaseous hydrogen during the electrodeposition of some metals or with partial electron conduction [4].

Many metals can be used for the electrodeposition like Cr, Ni, Ag, Au Zn etc and alloys. Among these coatings, electrodeposited nickel coatings are of technological importance.

Nickel plating is a method of deposition of nickel on a cathode, and cathode part is immersed into a nickel based electrolyte solution. When the nickel ions from the solution it travels and gets deposited on the cathode surface, the anode dissolves into the electrolyte in the form of the nickel ions and hence by maintaining the concentration of nickel ions in to the solution [5].

Many number of nickel plating baths are available for electrodeposition of nickel. The important baths are as follows.

1. Hard nickel bath
2. Sulfate –chloride bath
3. All-chloride bath
4. Watts nickel bath and
5. Nickel Sulphamate bath

Among all above baths the most widely used are watts nickels plating bath and Sulphamate bath solutions. By using watts bath the nickel can be deposited in two forms as bright and semi bright. Bright nickel is typically used for the corrosion protections and decorative purposes. Whereas semi bright nickel are used for the engineering process.

Sulfamate nickel plating baths have no more noticeable effect upon producing skin irritations and odorless when compare with the other nickel plating bath formulations of the Watts type. The other advantages of sulfamate baths over conventional nickel baths are high current density operation at low temperatures, stress-free deposits

(by the use of stable addition agents the compressive stress deposits can be easily done), Simplicity of bath composition, control, and maintenance, low sensitivity to impurities [6].

The advantages of Nickel Electrodeposition are as below,

Coatings can be done on the Electrical contacts and it can be operated at the minimum electrical loads with the temperature near to 200°C. And it leads to good contact resistance and electrical conductivity [7].

The coating obtained by the Nickel electrodeposition will give high thickness so it will possess low internal stress. Hence we can find many applications through nickel electrodeposition.

Nickel deposited coatings will provide better strength.

The coating obtained by nickel electrodeposition will be smooth hence it provides high reflectance [8].

In order to increase wear resistance and to provide surface lubrication the dispersed phase in composite coatings are used [9].

It provides better corrosion resistance.

Nickel is a harder metal and hence possesses high hardness [10].

The disadvantages of Nickel Electrodeposition

By using nickel electrodeposition good adhesion cannot be achieved because the nickel coating may be removed from the substrate.

By using nickel electrodeposition steel cannot be protected from the sacrificial corrosion [11].

Mechanical works like elongation, beading cannot be applied on nickel deposited from the electrodeposition.

Electro deposited nickel are highly sensitive to the impurities in the electrolyte.

In the case of bright nickel deposited on steel then the substrate mechanical properties will be worsen. This is one of the main reasons where hydrogenation occurs [12].

Electrodeposited metal matrixes composite are described as hard chrome coat. Hard

chrome coat is widely used in various engineering coatings now it has been replaced by Nickel coating. It is done in the form of composite coatings (Metal matrix and inert particles). This enhances the mechanical and tribological properties. They can be used in wear resistance, corrosion resistance and high temperature oxidation. And its applications involved in aerospace, automotive, manufacturing and chemical processing.

A metal matrix composite is characterized by the amount of composite particles incorporated in matrix. The deposited particle concentration mainly depends on the parameters like particle properties, bath composition and deposition variables [13].

Applications of composite coatings can be applied in the in many industries like general mechanics, automobiles, aerospace, food and textile, electronic and computer components.

There are several variables that may effect to the electro deposition. The important parameters affecting the electrodeposition and co deposition of particles are as follows:

1. Current Density
2. Plating metal ion concentration
3. pH
4. Conductivity
5. Temperature
6. Agitation
7. Effect of particle characteristics
8. Material and Surface finish of the substrate [14].

During electrodeposition of composite coating the insoluble solid materials will get suspended into an electrolyte and growing metal film will be captured. For electrodeposition of nickel composite coatings many particles are used such as carbon nano tubes, pumice diamond, hard oxides, carbides etc. have been used. A metal matrix composite are characterized by the amount of composite particles incorporated within the matrix.

The deposited particle concentration mainly depends on parameters like properties of the particles, bath composition, and deposition variables. Among all these parameters the most controllable process parameters are the properties of the particles. Compared to plain coatings, composite coatings will improve physical and electrochemical properties. Based on the properties of different particles used in the bath, their applications will be decided.

Applications of Composite coatings are classified into following categories like electrochemical process, dispersion hardening process and wear resistance process are the three important classifications. The life time tools of surface, engineering parts that are in moving condition and can undergo wear, can be increased using these composite coatings. Some researchers have also come out with new distributed phases for incorporation in to the Ni-matrix like pumice, cenospheres, graphene etc. [15].

Surfactants are also called as surface active agents. These are the substances which greatly reduce the surface tension of water. It leads to the smooth surface of coatings with their microcrystalline microstructure and their bright macroscopic appearance. They act as both leveler and brightener. They will absorb fine particles from the matrix and this increases the repulsion force between particle charges. And it avoids the agglomeration of particles suspended in the plating solutions. Because of high surface free energy the ultrafine particles from electrolyte bath will get agglomerated [16].

Different surfactants like anionic and cationic surfactants are used in the literature. The cetyltrimethyl ammonium bromide is used as a cationic surfactant and sodium dodecyl sulphate is used as the anionic surfactant. CTAB is widely used as topic antiseptic, and may be found in many household products such as shampoos, hair conditioner products and cosmetics [17].

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There are many surfactants such as CTAB, Coumarin, sodium dodecyl sulfate. The hardness study of the coatings were studied by microhardness study, wear test and corrosion were also done for the analysis of properties of the coatings with surfactants.

Effect of CTAB surfactant on electrodeposited nanoparticle SiC reinforced on Nickel metal matrix composite (MNC) coatings

A nickel sulfate bath containing SiC nanoparticles was used to obtain hard and wear-resistant nano particle reinforced Ni SiC MMCs coatings on steel surfaces which are used for anti-wear applications, such as in dies, tools and working parts. The study was on the influence of stirring speed and surfactant concentration on particle distribution, micro hardness and wear resistance of nano-composite coatings. The nickel films were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The depositions were controlled to obtain a specific thickness (between 50 and 200 μ m) and particle volume fraction in the matrix (between 0.02 and 0.12). The hardness of the coatings was measured and found to be 280–571 Hv, this is dependent on the particle volume in the Ni matrix. The effects of the surfactant on the zeta potential, co-deposition and distribution of SiC particles in the nickel matrix, as well as the tribological properties of composite coatings, were also investigated. All friction and wear tests were performed without lubrication at room temperature and in the ambient air (relative humidity 55–65 %). The results showed that wear resistance of the nano composites was approximately 2–2.2 times higher than unreinforced Ni deposited material.

The SiC nano particle-reinforced (100–1000 nm) Ni metal matrix composites were successfully deposited by D.C. electroplating, with the

concentration up to 11.37 vol.% particle co-deposition. By increasing the CTAB surfactant content resulted in an increase of the SiC vol. % within the Ni metal matrix and there was segregation-free dispersion of nano particle deposition. The hardness values of the nano SiC-reinforced electrodeposited coatings were as high as 571 Hz because of unique dispersion effects. It was also observable that the volume percentage of SiC in coatings increases with increasing surfactant (CTAB) concentration. Increasing the surfactant (CTAB) concentration resulted in the lattice distortion of the Ni matrix. Wear resistance of the coatings was increased with increasing surfactant (CTAB) content up to 300 mg/l in the electrolyte, but beyond this concentration, the wear resistance decreased. The co-deposited Ni-SiC nanocomposite coatings show higher friction coefficients and better wear resistance compared to the as-deposited Ni film, which can be attributed to the incorporation of nano-sized SiC particles in the deposit. These nanoparticles greatly increase the hardness of the composite coating through grain refinement strengthening and dispersion strengthening mechanisms [18].

Effect of sodium dodecyl sulfate surfactant on electrodeposited Ni-Al₂O₃ composite coatings

Ni-Al₂O₃ composite coatings were electrodeposited from a Watts-type bath containing particles in suspension. To 250 ml of the nickel bath, surfactant hexadecylpyridinium bromide was dissolved followed by the addition of Al₂O₃ particles. The solution containing Al₂O₃ particles was ultrasonically dispersed for several minutes and then was stirred for 3 h before the co-deposition process. Steel plate was used as the cathode; a pure Ni plate was used as the anode. Prior to electroplating, the substrates were mechanically polished for surface roughness. The steel substrate was activated in a mixed acidic bath before electroplating. During co-deposition process, the plating bath was stirred by a magnetic stirrer. The amount of co-deposits was examined at five different locations of each coating. The addition of surfactant HPB in plating bath increased the zeta

potential of Al₂O₃ particles, and promoted the co-deposition of Al₂O₃ particles with nickel to achieve a more uniform distribution of Al₂O₃ particles in metal matrix. The wear resistance of Ni-Al₂O₃ composite coatings was found to be increased with increasing concentration of HPB up to a certain optimum of 150 mg/l, beyond which a decreasing trend of wear resistance was observed under dry sliding and oil-lubricated conditions. This is probably due to the brittleness of nickel matrix increases when the concentration of surfactant exceeded the optimum.

Effect of sodium dodecyl sulfate surfactant on electrodeposition was studied. All solutions were prepared with analytical-grade chemicals and de-ionized water. Electrolysis was carried out in a glass container fixed with a wooden cover containing holes to insert connecting rods to the electrodes. Rectangular steel sheets were used as cathode (substrate). Steel specimen had the several weight percent of chemical composition C, Si, Mn, P, S, Ni, Cr, Mo, V, Cu and remainder Fe. Prior to electroplating, the steel substrates were mechanically polished with silicon carbide papers and subsequently rinsed with distilled water. A sequence of cleanings to remove the contamination on the substrate surface was done as follows: All specimens were etched in diluted HCl solution and then rinsed with distilled water, degreased in 10% w/v NaOH solution, washed thoroughly with distilled water, dipped in acetone, and dried at room temperature. They were then placed in desiccators and weighed prior to and subsequent to the experiment. A nickel sheet was used as anode. Nickel alumina composite coatings were obtained from nickel sulphamate bath containing suspended nano-alumina particles. As SDS concentration was increased in bath up to an optimum level (125 mg l⁻¹), nano-alumina particles participation in the coatings was enhanced and improved the micro hardness of the coatings to 492 HV. Beyond this level, increased surfactant concentration caused lower micro hardness. Nano-composite coatings obtained from a bath containing optimum concentration of SDS had the most positive

corrosion potential (0.209 V) and the lowest corrosion current ($1.141 \times 7 \text{ A cm}^2$). Further increase of SDS concentration had unfavorable effects on corrosion potential and corrosion current density shifted the potential to more negative values, and the current density to higher values [19].

Effect of surfactant on the co-electrodeposition of the nano-sized ceria particle in the nickel matrix

Pulse electrodeposited Ni-CeO₂ nanocomposite coatings are utilized in large applications because of its high strength, toughness and resistance to corrosion/wear[20]. Shrestha et al. [21] have studied the influence of the hydrophobic tail length of a cationic surfactant containing an azobenzene group (AZTAB) on the extent of co-deposition of SiC particles in the nickel matrix and found that an AZTAB with shorter tail can codeposit a higher amount of SiC particles than the surfactant with a longer tail. Ger [22] has investigated the effect of the surfactant cetyl trimethyl ammonium bromide (CTAB) related with the codeposition of SiC in the Ni matrix and found that the addition of CTAB in the electrolyte reduces the agglomeration of SiC particles in the plating bath resulting high percentage of uniformly distributed. The investigation is to study the influence of the concentration of surfactant (SLS) on the amount of co-deposition of nano-sized CeO₂ particles in the nickel matrix and its subsequent effect on the hardness of Ni-CeO₂ nanocomposite coatings. HEBM of CeO₂ is carried out using cemented tungsten carbide milling media with toluene as the process control agent for the production of nanocrystalline ceria powders. The mill is operated at a speed of 300rpm and the ball to powder. The powders are milled and samples are collected regularly during milling to observe the progress of the size reduction. The ball milled powder is washed and drying. The electrolytic solution is prepared by adding chemicals to the distilled water. The bath additives like saccharin sodium (Loba Chemie) as a brightener and an extra pure sodium lauryl sulphate (Loba Chemie) as an antipitting agent/surfactant are added to the bath.

The CeO₂ powders are added to the electrolytic solution and stirred to improve the uniformity of distribution within the bath before plating. The plating bath for deposition of the composite coatings is agitated prior to the electrodeposition and also during plating. The electroplating is carried out in electrolyte using parallel electrodes. The Ph level is regulated. An electrolytic quality nickel plate is used as an anode. The cathode is a cold pressed titanium plate. The titanium substrates, mounted in a cold setting polymer, are subjected to a range of pre-treatment like polishing and ultrasonic cleaning to eliminate the surface irregularities like scratches, dirt and contaminants and also to facilitate the stripping of the deposited coatings.

The particle size distribution of the ceria powders in the suspension has been determined by particle size analyzer and the ceria particles size varies from 20 to 51 nm. The crystallite size of Ni, as determined by the classical and modified Williamson-Hall method, varies from 30-50 to 21-30 nm, respectively. The modified method gives smaller crystallite size, since this method is free from strain anisotropy. The presence and size distribution of the ceria particles in the coating has been confirmed by the TEM analysis. The addition of surfactant SLS in the electrolyte increases the zeta potential of ceria particles and promotes the co-deposition of CeO₂ particles in the nickel matrix. The maximum amount of CeO₂ incorporation with a uniform distribution occurs, when the amount of SLS in the electrolyte is 0.1 g/l. The microhardness of the nanocomposites increases with the amount of SLS up to 0.10 g/l in the electrolyte. Beyond this amount, the hardness decreases due to agglomeration of the ceria particles in the nickel matrix.

Effect of nickel-BN composite coatings

Nickel-boron nitride (Ni-BN) composites are gaining importance for potential engineering applications due to their high hardness and anti-wear properties [23, 24, 25]. The electrodeposition of nickel-BN composites from a

sulfamate bath is obtained Demineralized water and chemicals of analytical grade were used for the preparation of baths. Brass foils were used as substrate for deposition and a nickel foil was used as soluble anode. The average size of hexagonal boron nitride particles, was 0.5 μ m. Deposition was carried out in a Pyrex beaker with magnetic stirrer and automatic temperature control unit. The solution was preheated at process temperature and then boron nitride particles were added to the bath. Before deposition, solution was sonicated. After electrodeposition, deposits were cleaned and dried.

Grain size and orientation of nickel matrix were detected by X-ray diffraction. The concentration of the boron nitride particles in the plating solution is limited by the solubility of the surfactant. Its presence in the electrolyte decreases the grain size and increases the weight loss of the deposits compared with a pure nickel deposit obtained without additives. Morphology is not affected by the presence of the surfactant in the plating solution. Compared to pure Ni coatings, Ni-BN composites show higher Microhardness up to over 500 HV and improved wear resistance. Both the properties improve increasing the boron nitride particles concentration in the electrolyte up to 10 g/l.

Effect of Co-Ni-Cu alloys nanoparticles in the presence of alkyl polyglucoside surfactant

Recently, there is an increasing interest in the synthesis of the Co-Ni-Cu alloys nanoparticles due to its unique magnetic and magnetoresistive properties, which depend on the composition, for used in magnetic device applications such as MEMS [26], magnetic recording and magnetic data storage [27]. The starting materials were used as alkyl polyglucoside (APG), boric acid (H₃BO₃) and all metal salts. The electrolytes containing CoSO₄, NiSO₄, CuSO₄ and H₃BO₃ were prepared using pure water. Electrodeposition of Co-Ni-Cu was carried out in a three electrode cell with ITO on glass plate, platinum wire and saturated calomel electrode (SCE) as working electrode, counter electrode and

reference electrode, respectively. A Solartron potentiostat was used to perform all the electrochemical experiments. Prior to each experiment, the electrolyte solution was purged with a flow of pure argon gas to remove any oxygen contain in the electrolyte. The cyclic voltammetry studies were performed with a potential window of 400 to -1100mV vs. SCE and the scan rate of 10mVs⁻¹. Finally, for the Co-Ni-Cu nanoparticles electrodeposition, a potentiostatic experiment was used in the presence of different concentrations of the APG surfactant. The deposition time was 150 s.

By controlling the APG concentration, the Co-Ni-Cu alloys nanoparticles with excellent growth characteristic can be prepared. The metal with lowest reduction potential (Cu) become the dominant product. Since high APG concentration as well as high deposition potential was found to be very effective for the preparation of the Co-Ni-Cu alloys nanoparticles with excellent growth characteristic. The present approach can be used to prepare magnetic nanoalloys for used in the currently existing application. The effort to produce the nanoalloys both with excellent chemicals composition and the growth characteristic are in progress.

III CONCLUSION

Electrodeposition process is one of the good coating technology which are widely used with the Nickel composite coatings using different surfactants are studied. Nickel composite coatings are used because of their good coating properties. Surfactants are used with the composite coatings to improve their properties. SiC nanoparticle-reinforced (100-1000 nm) Ni metal matrix composites were successfully produced by D.C. electroplating, up to 11.37 vol.% particle co-deposition. Increasing the surfactant (CTAB) content resulted in an increase of SiC vol. % within the Ni matrix and a segregation-free dispersion of nanoparticle deposition. The hardness values of the nano SiC-

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