وزارة التعليم العالي والبحث العلمي

جامعة ديالى

كلية الهندسة

تصنيع مواد طبية ذات اساس فولاذ مقاوم للصدأ 316 l مطليه بمواد حيويه نانويه مركبه من الفضه / سيراميك باستخدام تقنية الطلاء اللاكهربائي

رسالة مقدمة الى كلية الهندسة /جامعة ديالى

وهي جزء من متطلبات نيل درجة الماجستير في علوم هندسة المواد

من قبل

(بكالوريوس في هندسة المواد)

إشراف

أ.د.عادل خليل محمود　　　　أ.م.د.سهى ابراهيم عبد اللطيف

1444 هـ　　　　العراق　　　　2023م

Ministry of Higher Education

University of Diyala

College of Engineering

Synthesis of Stainless Steel 316 L Based-Ag/Ceramic Bio-Nano Composite Coatings by Electroless Deposition Technique

A Thesis Submitted to the Council of College of Engineering, University of Diyala in Partial Fulfillment of the Requirements for the Degree of Master of Science in Materials Engineering

By

Basma Zuher Thabet

(B.Sc. Materials Engineering, 2018)

Supervised by

Prof. Dr. Adel K. Mahmoud **Assist. Prof. Dr. Suha I. Al-Nassar**

1444 A.H. 2023 A. D.

Chapter One

Introduction

Chapter One

Introduction

1.1 Motivation

The electroless deposition is the highly significant method to produce the nano composites of the non-metallic and metallic components and this process can be used without the application of electric current from external source [1]. Development of the functional materials by the electroless deposition without the external energy requirement is an attractive idea. The electroless deposition can be sub-classified into deposition in the reducing agent’s existence, the disproportionation reaction and the galvanic displacement reaction [2]. The microbial adhesion as well as the creation of biofilm were known as a prevalent difficulty in the design and procedure of treating apparatuses, like cooling water system-like heat exchangers, and equipment of food processing apparatuses, so the samples are coated with silver because it is considered anti bacteria adhesion [3].

The damage of Deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA) as well as the protein inactivation via the particles of silver appeared to be the main bacteriostasis' mechanisms. The intracellular protecting mechanisms versus the silver varied in the Gram-negative and Gram-positive bacteria [4].

Carbon nanotubes (CNTs) can possess numerous uses due to the beneficial characteristics that get them a suitable material for a bio-medical use as they're further bio-compatible in comparison to the others, a broad no. of antibacterial as well as protein carriers, containing exposed functional groups, high tensile strength, chemical inertness, ultra-light weight, rapid electron transfer kinetics, etc. Also, there are antifungal properties, working as grasp semi and metallic conductive characteristics that make them an appropriate material for different uses, like ecological observing, clinical diagnostics, and safety of food. In addition, carbon nanotubes take an important part in the sensors synthesis to detect different pathogenic bacteria as well as aid in the cancer treatment. Even carbon nanotubes have a broad number of antimicrobial actions [5, 6].

Nano hydroxyapatite $Ca_5(OH)(PO_4)_3$ is a well-known bio-material for bone substitution that distributed into silver coating. It's a few bioactive implantation materials capable of making a straight and fixed bond with the tissue of bone [5]. The hydroxyapatite (HA) is alike to the crystal structure and the chemical composition of the human hard tissue, which possesses a sole biological action as well as biocompatibility [7]. And, the coating of hydroxyapatite upon the metallic material (like Ti and its alloys) can improve the excellent mechanical properties of the metallic materials and highpoint the virtuous hydroxyapatite biocompatibility and the good corrosion resistance [7].

Nano Alumina (Al_2O_3) ceramic is presently an accepted bio-material, especially for applying in prosthesis for entire joint replacement. Its high wear resistance, malleability, inertness, and excellent biocompatibility make it a perfect material for applying in the fixed friction areas and in positions where a good bone anchorage is required [8,9].The biomaterials in the implants form (dental implants, heart valves, joint replacements, bone plates, and so on) as well as the medical instruments (blood tubes, artificial hearts, biosensors, and so on) are broadly utilized for replacing and/or restoring the traumatized function or the de-generated organs or tissues. The metallic biomaterials are chiefly utilized to replace the damaged hard tissue. This is due to that if they are compared to the ceramic and polymeric materials, they have higher fracture toughness, fatigue strength, and tensile strength, as structural materials. Essentially, the nontoxic elements have to be chosen for the alloying elements of alloys for the biomedical uses. The chief metallic biomaterials are titanium and titanium alloys, Co-based alloys, and stainless steels (316L),The application of electroless deposition by uses of this materials in the orthopedic and dental devices,stents [10]. Stainless steel can be utilized for fabricating sturdy implant attempts; that means the not reusable low-cost copies of the real implants that can be employed via the surgeons through the chosen substitutes of joint for determining the precise implant dimensions [11]. The corrosion as well as abrasion is the two highly important causes of the degradation into the manufacturing components. Therefore, numerous studies were carried out for developing the approaches of decreasing the costs of wear and corrosion [12]. Lately the method of electroless nano-composite coatings has got a broad currency in tribology, biomedical applications.

1.2 Literature Review

Recent researches which have attracted much attention during the last decade on the preparation of nano composite coatings. However, the effect of the bath composition and the integration influences of (Al_2O_3, MWCNTs, and HA) at various concentrations (0.1 , 0.3 , and 0.5) g/l upon the phase structure, microhardness and corrosion rate is very important,

All these studies can be summarized in this following literature review.

J. E. Gray et al. (2003) [3] studied the Ag coating of catheters by electroless process that showed influences upon the bacterial growth as well as the adhesion to the catheter surfaces. The plasma alteration was utilized for enhancing the electroless silver coating adhesion upon the polyurethane. The antiadhesive and antibacterial characteristics of such coatings have been studied. The bacterial growth was reserved in the cultures subjected to the silver-treated polyurethane in comparison with the unchanged polyurethane. The higher growth reserve being noticed for the polyurethane surfaces with the less silver coverage. The bacterial adhesion was totally reserved upon the whole silver-coated surfaces.

Yi Li et al. **(2004) [13]** investigated the surface bound Ag nano-particles preparation upon polyimide via the surface adjustment technique as well as its use on electroless metal deposition. The consistently distributed Ag nano-particles, which aid the film to be functionalized via thiol-containing molecules, are developed and firmly bound upon the polyimide surface. And, the determined silver nano-particles/PI film isn't conductive and can be utilized as a substrate for the ED of metal, where the surface bound Ag nano-particles work as a catalyst and an adhesion promoter. And, the surface bound Ag nano-particles were permitted to the interface of the broad range of organic and biological thiol-containing molecules as well as could straight work as a catalyst location for the electroless metal plating.

YI FENG et al. (2004) [14] was investigated, a technique based on electroless plating of silver onto carbon nanotubes to increase composite interfacial adhesion. To provide a continuous coating layer, a number of techniques (oxidization, sensitization, activation, and adjusting the composition of the copper electroless plating fluid) are employed to enhance dispersion, increase activated sites, and decrease deposition rate.

In comparison to the pristine surface of the uncoated carbon nanotubes, the TEM image of a coated nanotube revealed that a coating layer seems to cover the whole surface of the nanotube with no voids or gaps. Because the diameter of the coated carbon nanotube was around 70-100 nm, the coating layer was determined to be (approximately 10-20 nm) thick. The chemical composition of the coating layer was analyzed using EDS, and only silver was discovered. TEM photos indicate that the surface of carbon nanotubes has been effectively coated with a continuous coating of silver, laying the groundwork for carbon nanotube applications in composite materials.

Hongfang Maa et al. (2008) [12] investigated the nanocomposite coating of Ni–P/Ag obtained by adding silver nanoparticles to the Ni–P by electroless technique. The results showed that the hardness of the composite coating is bigger than that of Ni–P alloy coating, the crystal structure revealed the transition of amorphous to crystalline with precipitation of Ni_3P and Ni at temperature about 335°C.

Lain Zhiyang1 et al. (2009) [15] investigated the Bio-limited Forming Technology based on the nano-composite (nano-Fe) coating by electroless process. Results displayed that the technique of stirring would cause an important influence upon the content of nanoparticles in the composite coating and were compared with the mechanical stirring. The magnetic stirring causes the nano-iron content in the composite coating increasing nearly double (Via blending the microorganisms as well as the nanoparticles prior to plating, the nanoparticles content in composite coating was augmented). For the meantime, the stirring technique influence upon the composite coating composition was investigated.

Weiwei Chen et al. (2010) [16] studied Ni–P–TiO_2 nano-composite coatings by electroless process. Such technique combines the electroless plating and the Sol-gel methods for preparing most dispersive oxide nanoparticle strengthened composite coatings. The transparent TiO_2 has been supplemented to the solution of standard electroless plated Nickel-Phosphor (Ni-P) at a rate organized for producing the Ni-P-TiO_2 nanocomposite coatings upon the alloys of magnesium. The coating was obtained for possessing a crystalline structure. The nano sized particles (about 15 nm) of TiO_2 properly distributed into the Ni–P coating matrix through the co-deposition procedure. Such method can efficiently prevent the agglomeration of nanoparticles into the coating matrix. Consequently, the microhardness of composite coatings was considerably augmented to about 1025 (HV200) in comparison with about 710 (HV200) of traditional composite coatings made with the solid-particle blending approaches. Respectively, the wear resistance of fresh composite coatings was highly enhanced as well.

Burcu Celena et al. (2011) [17] investigated a simple but multipurpose technique for developing supported-metal catalysts founded upon a polydopamine (PDOP) coating as well as the silver nanoparticles (Ag-NPs) electroless plating on nano-materials (for example, the Anodic Al Oxide (AAO) membranes and the Polystyrene (PS) nanotubes for the catalytic decrease were revealed). Results indicated that both AgNPs/PDOP/AAO/(200 nm) and AgNPs/PDOP/PS exhibited significantly higher catalytic activities than individual. Throw knowing their flexibility, simplicity, and efficiency, one believes that such green catalysts kinds might obtain a broad range of uses in the organic fabrication in addition to the catalysis.

Majid Montazer et al. (2012) [18] investigated a novel technique of manufacturing conductive polyester fabric via utilizing a new silver nanoparticles' electroless plating upon the fabric. Then, the fabric has first been processed with sodium hydroxide as well as silver nitrate at a temperature of 130°C for a time of one hour and after that with ammonia at the boiling for a time of one hour. Such processing improved the surface activity of fabric, generated the roughness of surface, enhanced the absorption of nanoparticle, and made ethylene as reducing agent. So, this resulted in that the creation of silver (Ag) nanoparticles upon the fabric surface of polyester resulted in a greater fabric weight with a lesser electrical resistance. Raising the ammonia quantity from (80 mL) to (150 mL) caused a lesser electrical resistivity of (1.3 Ω/square).

Nayan et al. (2012) [19] studied the silver reinforced with carbon nanotubes by electroless process, instead of graphite, to increase the electrical conductivity, hardness and wear resistance. In addition, the active use of CNTs in Ag/CNT composite depended strongly upon its homogenous spreading and a vigorous interfacial adhesion to the matrix of Ag and therefore needs for its adaptation of surface. For carrying out the CNTs surface adaptation also provided to them beyond the oxidation of liquid phase, the sensitization, and the procedure of activation. The chemical treatment at the room-temperature led to a nominally whole coating above the whole external surface of the multiwall CNT.

Sui Zhang et al. (2013) [20] investigated the Ag-PEGylated dendrimer nanocomposite coating for the anti-fouling thin film composite membranes to water treating. Such investigation suggested a facile technique for fabricating. The membranes of thin film composite (TFC) with the Ag-polyethylene glycol (PEGylated) dendrimer nanocomposite coatings upon the surface for reducing the protein fouling and bacteria in the maintainable methods of water processing. Interestingly, the TFC membranes surfaces were imparted with various functionalities, like PEG, amine, carboxylic acid, or the nanoparticles of Ag, which give good comparing of the anti-fouling characteristics of the functional sets four types. Important enhancements upon the hydrophilicity were obtained beyond the adaptations. The whole adjusted membranes depicted the decreased attachment of E. coli as well as bovine Serum Albumin (BSA). Among them, the Ag-PEGylated dendrimer nano-composite membrane was exposed to t-he minimum fouling via a (99.8%) ultimate fouling decrease. The PEG adhesion forces as well as the Ag nanoparticles adapted membranes being small, which will clarify the membranes' lower protein fouling.

Chengjiao Wu et al. (**2015) [21]** studied the Bio-inspired fabrication of the poly-dopamine/silver nano-composite particles with the anti-bacterial activities. The authors described a facile, mild and green method for fabricating the nano-composite particles of PDA/Ag via joining the mussel-inspired PDA chemistry as well as the silver electroless metallization**.** In such poly-dopamine-assisted electroless silver metallization process, no additional reductants, poisonous reagents and complicated devices being required. The X-ray diffraction outcomes that combine with the SEM and TEM remark proved the development of the single-crystal domain of the silver nano-particles, and obtained the nanoparticles size of silver also. Such composite particles of PDA/Ag revealed a fine cyto-compatibility against the human embryonic kidney cells(HEK293), while the initial antibacterial assays showed that the nanocomposite particles of PDA/Ag illustrated the extraordinary anti-bacterial actions against the Escherichia coli (Gram-negative bacteria) as well as the Staphylococcus aureus (Gram-positive bacteria). Concerning such benefits, these nanocomposite particles of PDA/Ag made in such ecologically friendly method are a perfect anti-bacterial material for different bio-medical uses.

Zaheruddin et al. (2016) [22] investigated the Cobalt-hydroxyapatite (Co-HA) composites that were positively produced via the simple procedure of the cobalt electroless deposition upon the hydroxyapatite (HA) particles surface. The deposition of cobalt was conducted in an alkaline bath with sodium hypophosphite as reducing agent. The procedure of electroless was conducted without the steps of sensitization as well as the activation. Results showed that the particles of cobalt were uniformly distributed in the matrix of HA beyond the sintering, and the composites' mechanical properties improved to (100wt %) with (3 g/l) cobalt and slowly reduced at the higher content of cobalt.

Bidhan Pandit et al. **(2017) [23]** studied the mostly conductive energy effective silver (Ag) nanoparticles upon the Multi-walled Carbon Nanotubes (MWCNTs) by electroless process as a super capacitive electrode. The simple, economical, and the room temperature procedure of the electroless reduction was developed for anchoring the nanoparticles of Ag above the MWCNTs. The nanoparticles of Ag were anchored homogenously above the whole MWCNTs surface for forming a hybrid electrode that revealed a superior specific capacitance (757 F/g), a rapid rate of charge and discharge with excellent cyclic performance owing to the conductive matrix as well as the mechanism of the double charge storage mechanism. A (60.7 Wh/kg) high specific energy with a (3.3 kW/kg) steady specific power can exposed a new possibility toward the applied method. Such electrode can provide a great potential in the upcoming as the energy storage electrode originates from the simple, cheap, and facile fabrication process for exhibiting the superior capacitive conduct as a function of the high energy as well as the power densities.

Fauzia Wahid et al. (2018) [24] studied the electroless deposition of silver nano particles (Ag-NPs) on multi walled carbon nano tubes (MWCNTS) treated with Thionyl Chloride and Hydrazine Monohydrate was investigated. The MWCNTs were oxidized with HNO_3 and H_2SO_4, according to the results. FTIR measurement indicated that the surfaces of MWCNTs were efficiently oxidized for feuture Ag-NP adhesion. MWCNTs had CNTs in single and cluster form, and the deposition of Ag-NPs on MWCNTs was compact, uniform, and homogeneous, with fewer extremely thin coated regions. MWCNTs had a lattice spacing of 0.3462 nm according to the XRD pattern,The deposition of 25nm sized Ag-NPs, the lattice spacing grew to 2.359 nm. The decreasing intensity of the distinctive peaks of Ag-NPs deposited MWCNTs is indicative of the formation of a compact and adherent layer of Ag-NPs on the surface of MWCNTs.

Matin Sadat Saneei Mousavi et al (2018) [25] studied sputtering and electroless plating processes were used to create an ionic polymer metal composite(IPMC) for bio-actuation applications. IPMC was enclosed by a polydimethylsiloxane (PDMS) thin layer to be used in biomedical devices, which not only makes it biocompatible but also reduces water loss from the IPMC channels, leading in prolonged IPMC actuation. The outcomes demonstrate However, as compared to the particle size(PS) of samples, the enhanced CEP approach produced effective electrodes appropriate for actuating applications with a 1.48 times greater actuation rate. Despite this, the output force of the PS of IPMCs was 1.33 times more than that of the (CEP) of (IPMC) due to their stiffness. To summarize, physically created IPMC was not as impressive as chemically prepared IPMC, not only due to the low adherence of the metal electrode to the nafion polymer, but also due to its high cost and reliance on machinery. In other words, the CEP approach provided high-quality IPMC while also being a low-cost, simple, and machine-free method.

Liyun Wang et all. **(2019) [26]** investigated the antibacterial and anti-encrustation performances of silver polytetrafluoroethylene nanocomposite coated urinary catheter in vitro by electroless technique. An effective silver-polytetrafluoroethylene (Ag-PTFE) nanocomposite coating was deposited onto the entire silicone (Si) catheters, and two in-vitro bladder models were intended for respectively testing the performances of the antibacterial (against Escherichia coli) as well as the anti-encrustation (against Proteus mirabilis). Every model was confronted with two various bacterial suspension concentrations. In comparison with the uncoated catheters, the coated catheters could considerably inhibit the bacterial immigration as well as the biofilm development along the exterior surfaces of catheter. Whereas, the coated catheter significantly resisted the encrustation and bacterial adhesion, respectively.

Eman M. Fayyad et al. (2019) [27] studied the novel electroless deposited corrosion resistant and anti-bacterial NiP-TiNi nanocomposite coatings are effectively created utilizing various concentrations of TiNi nanoparticles (0.2, 0.4, and 0.8 g/l in the bath). The effect of TiNi nanoparticles on the composition, deposition rate, thickness, and shape of the NiP coating is studied before and after 400C° annealing. The incorporation of TiNi nanoparticles into the NiP matrix causes the amorphous structure of the as-plated NiP to be transformed into a semi-crystalline structure. The microhardness of the composite coating improves dramatically when the TiNi content is increased to 0.4 g / l, and it improves even more following heat treatment. The results show that there is an optimal concentration for the addition of TiNi (0.4 g/l) that provides the composite coating with the best corrosion protection (about 98%). The corrosion protection of composite coatings improves somewhat below and above this concentration, as well as following heat treatment. Furthermore, the NiP-TiNi NCCs show excellent antibacterial activities, with Escherichia coli cell viability decreasing from 100% to 19%.

Hiba M. Algailani et al. (2020) [28] studied the Ni-MWCNTs nano composite coating via the technique of electroless deposition on the stainless steel (316L), where such method of coating is a substituting method for obtaining the coatings upon the different substrates. Nevertheless, the influence of the composition of bath upon the resistancto corrosion, phase structure, and microhardness was studied. The MWCNTs integration influences at various concentrations (1.25, 2.25, and 4.25) g/l upon the microstructure, the phase structure, and the electroless Ni–MWCNTs nanocomposite coatings morphology was compared. The nanocomposite coating of Ni-MWCNTs displayed remarkably more augmented hardness as well as enhanced resistance to corrosion.

Hiba M. Algailaniet al. (2020) [29] investigated the Ni-ZrO_2 nano-composite coating preparation via the technique of electroless deposition above a substrate of stainless steel (316L). The incorporation effects of ZrO_2 nano-particles at different percentages in the Nickel-based electroless deposition coating of nano-composite bath were compared. Results showed that the deposited nano-composite (Ni-ZrO_2) coating was completely distributed into the Nickel-based coating to become dense, as well as extremely adhesive surface and unceasing with a better uniform mix of the ZrO_2 nano particles coating without creating any agglomerations. The analysis of XRD depicted that the (Ni-ZrO_2) nano-composite coating being a crystalline structure. And, microhardness rises by raising the concentration of the 2nd phase strengthening the ZrO_2 nano-particles .

R. Radha et al. (2020) [30] investigated the electroless method that used to tin coated hydroxyapatite reinforced Mg-Sn alloy composite for improved bio corrosion resistance and bioactivity. Tin was coated on hydroxyapatite particles using an electroless coating technique. According to the findings, electroless coating is a promising technology for effectively coating Sn on HA particles, which aids in grain refinement and phase distribution uniformity. It also inhibits HA dissociation, which leads to the development of undesirable phases such as Ca-Sn, which can be harmful to corrosion characteristics owing to galvanic coupling. In compared to reinforcement of uncoated HA particles, the addition of Sn coated HA decreased biodegradation.

Silvia González et al. (2021) [31] investigated antimicrobial coating effectiveness on appropriately functionalized and nanostructured 316L food-grade stainless steel pipes. They used simple and low-cost electroless methods and surface modification technologies to create these functional coatings. Additional antibacterial and bactericide coatings, such as Ag nanoparticles, Ag films, or TiO_2 thin layers, can be applied to this nanostructure. The findings of this work showed that nano structuring and surface functionalization procedures are a viable path to creating innovative functional materials with extremely effective antibacterial properties. Indeed, They demonstrated that our utilization of an applicable combination of TiO_2 layer and Ag nanoparticle coatings atop nanostructured 316L stainless steel displayed outstanding antibacterial

Abstract

Silver-bio nanocomposite coating on stainless steel (316L) sheets was prepared by electroless deposition technique. The bath composition influences on the characteristics of Ag based Multi wall carbon nanotube(MWCNTs), Hydroxyapatite (HA) and Alumina (Al_2O_3) bio nanocomposite coating produced by electroless deposition technique,The variable of this process are (Temperature ,Speed ,pH ,Concentrations) therefore, the present work aims to comparing the influences of the Multi-wall carbon nanotube (MWCNTs) ,Hydroxyapatite(HA), and Alumina (Al_2O_3) nanoparticles incorporation at various concentrations (0.1, 0.3 and 0.5)g/l on the mechanical property (microhardness) , chemical properties (corrosion resistance and ion release) , surface morphology and crystal structure of Ag- nanocomposite coatings as well as biological property(anti-bacterial property) for the coated substrate ,The application of this work in orthopedic and dental devices,stent .

From the EDS results, it's obvious that the nanocomposite coatings comprise a silver matrix with (MWCNTs, HA and Al_2O_3) strengthening nanoparticles.

The scanning electron microscope (SEM) analysis results showed that the coatings are uniform and covers the stainless steel (316L) substrate, and showed that the uniform distribution of nano particles in the Ag matrix coating.

While X-ray diffraction(XRD) results, showed that the nanocomposite coatings Ag- (, Hexagonal-MWCNT, HA and Alpha-Al_2O_3) being nano-crystalline structures.

The microhardness tests outcomes manifested an important enhancement in the property of the hardness of (Ag- MWCNTs), (Ag-HA) , (Ag- Al_2O_3)

with increasing the concentration of nano particles, Which it is compared with stainless steel 316L without coating (104.6 Hv). Where, the (Ag-0.5 MWCNTs) nanocomposite coating overhead registered the uppermost values (204.9 Hv) in comparison with HA and Al_2O_3 nanocomposite coating.

The corrosion rate (by Tafel extrapolation method) of the coated specimen by (Ag–0.5MWCNT) nano-composite coating possess lower rate of corrosion (1.083×10^{-1} mpy), It is less than the rate of the corrosion of uncoated Stainless steel(316 L) (6.313×10^{-1} mpy).

The ions release for the coated substrate (Ag-0.5 MWCNTs, Ag-0.5 HA, Ag-0.5 Al_2O_3) nanocomposite coatings of two elements (Ni ,Cr) in the tests of immersion sample in Ringer solution .The release of Ni was obtained about (0.17-0.26) % within the allowable limit in accordance with the amount of Ni permitted to be inside the human body. The ions for chromium weren't released owing to a passive film shaped upon the surface of the samples.

The anti-bacterial evaluated for the coated substrate via electroless 0.5 (Ag-MWCNTs ,Ag-HA andAg-Al_2O_3) bio nano composite coatings that immersed in E. coli (gram-negative) bacteria results are show the clear zone formation around the disc denotes bacterial inhibition. Where was the best rate of killing bacteria in Ag-0.5 MWCNTs, which about (13mm). The difference in the killing area for bacteria was small and close, and the killing rate for bacteria was good. This indicates the good effectiveness of silver towards killing bacteria.