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Characterization of Corrosion Resistance of Silver-Hydroxyapetite (Ag-HA) Bio-Nanocomposite Coating

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ABSTRACT

Silver-. Hydroxyapatite (Ag-HA) nanocomposite coating on stainless steel (316L) sheets was prepared by electroless deposition technique. A few researches were studied the bath composition influence upon the corrosion behavior of Ag-HA bionanocomposite coating produced by electroless deposition technique, therefore, the current investigation will compare the influences of the Hydroxyapatite nanoparticles incorporation at various concentrations (0.1, 0.3 and 0.5) g/l on the mechanical property (microhardness) and chemical properties (corrosion resistance and ion release) of Ag-HA nanocomposite coating. Ag-HA nanocomposite coating exhibits much-increased on the microhardness from 104.7 Hv to 139.9 Hv at (0.5g/l) concentration of HA nanoparticles and remarkably improved corrosion resistance, where the corrosion rate was improved for the coating from (5.954×10-1, to 2.633×10-2) mpy in the presence of nano-HA contents respectively. Also, from ion release analysis of the element coating was found the nickel content within the permissible limit in accordance with the amount of Ni permitted to be existed inside the human body and the chromium element was not found.

1. Introduction

Electroless deposition is the most important technique to manufacture nano composites of metallic as well as non-metallic constituents [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 a gent's existence, the disproportionation reaction and the galvanic displacement reaction [2]. Q. Zhao and et al. studied the Silver-Polytetrafluoroethylene (PTFE) composite coatings by electroless technique, for enhancing the coating mechanical properties. And, 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 were coated with silver because it was considered anti bacteria adhesion (The components of Ag bath and work conditions, they are from previous studies from this Reference [3]. L. Zhao and et al. studied the antioxidant, corrosion resistance of Ag-HA nanocomposite coating by electroless deposition technique [4]. Shuai Zhang investigated the silver nanoparticle/polytetrafluorethylene (Ag

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NP/PTFE) coating with improved antibacterial as well as anti-corrosive properties. The silver (Ag)-based coatings have roused concentrated attention as silver possesses a wide-spectrum antibacterial action and a less risk of evolving bacterial resistance [5]. A. M. Sadoun studied influence of nano Al_2O_3 coated Ag supplement upon the resistance to corrosion, and silver was considered the best choice to resist the corrosion and bacterial adhesion [6]. L. Zhao have investigated the effect of Silver-hydroxyapatite nanocomposite coating upon the biofilm development of joint prosthesis as well as its mechanism. Silver-hydroxyapatite nano composite coating can clearly prevent the biofilm development. The bacterial adhesion was decreased [7]. The damage of DNA and 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 [8]. 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 [9]. Hydroxyapatite (HA) is alike to the chemical composition as well as a crystal structure of the human hard tissue, which possesses an irreplaceable biological action and biocompatibility [7]. The HA coating upon the metallic material (like Ti or Ti alloy) can improve the brilliant mechanical properties of metallic materials and highpoint the virtuous HA biocompatibility and good corrosion resistance [7]. 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) is 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. And, 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 [10]. 316L 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 abrasion and corrosion are the two most important degradation causes in the manufacturing components. Therefore, the wide investigations were carried out for developing the decreasing approaches of wear and corrosion costs. The corrosion rate (CR) in a certain atmosphere is straight proportional to its corrosion current density (I_{corr}) according to the relationship:

$$CR=0.13\times I_{corr} \times (e / \rho) \quad (1)$$

This equation relates to calculate the CR in mil per year (mpy), where (ρ) and (e) are the density and weight of coating elements, respectively (The ρ of Ag is 10.49 g/ cm^3, the e of Silver is 107.868 grams) [12]. The common law was issued by Bockris and Reddy in electrochemistry, where the logarithm of current varies directly with the electrode voltage; however, many developments were made on the electrode process, which includes a slow reaction step on the electrode surface, which is known as polarization activation [13]. Its lately the method of electroless nano-composite coatings have acquired a broad currency in corrosion, tribology and biomedical aerospace uses, because the corrosion and low hardness of the biomaterials that used in human body cause health problem and own a little age and thus is a healthy body problem. The metal ions release can result local as well as systemic health difficulties owing to the diffusion of ions throughout the entire body [14]. This work is devoted for the preparation of (Ag-HA) nano-composite using coating on substrate from stainless steel (316L) sheets by an electroless deposition technique. The objective of present work is to study the effect of the incorporation of Hydroxyapatite nanoparticles at different concentrations (0.1, 0.3 and 0.5 g/l) on the

microhardness, corrosion resistance and ion release characteristics. Silver coating was used on the surface of 316L to protect it from bacteria adhesion, because silver is antibacterial as well as to prevent the release of nickel ions from the metal over time.

2. Methodology

Stainless steel AISI 316L, Fe/Cr18%/Ni 10%/Mo 3% specimens with dimensions of (20 mm x 20 mm x 2 mm) were used as a substrate material for Ag-HA nanocomposite coatings in this study. Table (1) shows the experimentally chemical analysis of the substrate of SS (316L) which was carried out in the State Company for Examination and Engineering Rehabilitation, Baghdad-Iraq. Molding, separating, and confronting techniques were all used in the preparation of the sample. The sample was then given to a surface crushing contact with (400-600) grade emery paper from that point forward. Unfamiliar materials and consumables were meticulously removed. Sheets have been initially cleaned by alkaline solution at (60-80°C) for a time of (10-20 min) and finally washed by water. And, the alkaline solution composition comprised Na_2SiO_3: 8 g/l, Na_3PO_4: 30 g/l, Na_2CO_3: 25 g/l;, and NaOH: 25 g/l. Then, they have been immersed into a dilute HCl solution (1M) for a (30 sec) time and finally rinsed by cold water as well as de-ionized water, correspondingly. The stimulated surface substrate is dipped into a chemical bath at 25ºC for two hrs for completing the procedure of the deposition of silver. Beyond many experiments, the working circumstances as well as the bath chemical composition of the electroless Ag-nanocomposite coating strengthened via HA nanoparticles were chosen. The working circumstances and the bath chemical composition for the electroless Ag-HA nanocomposite coatings utilized are listed in the Table (2). For reducing the silver coating oxidation, a 0.2 g/l from $C_4H_6O_6$ was added to the bath (Solution B was used as reducing agent to reduce the oxidation of silver, and solution A is considered the basic materials without which the coating process will not take place, especially ($AgNO_3$). After that, a round nanoparticle was found into the similar Ag bath with the sub-sequences for achieving the Ag-HA nanoparticle code position. Beyond completing the procedure of electroless coating, the all samples were washed with the distilled water for cleaning purpose. Solutions (300 ml) strengthened by HA nanoparticle were taken and blended utilizing a magnetic stirrer for getting the best consistent and totally uniform suspension HA nanoparticle powder in the bath. And, at the initial stage, a silver layer was deposited at the initial period for preventing the uniform porosity in the layer of coating, and after that, the silver bath strengthened by the HA A and B in the Table 1 represents a solution of silver ion and a solution of reducing agent, respectively. These solutions were arranged discretely. Such solutions have been blended just prior to plating. After the time of silver coating ends, the nano hydroxyapatite (0.1, 0.3, and 0.5 g/l) was added to a silver bath for 30-60 min, where each sample that is to be coated was added to its solution with a certain proportion of nanoparticle different from the other and separate solutions. The microhardness was measured by Vickers hardness, the parameters of corrosion for of Ag-HA nanocomposite coating was computed via the technique of Tafel extrapolation in Ringer's solution and at a temperature of 37°C. Ion release analysis of the element coating was done after submerging the sample for (3-7) days in Ringer's solution. Since, SS was used and among the components of this alloy is nickel and chromium, and because these elements contain toxicity, it is wanted to know if the material as a result of corrosion released these ions. Therefore, this examination was carried out. The device contains a stander, where the solution is brought and turned into a filament where the heat is applied to it, so that it vaporizes, and the ratio is measured here. If it is within the permissible limit, it is non-toxic, and if it is more than the stander, it is considered toxic.

Table 1: Experimentally chemical analysis of the substrate of SS (316L)

Element	Carbon	Manganese	Silicon	Chromium	Nickel	Molybdenum	Phosphorus	Sulfur	Iron
316 L	0.027	1.01	0.484	17.00	10.18	2.30	0.035	<0.002	Bal.

Figure 1. Coating bath

Table 2. Electroless bath composition and operating conditions

Compositions	Solution (A)	Solution (B)
$AgNO_3$	3.0 g/l	
$Na_2S_2O_3$	2.1 g/l	
NH_4OH	60 ml	
$C_6H_{12}O_6$		2.25 g/l
$C_4H_6O_6$		0.2g/l
C_2H_5OH		5 ml
H2O	450 ml	450 ml
pH	12	
Temperature	20-250C	
Coating time	30-60 min	
Particle size of HA nanomaterial	20 nm	

3. Results and discussion

3.1. Microhardness of nanocomposite coating

The Vickers microhardness test was applied for a stainless-steel plate coated with Ag-HA nanoparticles. Samples without coating have the lowest value (104.7 Hv) of microhardness in comparison to the else samples' values of the coatings that increased via coating at a (0.5 g/l) concentration HA nanoparticle. The electroless Vickers microhardness of Ag- (0.5 g/l) HA nano-composite attained H_V=139.9 and increased in comparison to that of Ag-(0.1, 0.3) HA that reached Hv=109.2 and 117.6 respectively. This means that the HA nanoparticles' higher content may influence the Ag crystal structures resulting in a promising performance of the nano-composite coatings.

3.2. Corrosion results

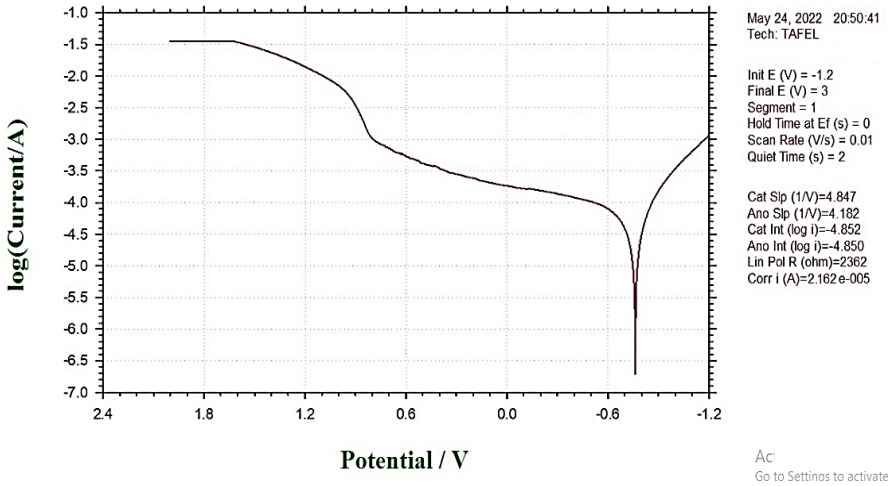
The reinforced nanoparticles serve as physical barriers to the procedure of corrosion attack of filling in micron holes or crevices as well as guard the surface owing to the best entrenched occurrence, especially for the HA nanoparticles reinforcement Ag-based nanocomposite coating considerably leading to raise the value of corrosion resistance. And, the virtuous characteristics of the biological barrier of the coating regimes can be enhanced with nano-sized fillers having greater barrier characteristics. The nanoparticles of HA were conducted an important advantage to reinforcement in the metallic coatings [8].

Figure 2 and Table 3 depict the factors of corrosion for the Ag-HA nano-composite

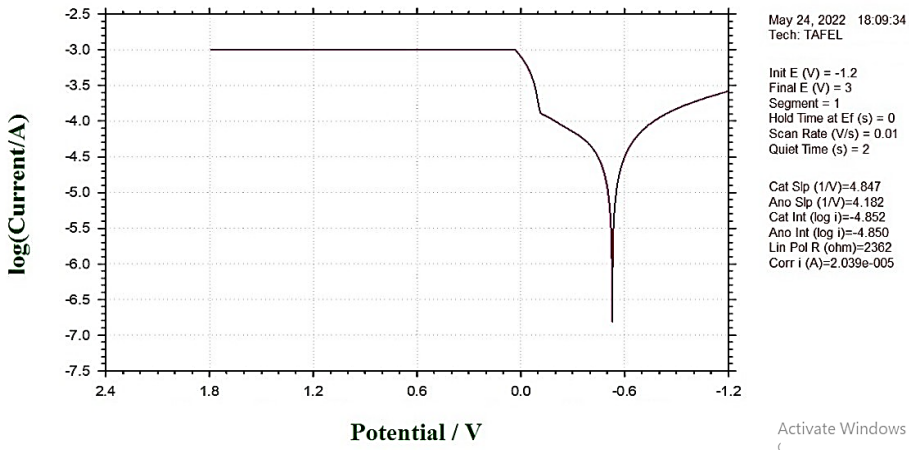
coating computed via Tafel extrapolation technique in Ringer's solution and temperature 37°C and the corrosion test instrument used as shown in the Figure 3. Such factors comprise the Tafel slopes (bc and ba), the current density of corrosion (I_{corr}), potential (E_{corr}), and the rate of corrosion. And, the rate of the corrosion of the coated sample electroless Ag-HA nano-composite coatings upon the various quantities of the nanoparticles of HA, the surface area exposed to corrosion is 1 cm and does not need to covered with polymeric material during the corrosion examination. The corrosion rate was decreased for the coatings from 5.954×10^{-1}, to 2.633×10^{-2} mpy in the presence of nano-HA contents. At the 0.5%, the HA nanoparticle improves the coating performance manifested the best corrosion safeguard.

3.3. Ion release results

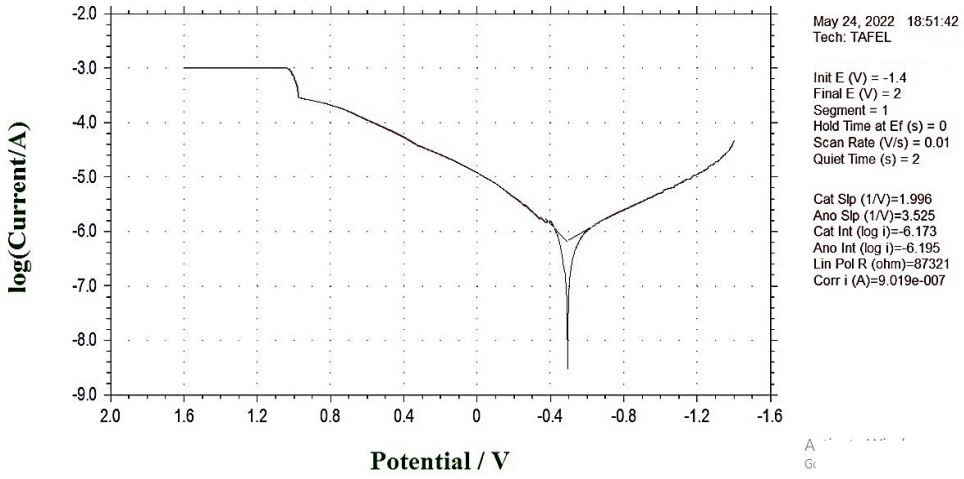
The (Ni, Cr) ions quantities that were released from the (0.5 HA) of implant sample in the Ringer's solution were measured. And, for the biomedical uses the substrate that coated via electroless Ag coating, the analysis of ion (nickel, chrom) released in the immersion test was for three and seven days in the Ringer's solution. The result of ions release of 0.5 Ag-HA nano composite coating was found around 0.26%Ni within the permissible limit according to the quantity of nickel allowed to exist within the human body. The Cr was not released due to a passive film formed on the surface and on not damaged by friction and micro-movements in this medium through the immersion time.



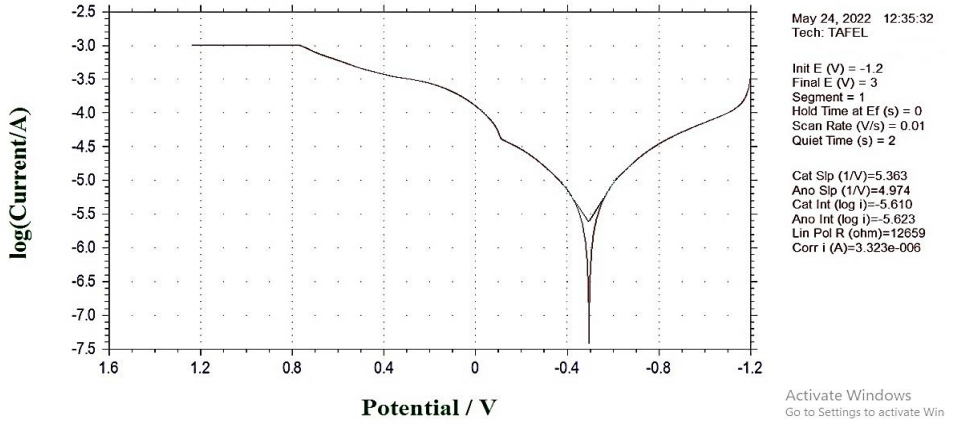
a. 316 L substrate without coating



b. Ag-0.1 wt % HA



c. Ag-0.3 wt % HA



d. Ag-0.5 wt % HA

Figure 2. Tafel plot for the Ag-based HA nanocomposite coating sample in (500 ml) Ringer' ıperature (37°C) of body human at various concentrations of HA

Table 3: Influence of the changing the concentration of the nanoparticles of Ag-HA upon the conduct of corrosion compared to the corrosion of 316 L without coating

ITEM	$E_{corr.}$ (volt)	$I_{corr.}$ (Amp)	Corr rate (mmpy)	βc	βa	OCP (volt)	E_{pit}	E_b
Base	-0.759	2.162×10^{-5}	6.313×10^{-1}	0.206	0.239	-0.520	0.781	1.648
0.1% HA	-0.523	2.039×10^{-5}	5.954×10^{-1}	0.206	0.239	-0.476	-0.106	0.050
0.3% HA	-0.500	3.323×10^{-6}	9.703×10^{-2}	0.186	0.201	-0.441	-0.084	0.771
0.5% HA	-0.500	9.019×10^{-7}	2.633×10^{-2}	0.501	0.283	-0.270	-0.974	1.041

Figure 3. The corrosion test instrument (CHI 604e)

4. Conclusions

The present work studies the effect of various concentrations (0.1, 0.3 and 0.5 g/l) of nano-hydroxyapatite particles on the mechanical property (microhardness) and chemical properties (corrosion resistance and ion release) of Ag-HA nanocomposite coating, therefore may be drawn the following conclusions:

1. The Corrosion rate was enhanced for the coatings from 5.954×10-1 mpy, to 2.633×10-2 mpy in the presence of nano-HA contents, that is mean the corrosion rate decreases when increase the concentration of nano hydroxyapatite particles.
2. The microhardness increases with increasing nano-HA concentration.
3. The resulted of ions release for substrate coated by electroless (Ag-HA) nanocomposite coating when analysis of the element coating in Ringer' s solution within the permissible limit in accordance with the amount of Ni permitted to be existed inside the human body and the chromium element was not found.

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