

بسم الله الرحمن الرحيم

Sudan university of science and technology

College of Graduate studies

Electrodeposition of Nickel and Titanium

Dioxide from Electrolytic Glycine Bath

الترسيب الكهربى للنكل وأكسيد التيتانيوم فى حمام الجلايسين الالكتروليتى

**A Thesis Submitted in Partial Fulfillment for the
Requirements of the Degree of M.Sc in Chemistry**

By :

B.SC. Honours . Hassan Ataa Awad Elkareem
Mohamed

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الآية

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قال تعالى :

{ وَأَنْزَلْنَا الْحَفِيَّةَ بِأُتْسٍ شَدِيدٍ وَمَنْفَعٌ لِلنَّاسِ وَلِيَعْلَمَ اللَّهُ مَنْ يَنْصُرُهُ وَرُسُلَهُ بِالْغَيْبِ إِنَّ اللَّهَ
قَوِيٌّ عَزِيزٌ }

سورة الحديد

الاية 25

صدق الله العظيم

Dedication

This work is dedicated to my father, my mother and my married sisters and brothers for their love and support.

Also to my fiancée for the believing in me, accepting me just as way I am and for their infinite and sincere caring ,loyalty and kindness

Acknowledgment

First I thank Allah for grating me the strength to do this study.

*I would like to express my immense gratitude and appreciation to my wonderful supervisor **Dr. Mohammed Suliman** for his help, suggestions and close supervision throughout the study.*

Finally all my thanks go to everyone who supported and helped me to accomplish this study.

Abstract

This research aims to study the electrodeposition of nickel-titania coatings from glycine bath. Ni-TiO₂ coatings with varying Titania content were electrodeposited on copper substrate employing glycine electrolyte. The different conditions which affect the deposition process such as current, plating time, concentration of nickel and glycine, PH and temperature were investigated. The Titania content in the coatings increased with increasing Titania content in the bath and decreased at high current density, the effect of pH shows an increase in Titania up to pH 8, Enhancement of thickness of the coating show whenever increase of the percentage of contents of the electrolyte bath, time and temperature. The obtained coatings were characterized using x-ray fluorescence (XRF) and Atomic absorption Spectroscopy (A.A.S). The optimum conditions of this bath were found as follow: PH 8, current 0.4 A/cm². The percentage, of the incorporated TiO₂ was 2.7695%.

المستخلص

هدف هذا البحث للترسيب الكهربائي للنكل وأكسيد التيتانيوم في حمام الجلايسين الالكتروليتي, تم دراسة عدد من العوامل المختلفة (الأس الهيدروجيني, كثافة التيار, الزمن, درجة الحرارة, تركيز النكل وتركيز أكسيد التيتانيوم) لمعرفة تأثيرها علي عملية الترسيب.

تم ترسيب سبيكة النكل والتيتانيوم علي سطح النحاس وذلك باستخدام كميات مختلفة من اكسيد التيتانيوم. ووجدنا ان نسبة اكسيد التيتانيوم في طبقة النحاس تزيد بزيادة في المحلول الالكتروليتي, وتنخفض عند كثافة التيار العالي وكذلك بزيادة التركيز والاس الهيدروجيني حتي 8 . ووجدنا ان سمك الطلاء يزيد بزيادة كمية اكسيد التيتانيوم ومحتويات المحلول الألكتروليتو درجة الحرارة والزمن. وتم دراسة خواص الطبقة عن طريق جهاز طيف الامتصاص الذري وطيف الاشعة السينية ووجد ان الظروف القياسية لهذا البحث عند أس هيدروجيني 8 وكثافة تيار 0.4 أمبيرو ان نسبة التيتانيوم هي 2.7695%.

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Chapter One

Introduction and literature review

Chapter One

Introduction

1.1 Introduction:-

Electroplating is a process that uses electric current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The term is also used for electrical oxidation of anions onto a solid substrate, as in the formation of silver chloride on silver wire to make silver/silver-chloride electrodes. Electroplating is primarily used to change the surface properties of an object (e.g. abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.), but may also be used to build up thickness on undersized parts or to form objects by electroforming[1].

The process used in electroplating is called electrodeposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that it comprises and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode [1].

Other electroplating processes may use a non-consumable anode such as lead or carbon. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution [2].

The most common form of electroplating is used for creating coins such as pennies, which are small zinc plates covered in a layer of copper [3].

1.1.1 Electrotyping and Electroforming:-

The cations associate with the anions in the solution. These cations are reduced at the cathode to deposit in the metallic, zero valence state. For example, in an acid solution, copper is oxidized at the anode to Cu^{+2} by losing two electrons. The Cu^{+2} associates with the anion $(\text{SO}_4)^{-2}$ in the solution to form copper sulfate. At the cathode, the Cu^{+2} is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode.

The plating is most commonly a single metallic element, not an alloy. However, some alloys can be electrodeposited, notably brass and solder. Many plating baths include cyanides of other metals (e.g., potassium cyanide) in addition to cyanides of the metal to be deposited. These free cyanides facilitate anode corrosion, help to maintain a constant metal ion level and contribute to conductivity.

Additionally, non-metal chemicals such as carbonates and phosphates may be added to increase conductivity.

When plating is not desired on certain areas of the substrate, stop-offs are applied to prevent the bath from coming in contact with the substrate. Typical stop-offs include tape, foil, lacquers, and waxes [4]. The ability of a plating to cover uniformly is called throwing power; the better the "throwing power" the more uniform the coating [5].

Nickel electroplating is an important part of any engineering component. Nanocomposites consisting of advantageous used widely in many applications area due to their unique physical, chemical and electro-optical properties. Since the mechanical and electrical properties of TiO_2 films are dependent on their

composition, crystallinity, surface morphology and total surface area. Over the past few years, metal matrix composite coatings, especially nickel matrix composite coatings containing nano-particles which exhibit excellent properties, such as higher wear and corrosion resistance, higher hardness, and more excellent self lubricating in comparison with single metal coating, have been more widely studied. The coating properties improved with decreasing of deposited particles size. Corrosion resistance can be affected by microstructure, such as grain size, surface morphology and texture, which is closely related to the electrode position parameters, such as current density, pH, electrolyte temperature and particle concentration of the plating bath. Metal matrix composite coating containing alumina (Al_2O_3) and titanium (TiO_2) particles has been widely used in industry. Although Ni-Ti O_2 composites have been reported to be advantageous for high temperature [6]. Interesting photo electrochemical and photocatalytic behavior application [2,3,6]. Relatively little research effort has been dedicated to the electrode position of nickel titanium composites [2-7]. The electro co-deposition of Ni with second phase nano-particles such as aluminum oxide, titanium nitride, carbon nanotube (CNTs), diamond, silicon carbide, silicon nitride and zirconium oxide have been studied extensively over the past two decades. A variety of nanosized particles some such investigations with Ni- Al_2O_3 [8-12], Ni-CNTs [13,14], Ni- Si_3N_4 [15,16], Ni-diamond [7], Ni-SiC [8-11], Ni- ZrO_3 [14], Ni- TiO_2 [17, 18], Have been reported recently. These have the large projected applications for automotive parts, aerospace printed circuitry and electrical contacts, gold-silver wares and jewelry, musical instruments and trophies, soft metal gaskets, decorative door, light are bathroom fittings [7].

1.2 Electrochemical Methods of Analysis:-

The aggregate of methods of qualitative and quantitative analysis based on electrochemical phenomena occurring within a medium or at the phase boundary and related to changes in the structure, chemical composition, or concentration of the compound being analyzed. These methods are divided into five major groups: potentiometry, voltammetry, coulometry, conductometry, and dielectrometry. Potentiometry combines methods based on the measurement of the emf of reversible electrochemical circuits, when the potential of the working electrode is close to the equilibrium value. This method includes redox titration, ionometry, and potentiometric titration. Voltammetry is based on the study of the dependence of

polarization current on the voltage applied to an electrochemical cell when the potential of the working electrode differs significantly from the equilibrium value (Polarization, ELECTROCHEMICAL). Voltammetry, with its variety of methods, constitutes the largest group of electrochemical methods of analysis and is commonly used for the determination of compounds in solutions and melts (for example, polarography and amperometry). Coulometry combines methods of analysis based on the measurement of the amount of material deposited on an electrode in the course of an electrochemical reaction in accordance with Faraday's laws. In coulometry, the potential of the working electrode differs from the equilibrium value. A distinction is made between coulometry at constant potential and coulometry at constant current. The latter includes both direct and indirect methods, electro analysis, and coulometric titration[7].

Conductometry encompasses methods in which the electrical conductivity of electrolytes (aqueous and nonaqueous solutions, colloid systems, melts, and solids) is measured (Electrical Conductivity of Electrolytes). It is based on the change in the concentration of a compound or the chemical composition of a medium in the interelectrode space; it is not linked with the electrode potential, which is usually close to the equilibrium value. Conductometry includes both direct analytical methods (used, for example, in salinometers) and indirect analytical methods (for example, in gas analysis) using either direct or alternating current (low-or high-frequency current). It also includes chrono-conductometry and low-frequency and high-frequency titration. Dielectrometry combines analytical methods based on the measurement of the dielectric constant of a substance resulting from the orientation of particles (molecules or ions) that have a dipole moment in an electric field. These methods are used to monitor the purity of dielectrics, for example, to detect small amounts of moisture. Dielectrometric titration is used to analyze solutions[7].

1.2.1 Applications of Electrochemical Analysis :-

There are various extremely important electrochemical processes in both nature and industry, like the coating of objects with metals or metal oxides through electrode position and the detection of alcohol in drunken drivers

through the redox reaction of ethanol. The generation of chemical energy through photosynthesis is inherently an electrochemical process, as is the production of metals like aluminum and titanium from their ores. Certain diabetes blood sugar meters measure the amount of glucose in the blood through its redox potential. As well as the established electrochemical technologies (like deep cycle lead acid batteries) there is also a wide range of new emerging technologies such as fuel cells, large format lithium ion batteries, electrochemical reactors and super-capacitors that are becoming increasingly commercial. Electrochemistry has also important applications in the food industry, like the assessment of food/package interactions, the analysis of milk composition, the characterization and the determination of the freezing end-point of ice-cream mixes, the determination of free acidity in olive oil[4].

1.3 Nickel, Titanium and Copper Composites:-

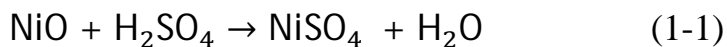
1.3.1 Nickel Metals:-

Nickel is an element with the symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals and is hard and ductile. Pure nickel, powdered to maximize the reactive surface area, shows a significant chemical activity, but larger pieces are slow to react with air under standard conditions because an oxide layer forms on the surface and prevents further corrosion (passivation). Even so, pure native nickel is found in Earth's crust only in small amounts, usually in ultramafic rocks [8][9] and in the interiors of larger nickel-iron meteorites that were not exposed to oxygen when outside Earth's atmosphere. Nickel oxidizes slowly at room temperature and is considered corrosion-resistant. Historically, it has been used for plating iron and brass, coating chemistry equipment, and manufacturing certain alloys that retain a high silvery polish, such as German silver. About 6% of world nickel production is still used for corrosion-resistant pure-nickel plating. Nickel-plated objects sometimes provoke nickel allergy. Nickel has been widely used in coins, though its rising price has led to some replacement with cheaper metals in recent years.

Nickel is one of four elements (iron, cobalt, nickel, and gadolinium)[7] that are ferromagnetic around room temperature. Alnico permanent magnets based partly on nickel are of intermediate strength between iron-based permanent magnets and rare-earth magnets. The metal is valuable in modern times chiefly in alloys; about 60% of world production is used in nickel-steels (particularly stainless steel). Other common alloys and some new super alloys comprise most of the remainder of world nickel use, with chemical uses for nickel compounds consuming less than 3% of production[8]. As a compound, nickel has a number of niche chemical manufacturing uses, such as a catalyst for hydrogenation. Nickel is an essential nutrient for some microorganisms and plants that have enzymes with nickel as an active site.

1.3.2 Nickel(II) Ions:-

Nickel(II) fluoride is made by fluorination of NiCl_2 ; it is a yellow solid with a futile structure. Both NiF_2 and its green tetra hydrate are commercially available. Anhydrous NiCl_2 , NiBr_2 and NiI_2 are made by direct combination of the elements; NiCl_2 and NiI_2 adopt a CdCl_2 structure, while NiBr_2 has a CdI_2 structure. The chloride is a useful precursor in Ni(II) chemistry and can be purchased as the yellow anhydrous salt or green hydrate. The hex hydrate contains the $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ ion in the solid state, but the dihydrate (obtained by partial dehydration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) has a polymeric one word structure analogous to 21.36. Anhydrous NiBr_2 is yellow and can be crystallized as a number of hydrates; black NiI_2 forms a green hex hydrate. The water-insoluble, green NiO is obtained by thermal decomposition of NiCO_3 or $\text{Ni}(\text{NO}_3)_2$ and crystallizes with the NaCl structure; thin amorphous films of NiO exhibiting electro chromic behaviour may be deposited by CVD (chemical vapour deposition, starting from $[\text{Ni}(\text{acac})_2]$). Nickel(II) oxide is antiferromagnetic. Nickel(II) oxide is basic, reacting with acids e.g. reaction 1



Although NiS is not precipitated in acidic solution, after exposure to air it is insoluble in dilute acid. Addition of $[\text{OH}]^-$ to aqueous solutions of Ni^{+2} precipitates green $\text{Ni}(\text{OH})_2$ which has a CdI_2 structure; it is used in NiCd batteries [10]. or just nickel sulfate, usually refers to the inorganic compound with the formula $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. This highly soluble blue-coloured salt is a common source of Ni^{+2} ion for electroplating. Approximately, 40,000 tonnes were produced in 2005. It is mainly used for electroplating of nickel [1]. In 2005–06, nickel sulfate was the top allergen in patch tests (19.0%) [2]. These salts differ in terms of their hydration or crystal habit. The common tetragonal hex hydrate crystallizes from aqueous solution between 30.7 and 53.8 °C. Below these temperatures, a heptahydrate crystallizes, and above these temperatures an orthorhombic hex hydrate forms. The yellow anhydrous form, NiSO_4 , is a high melting solid that is rarely encountered in the laboratory. This material is produced by heating the hydrates above 330 °C. It decomposes at higher temperatures to nickel oxide [1]. X-ray crystallography measurements show that $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ consists of the octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ ions. These ions in turn are hydrogen bonded to sulfate ions [3]. Dissolution of the salt in water gives solutions containing the aqua complex $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$. All nickel sulfates are paramagnetic. The salt is usually obtained as a by-product of copper refining. It is also produced by dissolution of nickel metal or nickel oxides in sulfuric acid. Aqueous solutions of nickel sulfate reacts with sodium carbonate to precipitate nickel carbonate, a precursor to nickel-based catalysts and pigments. [4] Addition of ammonium sulfate to concentrated aqueous solutions of nickel sulfate precipitates $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. This blue-colored solid is analogous to Mohr's salt, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. [1] Nickel sulfate is used in the laboratory. Columns used in polyhistidine-tagging, useful in biochemistry and molecular biology, are regenerated with nickel sulfate. Aqueous solutions of a $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ And related hydrates react with ammonia to give $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$ and with ethylenediamine to give $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]\text{SO}_4$.

1.3.3 Types of Nickel Plating Solutions:-

Choice of bath composition is indicated primarily by the mechanical properties desired in the deposits. Electrodeposited metals can often be varied over wide limits than those of the same metals produced by conventional means [11]. The various Types of nickel bath used for production are listed in table(1) .

(I) Watts bath :

while the Watts nickel solution is the most popular one used for deposition of heavy nickel coating, other baths are employed when their specialized advantages are desired as shown in table (1).

Table (1) Composition of Bath used for Nickel Deposition

Type of bath	Nickel sulfate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	Nickel chloride NiCl_2	Nickel Sulfamate $\text{Ni}(\text{SO}_3\text{NH})_2 \cdot 4\text{H}_2\text{O}$	Boric acid H_3B_3
Watts	240-330	37-52	-	30-40
Hard watts(containing ammonia)	180-230	-	-	30
All chlorides	-	250-300	-	20-30
Conventional Sulfa mate + organic stress-reliever	-	30	300-450	30-45
Concentrated sulfa mate	-	5-15	550-650	30-40

Variations in the plating conditions cause variation in the mechanical properties.

These conditions may be solution composition, acidity, temperature and current density [12,13] .watts bath is so simple to control, and maintains in its optimum condition and is still recommend in the heavy nickel field .

Although the deposits obtained from it are fairly soft and have moderately high tensile strength. When harder plate is desired additives to Watts bath such as ammonium salt or organic compounds like as saccharin or p-toluene sulfamid can be added to this bath.

(II).Sulfamate Bath:

Sulfamic acid is the base of nickel sulfamate plating solutions .commercial use this type of bath started about 1949. The standard sulfamate solution gives deposits having a lower stress than those from Watts bath but with somewhat lower ductility. This makes this process suitable for electroforming . But, harder and stronger deposits having little or no internal stress are required .compounds such as naphthalene , sulfonic acid are added to the solution because nickel sulfamate bath are usually employed to produce deposits for engineering applications[14].

(III). All –Chloride Bath :

Allchloride solutions has little application for heavy nickel plating, although, it is possible to employ double the current density that can be used in a watts before result. Also, their throwing power is superior; the deposition has a high tensile stress and low ductility[14].

(IV). Fluoborate Bath:

Flu borate bath have not achieved much popularity for deposition of nickel although the deposits from them are slightly less stressed than those from a watts bath . The mechanical properties of the electroplating article from Fluoborate solution are excelled by those from a sulfamate bath . Except for some uses in the printing industry, the Fluoborate bath is of little use [14].

(V).Citrate Bath:

Citrate bath exhibits excellent cathode current efficiency and buffering for bath PH, which are comparable with those of the watts bath deposits obtained from citrate bath are a harder a deposits from the watts bath. A possible explanation for these characteristics is the fact that the citric acid in

the citrate bath reacts with nickel ions to form nickel citrate complexes which are adsorbed on the surface of cathode and contribute to electrode position of nickel and crystallization of the deposits [14].

(IV). Black Nickel:

Solution in table (2) is for deposition of a decorative black finish, which contains only nickel but also large amounts apart from some limited use on optical equipment or for solar collectors, black nickel has chiefly applied for decorative purpose.

Table (2) Black Nickel Bath Electroplating Conditions

Solution	Ingredients	Concentration g\L	PH	Temp °C	Current density A\dm ²
Black nickel	NiSO ₄ . 6H ₂ O NH ₄ Cl NaCNS ZnCl ₂	75 30 15 30	5	24-32	0.15

Nickel plating is used, extensively, for decorative, engineering and electroforming purposes because the appearance and other properties of electrodeposited nickel can be varied over wide ranges by controlling the composition and the operating parameter of the plating solution. Decorative applications account for about 80% of the nickel consumed in plating ; 20% is consumed for engineering and electroforming purposes [15] . Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of direct current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of

direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with with nickel. The nickel in the solution is present in the form of divalent positively charged ions (Ni^{2+}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode where metallic nickel is dissolved to form divalent positively charged ions which enter the solution; nickel ions discharged at the cathode are replenished by those formed at the anode.

1.3.4Titanium:-

Titanium is a chemical element with symbol Ti and atomic number 22. It is a lustrous transition metal with a silver color, low density and high strength. It is highly resistant to corrosion in sea water, aqua regia, and chlorine. Titanium was discovered in Cornwall, Great Britain, by William Gregor in 1791 and named by Martin Heinrich Klaproth for the Titans of Greek mythology. The element occurs within a number of mineral deposits, principally rutile and ilmenite, which are widely distributed in the Earth's crust and lithosphere, and it is found in almost all living things, rocks, water bodies, and soils[3]. The metal is extracted from its principal mineral ores by the Kroll[4].and Hunter processes. The most common compound, titanium dioxide, is a popular photocatalyst and is used in the manufacture of white pigments[5]. Other compounds include titanium tetrachloride (TiCl_4), a component of smoke screens and catalysts; and titanium trichloride (TiCl_3), which is used as a catalyst in the production of polypropylene[3].

Titanium can be alloyed with iron, aluminium, vanadium, and molybdenum, among other elements, to produce strong, lightweight alloys for aerospace (jet engines, missiles, and spacecraft), military, industrial process (chemicals and petro-chemicals, desalination plants, pulp, and paper), automotive, agri-food, medical prostheses, orthopedic implants, dental and endodontic instruments and files, dental implants, sporting goods, jewelry, mobile phones, and other applications [3].

The two most useful properties of the metal are corrosion resistance and the highest strength-to-density ratio of any metallic element[6]. In its unalloyed

condition, titanium is as strong as some steels, but less dense[7]. There are two allotropic forms[8].and five naturally occurring isotopes of this element, $^{46}_{22}\text{Ti}$ through $^{50}_{22}\text{Ti}$, with $^{48}_{22}\text{Ti}$ being the most abundant (73.8%)[9]. Although they have the same number of valence electrons and are in the same group in the periodic table, titanium and zirconium differ in many chemical and physical properties.

1.3.4.1 Physical Properties:-

A metallic element, titanium is recognized for its high strength-to-weight ratio[8]. It is a strong metal with low density that is quite ductile (especially in an oxygen-free environment)[3] lustrous, and metallic-white in color[10]. The relatively high melting point (more than 1,650 °C or 3,000 °F) makes it useful as a refractory metal. It is paramagnetic and has fairly low electrical and thermal conductivity[3]. Commercial (99.2% pure) grades of titanium have ultimate tensile strength of about 434 MPa (63,000 psi), equal to that of common, low-grade steel alloys, but are less dense. Titanium is 60% denser than aluminium, but more than twice as strong[7].as the most commonly used 6061-T6 aluminium alloy. Certain titanium alloys (e.g., Beta C) achieve tensile strengths of over 1400 MPa (200000 psi)[11].However, titanium loses strength when heated above 430 °C (806 °F)[12]. Titanium is not as hard as some grades of heat-treated steel, is non-magnetic and a poor conductor of heat and electricity. Machining requires precautions, because the material might gall if sharp tools and proper cooling methods are not used. Like those made from steel, titanium structures have a fatigue limit that guarantees longevity in some applications[10] Titanium alloys have less stiffness than many other structural materials such as aluminium alloys and carbon fiber.

1.3.4.2 Chemicals Properties:-

Like aluminium and magnesium, titanium metal and its alloys oxidize immediately upon exposure to air. Titanium readily reacts with oxygen at 1,200 °C (2,190 °F) in air, and at 610 °C (1,130 °F) in pure oxygen, forming titanium dioxide[8] It is, however, slow to react with water and air at ambient temperatures because it forms a passive oxide coating that protects

the bulk metal from further oxidation[26] When it first forms, this protective layer is only 1–2 nm thick but continues to grow slowly; reaching a thickness of 25 nm in four years. Atmospheric passivation gives titanium excellent resistance to corrosion, almost equivalent to platinum, capable of withstanding attack by dilute sulfuric and hydrochloric acids, chloride solutions, and most organic acids. However, titanium is corroded by concentrated acids . As indicated by its negative redox potential, titanium is thermodynamically a very reactive metal that burns in normal atmosphere at lower temperatures than the melting point. Melting is possible only in an inert atmosphere or in a vacuum. At 550 °C (1,022 °F), it combines with chlorine[27]. It also reacts with the other halogens and absorbs hydrogen[5].

Titanium is one of the few elements that burns in pure nitrogen gas, reacting at 800 °C (1,470 °F) to form titanium nitride, which causes embrittlement[17]. Because of its high reactivity with oxygen, nitrogen, and some other gases, titanium filaments are applied in titanium sublimation pumps as scavengers for these gases. Such pumps inexpensively and reliably produce extremely low pressures in ultra-high vacuum systems.

1.3.5 Copper:-

Copper is the most common metal plated, exclusive of continuous strip plating and nickel [10]. The major uses of electroplated copper are plating on plastics, printed wiring boards, zinc die castings, automotive bumpers, rotogravure rolls, electro refining, and electroforming [11]. Electroplated copper is playing a major role in the change from aluminum to copper in semiconductor interconnect technology. This materials change was heralded as a “major breakthrough” in The New York Times (September 22, 1997) and a “dazzling technical advance” by Time magazine (October 10, 1997) . It signals one of the most important changes in materials that the semiconductor industry has experienced since its creation [2b] Copper is electrodeposited for numerous engineering and decorative applications requiring a wide range of mechanical and physical properties. The range extends from properties superior to full-hard wrought copper to properties equivalent to annealed pure copper [12]. Copper is an excellent choice for an underplate, since it often covers minor imperfections in the base metal. It is

relatively inert in most plating solutions of other common metals; it has a very high plating efficiency, resulting in excellent coverage even on difficult-to-plate parts; and lastly, it is highly conductive, making it an excellent coating for printed wiring boards or as a coating on steel wire used to conduct electricity [10]. Copper deposits also act as thermal expansion barriers by absorbing the stress produced when metals with different thermal expansion coefficients undergo temperature changes, and this is particularly helpful with plastic substrates. The leveling and brightness properties of copper deposits can be further enhanced by buffing, and since copper is much softer than steel or nickel, it is easy and relatively inexpensive to buff [13].

Of the plating systems that have been studied, only relatively few have revealed a stage of commercial importance for electrode position of copper. These are the alkaline cyanide and pyrophosphate complex ion systems and the acid sulfate and fluoborate simple ion systems. Other types of solutions have been too unstable or lacking in good deposit characteristics over sufficiently wide current density ranges [14]. In recent years some alkaline noncyanide systems have been developed for replacing cyanide. The areas of application of the various copper plating solutions overlap somewhat, but each has its fairly well defined area of usefulness. Clearly, the most heavily used are the acid copper sulfate solutions. Open literature publications and patents for sulfate solutions since the 1974 edition of this book in [15] far outnumber those of all the other solutions combined. Deposits produced in cyanide solutions are typically thin (<12.5 mm) and are used as an undercoating for nickel and chromium, as a heat treatment slop-off for selective hardening of ferrous parts, or as an intermediate step prior to additional plating. For example, a copper cyanide deposit is typically a key part of the activation cycle for preparing aluminum, beryllium, and zinc die castings for plating. Copper deposits from cyanide solutions are not generally suitable for deposition of relatively thick deposits for electroforming and similar applications. Cyanide solutions are finding less and less favor because of their toxicity and waste treatment problems and are being replaced by noncyanide solutions. Pyrophosphate solutions, once used heavily for plating through holes on printed wiring boards, have been almost completely replaced by high-throw acid sulfate solutions. Flu borate

solutions have been advertised for many years as having the capability to deposit copper at very high current densities.

1.3.5.1 Application:-

Electrode position of copper from acid solutions is extensively used for electroforming, electro refining, and electroplating. Refiners and electro formers, in particular, employ acid solutions because costs of chemicals and power are low and because the solutions are simple and easy to control. In the electro winning and electro refining industries, acid solutions are employed exclusively. More than 80% of the domestic production of primary copper is refined electrolytically.

Acid copper sulfate solutions are widely used for plating of printed wiring boards and for semiconductor interconnect technology. Electroformed copper articles include band instruments, heat exchangers, reflectors, and a variety of articles for military and aerospace applications. All three main types of printing processes (electrotyping, rotogravure work, and lithography) use copper and sometimes nickel and chromium [16]. Acid copper solutions containing organic brightening and leveling agents are used extensively to deposit smooth copper on rough steel and etched plastics. Zinc die castings are plated with approximately 15 mm of leveling acid copper [17, 18] before nickel and chromium plating, to eliminate buffing before plating. Because of the excellent micro throwing power of the acid copper, pits, pores, or crevices in either steel or zinc surfaces are well filled with copper, and this improves resistance to corrosion or blistering [19–20]. Acid copper deposits are one part of the sequence for decorative plating of aluminum wheels for automotive applications. In some cases the copper is buffed to add luster to the low-current-density areas of the wheel and to flow some of the copper over small pits and voids [21]. Coatings on plastics need to be bright and ductile and have the capability to expand and contract with the thermal expansion of the plastic without cracking, blistering, or peeling. Bright decorative acid copper deposits meet these requirements [13, 22]. One of the most important steps in the production of plated wire for memory use is copper plating in acid sulfate solution [23]. Many kilometers of steel wire are given a copper cyanide strike and plated with copper in acid solution to produce a high-strength electrical cable. Thick deposits (200 mm) of copper

are applied to steel rolls and then engraved for use in printing and marking papers and textiles. Stainless steel cooking vessels are copper plated in acid solutions to improve the heat diffusion characteristics of outer surfaces and avoid local hot spots. Copper plating for stopping off carburizing on selected areas is accomplished by striking in a cyanide solution followed by plating in acid solutions. Acid copper plating is sometimes used for building up worn or over machined parts, especially when copper surfaces are desired for protection against fretting corrosion. Optical surfaces can be produced on parts by single-point diamond turning specific acid copper deposits [24–25]. Metal powders produced by deposition in acid solutions are used for making sintered compacts and pigments.

1.4 Glycine:-

Glycine is of the simplest structure in the 20 members of amino acid series, also known as amino acetate. It is a non-essential amino acid for the human body and contains both acidic and basic functional group inside its molecule. It exhibits as a strong electrolyte in an aqueous solution, and has a large solubility in strong polar solvents but almost insoluble in non-polar solvents. Moreover, it also has a relative high melting point and boiling point. The adjustment of the pH of the aqueous solution can make glycine exhibit different molecular forms. The side chain of glycine contains only a hydrogen atom. Owing to another hydrogen atom connecting to the α -carbon atom, the glycine is not optical isomer. Since the side bond of glycine is very small, it can occupy space which can't be occupied by other amino acids, such as those amino acids located within the collagen helix. At room temperature, it exhibits as white crystal or light yellow crystalline powder and has a unique sweet taste which can ease the taste of acid and alkaline taste, masking the bitter taste of saccharin in food and enhance the sweetness. However, if an excessive amount of glycine is absorbed by body, they not only can't be totally absorbed by the body, but will also break the balance of the body's absorption of amino acids as well as affect the absorption of other kinds of amino acids, leading to nutrient imbalances and negatively affected health. The milk drink with glycine being the major raw material can easily do harm to the normal growth and development of young people and children. It has a density of 1.1607, melting point of 232 ~

236 °C (decomposition). It is capable of acting together with hydrochloric acid to form hydrochloride salt. It is presented in the muscles of animals. IT can be produced from the reaction between monochord acetate and ammonium hydroxide as well as from the hydrolysis of gelatin [14]. Nanocomposites have attracted extensive interest because of their beneficial electrical, optical, magnetic and mechanical properties[28].

Ni-TiO₂ nanocomposites with varying titanium content were electrodeposited on copper substrates employing a gluconate electrolyte. The changes in microstructure and corrosion behavior of electrodeposited nickel with respect to titanium addition were studied. The titanium content in the coatings increased with increasing titanium content in the bath and decreased at high current density. The effect of pH shows an increase in titanium up to pH8. Enhancement of hardness and corrosion resistance was observed via incorporation of titanium in the nickel matrix. The addition of TiO₂ nanoparticles to the bath affects the microstructure and morphology of the nickel matrix, as indicated by x-ray diffraction (XRF) and scanning electron microscopy (SEM)[29].

1.5 Objectives of The Study:-

-The objectives of this research are:

-To Electrodeposit Ni-TiO₂ from glycine baths at different condition such as concentration of nickel ions, titanium oxide, glycine, temperature, current and time.

- To Calculate the obtained coating thickness.

-To characterize of the obtained Ni-TiO₂ deposits using XRF and A.A.S.

Chapter Two

Materials and Methods

Chapter Two

Materials and Methods

2.1 Chemicals and Materials:-

2.1.1 Chemicals:-

All chemicals used in this research were of Analytical grade type. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, Glycine, NaOH, HCl con-, H_3NO con-, H_3PO_4 , TiO_2 , sheet of copper, sheet of Ni, H_2SO_4 con-, ammonia solution, EDTA, EBT reagent, Distilled Water.

2.1.2 Materials and Glass Ware:-

Beakers, 50ml, 100ml, 250ml, conical flask 100ml, titration flask 250ml, glass rod, funnel, filter paper, PH paper, thermometer, and pipette.

2.2 Instruments:-

Water bath, DC-power supply, X-ray fluorescence XRF(OXFORD/X-Supreme/00595), Atomic absorption Spectrophotometer A.A.S(GBC/Sauant/A7703) .

2.3 Preparation of Solutions:-

2.3.1 Preparation of Nickel Sulfate(0.2M) Solution:-

5.257g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was weighed in beaker 100ml, and dissolved in 10ml of distilled water and the solution was transferred quantitatively to the flask 100ml, and filled with distilled water to the mark.

2.3.2 Preparation of Ammonium Sulfate(0.2M) Solution:-

1.53g of $(\text{NH}_4)_2\text{SO}_4$ were weighed in beaker 100ml, and dissolved in 10ml of distilled water and the solution was transferred quantitatively to a 100ml flask, was filled with distilled water to the mark.

2.3.3 Preparation of glycine (0.2M) Solution:-

2.28g of glycine was weighed in beaker 100ml, and dissolved in 10ml of distilled water and the solution was transferred quantitatively to the flask 100ml, and filled with distilled water to the mark.

2.4 Methods:-

Solution bath contains $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.2M), $(\text{NH}_4)_2\text{SO}_4$ (0.2M), and Glycine (0.2M).

Copper sheet cathode and nickel sheet anode both of dimensions $1.5 \times 1.5 \text{ cm}^2$ were used. The copper sheet cathodes were mechanically polished with different grade emery papers and then immersed in pickling solution (300ml H_2SO_4 + 595ml distilled water) for 1min, washed with distilled water, rinsed with acetone, dried and finely weighed. The pH was measured using Microprocessor PH meter and adjusted by NaOH 20% addition, the temperature was controlled by using thermometer. Direct current was supplied by a D.c power supply unit (GP-4303D). The copper cathodes were weighed before and after electrode position for a certain period of time and at fixed current density. From the change in weights of the cathodes, the deposited weight was calculated. the composition was examined using the following procedures:

- The coating layer is stripped using 10% H_2SO_4 solution. The object is then put as anode in an electroplating cell by which the coating layer will be dissolved in the solution, which is then diluted to 250ml with distilled water.
- The analysis was done using Atomic absorption Spectrophotometer.
- The solution obtained is further diluted by dissolving 5ml in distilled water to 250ml.
- The Titanium weight was calculated by subtracting the obtained nickel weight from the total deposit weight.

The surface of the as-deposited nickel and nickel-titanium, on copper substrates was inspected using Atomic Absorption Photometer, and X-Ray fluorescence, with a copper target ($\text{Cu}_{\lambda} = 1.5406 \text{ \AA}$) and Nickel filter.

Table 3 - The Bath Composition and Operating Conditions of Nickel-Titania Electrodepositing Process.

Nickel sulfate	0.1-0.5mol/L
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Ammonium sulfate	0.2mol/L
Titanium	1 – 4g/L
Temperature	30 -100°C
Current density	0.1-0.5 A/cm ²
PH	2-10
Time	10-60 min

Chapter Three

Results and Discussion

Chapter Three
Results and Discussion

3.1 Optimization of Nickel-Titanium Electrode Position Parameters:

From Fig.1 and Table.1 show the thickness of the coating is increased with increasing pH up to pH 8, after which the coating thickness is decreased due to the nickel hydroxide precipitation.

Table. 3.1 Effect of pH on thickness of the Ni-TiO₂ coating.

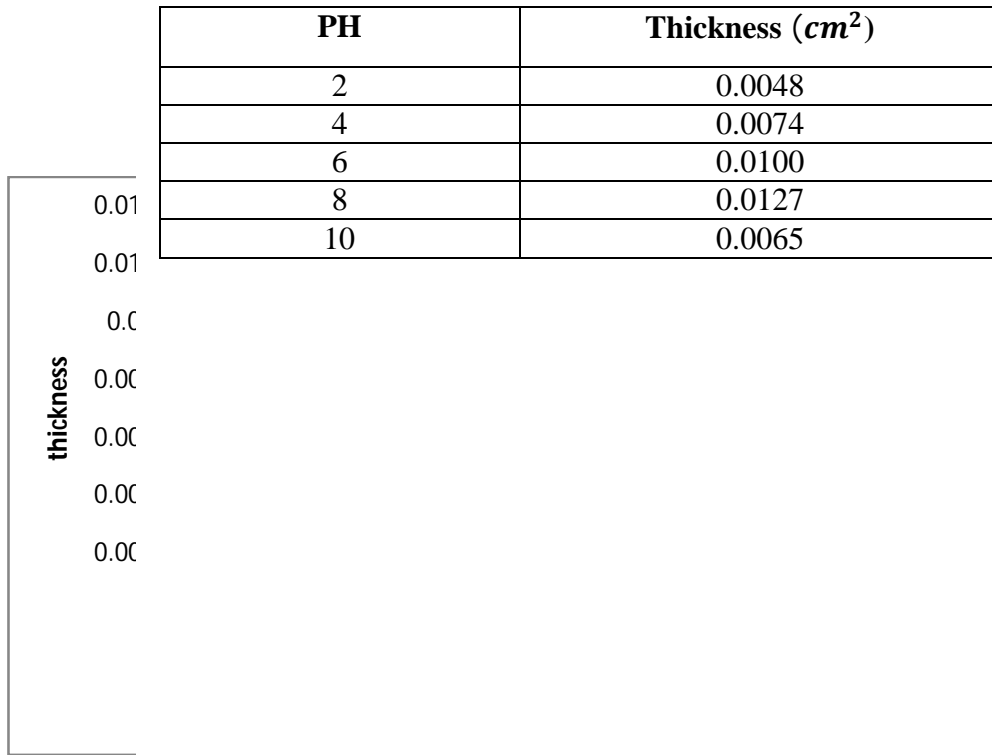


Fig.3.1 Effect of pH on thickness of Ni-TiO₂ coatings.

The effect of current density on the coating thickness is illustrated in Table.2 and Fig.2 It is clear from these results that the thickness increased with

increasing current density up to 0.4 A/cm^2 and beyond that decreased gradually. This may be attributed to the fact that an increase in current density results in more rapid deposition of metal matrix and fewer particles are embedded in the coating. Hence, the metal deposition dominates the co-deposition process.

Table3.2 Effect of current on thickness of Ni-TiO₂ coatings.

Current (A)	Thickness (cm ²)
0.1	0.0894
0.2	0.1143
0.3	0.1340
0.4	0.1454
0.5	0.1744
0.6	0.1208

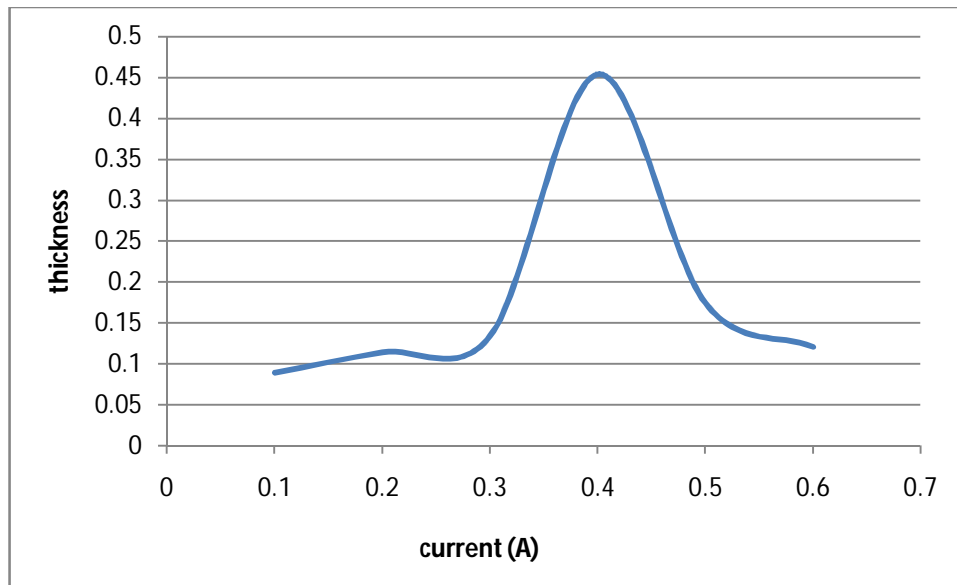


Fig3.2.Effect of current on The Thickness of Ni-TiO₂ coatings .

Table 3.3 and Fig 3. 3 shows the effect of plating time on the coatings thickness, These results indicate that the thickness of coating increased with increasing plating time in accordance with Faraday’s Law.

Table3.3 Effect of time on thickness of the Ni-TiO₂ Electrodeposition.

Time(sec)	Thickness (cm ²)
10	0.1972
20	0.2017
30	0.2259
40	0.2394
50	0.2584
60	0.2604

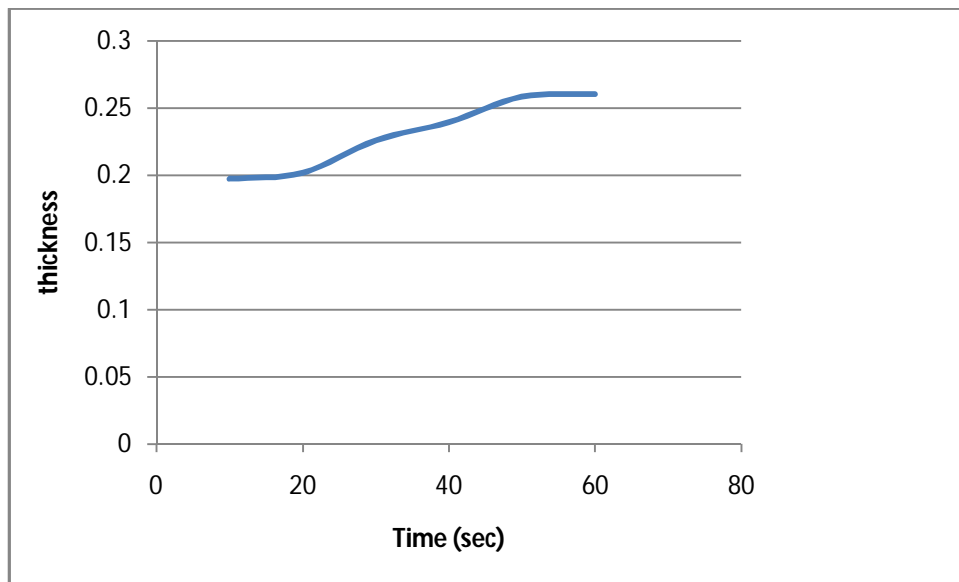


Fig3.3 Effect of time on The thickness of Ni-TiO₂ coatings .

Table3.4 and Fig3.4 shows that the coating thickness is increased with increasing temperature up to 100°C. Beyond that point, hydrogen evolution hinders the composite deposition.

One of the important parameter in electroplating is the bath temperature.

Table3.4 Effect of temperature on thickness of Ni-TiO₂ coatings.

Temperature (C°)	Thickness (cm ²)
30	0.0214
40	0.0439
50	0.0473
60	0.0463
70	0.0694
80	0.0701
90	0.0718
100	0.0787

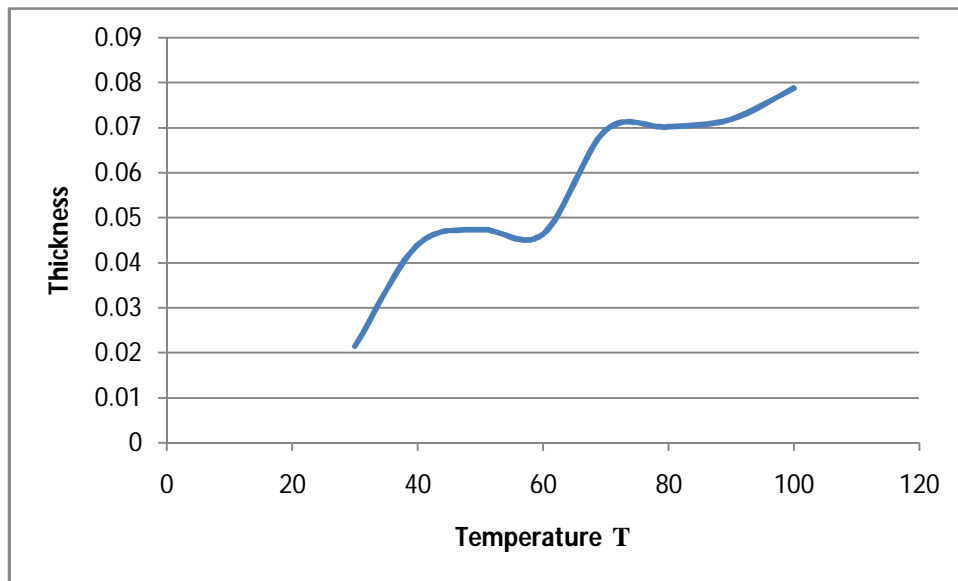


Fig3.4 Effect of The temperature on the thickness of Ni-TiO₂ coatings.

Table3.5. and Fig3.5 shows that the thickness of the coatings is increased with increasing concentration of the NiSO₄.6H₂O.

Table3.5 Effect of concentration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ g/L on thickness of the Ni-TiO₂ coatings.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ g/L	Thickness (cm ²)
0.1	0.0929
0.2	0.1875
0.3	0.1527
0.4	0.1917
0.5	0.2103

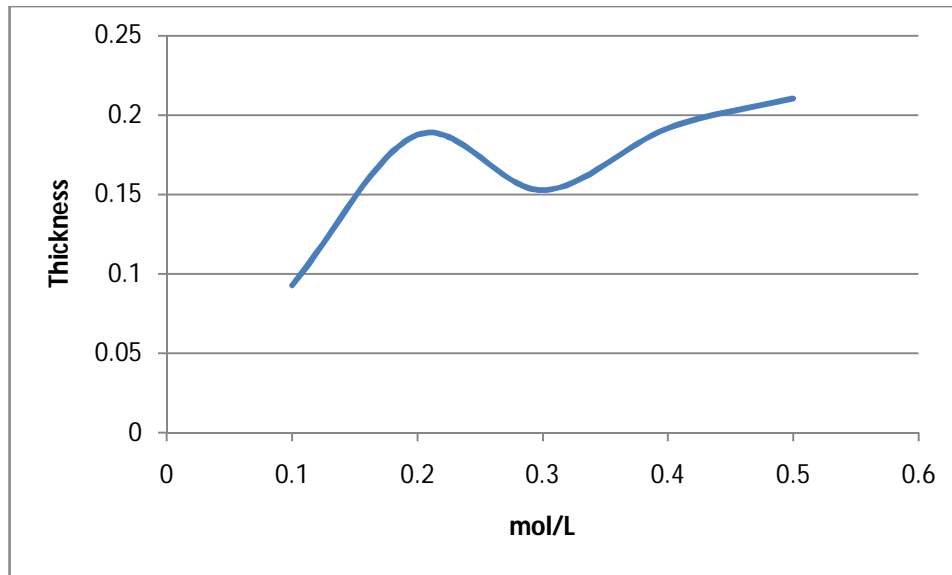


Fig 3.5 Effect of the concentration of the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ on the thickness of the Ni-TiO₂ coatings.

Table3.6 and Fig3.6 shows that the thickness of the coatings is increased with increasing concentration of the glycine.

Table3.6 Effect of concentration of Glycene on thickness of the Ni-TiO₂ coatings.

Glycine g/L	Thickness (cm ²)
1	0.0145
2	0.0172
3	0.01969
4	0.0563

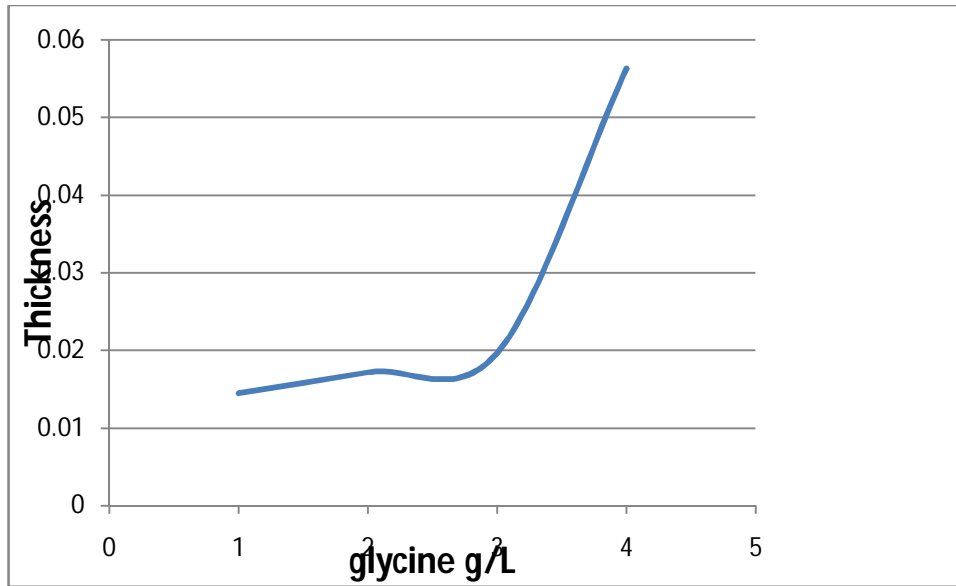


Fig 3.6 Effect of concentration of glycine on the thickness of the Ni-TiO₂ coatings.

Table3.7. and Fig3.7 Shows that the thickness of the coatings is increased with increasing concentration of TiO_2 .

Table3.7 Effect of concentration of TiO_2 on thickness of the Ni- TiO_2 coatings.

TiO_2 g/L	Thickness (cm^2)
1	0.0138
2	0.0418
3	0.0591
4	0.0663

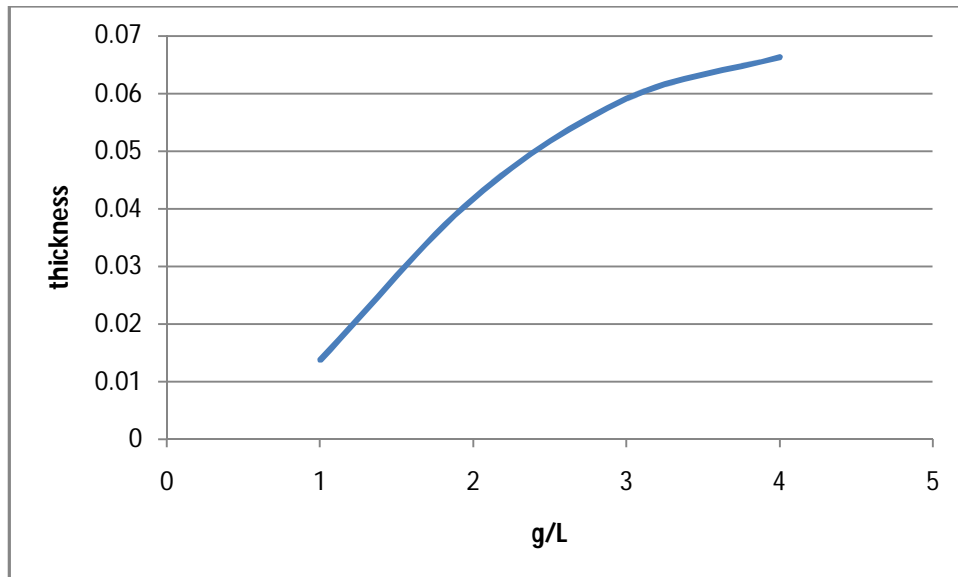


Fig3.7 Effect of the concentration of the TiO_2 on the thickness of the Ni- TiO_2 coatings.

3.2 Determination of Ni and TiO₂ in the Coatings Samples:

It is interesting to note that the rate of particle incorporation is higher at low current densities and levels off at higher current densities, as seen in Fig.3. 2. This dependence of particle incorporation on the current density is consistent with Guglielmi's model.²⁵ At low current densities, the codeposition process is controlled by particle adsorption and hence particle incorporation is dominant.

3.2.1 Determination of Nickel by A.A.S Instrument:

Percentage of Nickel is 0.72462%.

3.2.2 Determination of Nickel and Titanium by XRF Instrument:

Percentage of Nickel is 0.8745%.

Percentage of Titanium is 2.7695%.

Conclusions:-

In Ni- TiO₂ composite, the amount of TiO₂ incorporated is directly increased with increasing the amount of particles present in the bath, The applied current density and pH of the electrolytic solution critically affect this amount of incorporation because the particles amount in the deposits increased with increasing current density and pH to a certain degree and then decreased. Incorporation of TiO₂ particles affects the characteristics of the structure of Ni-matrix.

Determined the percentage of Ni by A.A.S (0.72462%), and by XRF (0.8745%), the percentage of TiO₂ by XRF (2.7695%).

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