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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. Several studies have analysed the influence of bath composition on the corrosion behaviour of Ag-HA bio-nanocomposite coating produced by electroless deposition. Therefore, the present study compared the influence of varying concentrations of HA nanoparticles (0.1, 0.3, and 0.5) g/L on the mechanical (microhardness) and chemical (corrosion resistance and ion release) properties of the Ag-HA nanocomposite coating. The Ag-HA nanocomposite coating exhibited a remarkable increase in microhardness from 104.7 Hv to 139.9 Hv at 0.5 g/L HA nanoparticles and improved corrosion resistance, where the corrosion rate was enhanced for the coating from 5.954×10-1 mpy to 2.633×10-2 mpy in the presence of nano-HA. The ion release analysis of the element coating revealed that the nickel content was within the permissible limit in accordance with the amount of Ni permitted to exist inside the human body, and chromium was not found.

1. Introduction

Electroless deposition is an important method for producing nanocomposites of metallic and nonmetallic constituents [1]. It's an interesting idea to use electroless deposition to make functional materials without using any outside energy. Electroless deposition can be divided into three types: deposition in the presence of a reducing agent, disproportionation reaction, and displacement reaction galvanic [2],[3]. Q. Zhao et al. investigated silver-polytetrafluoroethylene composite coating by electroless technique to enhance the coatings' mechanical properties. Microbial adhesion and biofilm formation are known challenges in the design and operation of treatment apparatuses, such as food processing apparatuses and heat exchangers, hence, silver is typically used to coat samples antibacterial adhesion (the components of Ag bath and work conditions were based on a previous study [4]). L. Zhao et al. investigated the antioxidant activity and corrosion resistance of Ag-hydroxyapatite (HA) nanocomposite coating by electroless deposition [5]. Shuai Zhang investigated Ag nanoparticle/polytetrafluorethylene (Ag NP/PTFE) coating with improved anti-bacterial and anticorrosive properties. The Ag-based coatings have aroused extensive attention because silver possesses a wide spectrum of antibacterial action and a low risk of bacterial resistance evolving [6]. A. M. Sadoun studied the influence of nano Al_2O_3-coated Ag

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supplement upon resistance to corrosion, and Ag was considered the best choice to resist corrosion and bacterial adhesion [7]. L. Zhao investigated the effect of Ag-HA nanocomposite coating upon the biofilm development of joint prosthesis and determined the underlying mechanism; they found that the Ag-HA nanocomposite coating can clearly prevent biofilm development, and bacterial adhesion decreased [8]. Damage to DNA and RNA, in addition to the inactivation of proteins by Ag particles, appears to be the primary mechanism of bacteriostasis. Gram-negative and Gram-positive bacteria have distinct intracellular defence mechanisms against silver. [9]. Nano-HA $Ca_5(OH)(PO_4)_3$ is a well-known bio-material for bone substitution that is distributed into Ag coating. It is a bioactive implantation material capable of making a straight and fixed bond with bone tissue [10]. The chemical composition and crystal structure of HA are similar to those of human hard tissue, which possesses irreplaceable biological action and biocompatibility [8]. HA coating on metallic material (like Ti or Ti alloy) can improve the brilliant mechanical properties of metallic materials and enhance HA biocompatibility and good corrosion resistance [8]. Biomaterials used in implants (e.g., heart valves, dental implants, bone plates, and joint replacements) and medical instruments (e.g., artificial hearts, blood tubes, and biosensors) are commonly used to replace and/or restore the function of injured or degenerating organs or tissues. Metallic biomaterials are primarily used to replace damaged connective tissue. In comparison to polymeric materials and ceramics, their fatigue strength, fracture toughness, and tensile strength are superior to those of structural materials. Notably, nontoxic elements must be selected for biomedical alloys. Titanium and its alloys, Co-based alloys, and stainless steel are the principal metallic biomaterials (SS) [3],[11]. 316L SS can be utilised to fabricate sturdy implant attempts; Thus, surgeons can use the non-reusable, low-cost copies of actual implants to determine the precise implant dimensions in the selected replacement joints [12]. Abrasion and corrosion are the two most important degradation causes in manufacturing components. Extensive investigations have been carried out to decrease wear and corrosion costs. The rate of corrosion (in mil/year) in a specified atmosphere is directly related to its corrosion current density (I_{corr}), as shown in the following equation:

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

where (ρ) and (e) are the coating element's density and weight, respectively (ρ of Ag is 10.49 g/cm^3, and e of silver is 107.868 g) [13]. 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 known as polarisation activation [14]. Electroless nanocomposite coatings have recently gained popularity in corrosion, tribology, and biomedical aerospace applications because the corrosion and low hardness of the biomaterials used in the human body cause health hazards. Due to the diffusion of ions throughout the entire body, the release of metal ions can result in local and systemic health difficulties [3],[15]. This work is devoted to the preparation of Ag-HA nanocomposites by electroless deposition coating on SS (316L) sheets. The objective of this study was to examine the effect of incorporation of HA nanoparticles at different compositions (0.1, 0.3, and 0.5) g/L on microhardness, corrosion resistance, and ion release characteristics. Silver coating was used on the surface of 316L to protect it from bacterial adhesion, because silver is antibacterial and can prevent the release of nickel ions from metal over time.

2. Methodology

SS AISI 316L, Fe/Cr 18%/Ni 10%/Mo 3% specimens with dimensions of 20 mm × 20 mm × 2 mm were used as a substrate for Ag-HA nanocomposite coatings in this work. Table (1) shows the findings of the chemical analysis of the substrate of SS (316L), which was carried out in the State Company for Examination and Engineering Rehabilitation, Baghdad, Iraq. In order to prepare the sample, processes like moulding, separating, and confronting were utilized. From that point forward, the sample was subjected to surface crushing with 400–600 grit fine sandpaper. Unfamiliar material and consumable were eliminated with care. The sheets were first cleaned with an alkaline solution at 60 °C–80 °C for 10 –20 minutes before being washed with water. The alkaline solution comprised 8 g/l Na_2SiO_3, 30 g/l Na_3PO_4, 25 g/l NaOH and 25 g/l Na_2CO_3. The sheets were then submerged in a diluted HCl solution (1M) for 30 seconds before being washed with deionized (DI) water. To finish depositing silver on the surface, two hours were spent immersing the substrate in a chemical bath at 25 °C. The electroless Ag-nanocomposite coating's operating circumstances and bath chemical composition improved with HA nanoparticles. Table (2) shows electroless Ag-HA nanocomposite coating working conditions and bath chemical composition. To reduce oxidation of the Ag coating, we added 0.2 g/L $C_4H_6O_6$ to the bath (solution B was used as reducing agent to reduce the oxidation of Ag, and solution A is considered the basic material without which the coating process will not take place, especially ($AgNO_3$)). A round nanoparticle was discovered in a similar Ag bath with the subsequences to achieve the Ag-HA nanoparticle code position. After electroless coating, samples were cleaned with distilled water. HA nanoparticle-enhanced solutions (300 mL) were mixed with a magnetic stirrer to obtain the most uniform HA suspension powder in the bath. To avoid uniform porosity in the coating layer, an initial silver layer was placed. Consequently, the silver bath strengthened by HA A and B in Table 1 represents, respectively, a solution of silver ion and a solution of reducing agent. These options were organized in a discrete manner. These solutions were combined before plating. When Ag coating was finished, nano-HA (0.1, 0.3, and 0.5) g/l was added to a silver solution for 30 - 60 minutes, with each coating sample added to its own solution having a different nanoparticle concentration. The microhardness was measured by Vickers hardness. The parameters of corrosion for the Ag-HA nanocomposite coating were computed via Tafel extrapolation in Ringer’s solution at 37 °C. Ion release analysis of the element coating was conducted after submerging the samplse for 3–7 days in Ringer’s solution. Given that SS was used, and this alloy contains nickel and chromium, which are toxic, we aimed to determine if the material as a result of corrosion released these ions. Therefore, this examination was carried out. The device contained a stander, where the solution was brought and turned into a filament where heat was applied to it, so that it vapourised, and the ratio was measured. If it was within the permissible limit, then it was non-toxic; if it was more than the stander, it was 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: Conditions for operation and electroless bath composition

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

3. Results and discussion

3.1. Microhardness of nanocomposite coating

The Vickers microhardness test was applied for an SS plate coated with Ag-HA nanoparticles. Samples without coating had the lowest microhardness (104.7 Hv) in comparison with the other samples' values with coating at 0.5 g/L HA nanoparticle. The electroless Vickers microhardness of Ag-(0.5 g/L) HA nanocomposite was H_V=139.9 and increased in comparison with that of Ag-(0.1, 0.3) HA, which reached Hv=109.2 and 117.6, respectively. Thus, high contents of HA nanoparticles may influence the Ag crystal structures, resulting in the promising performance of the nanocomposite coatings.

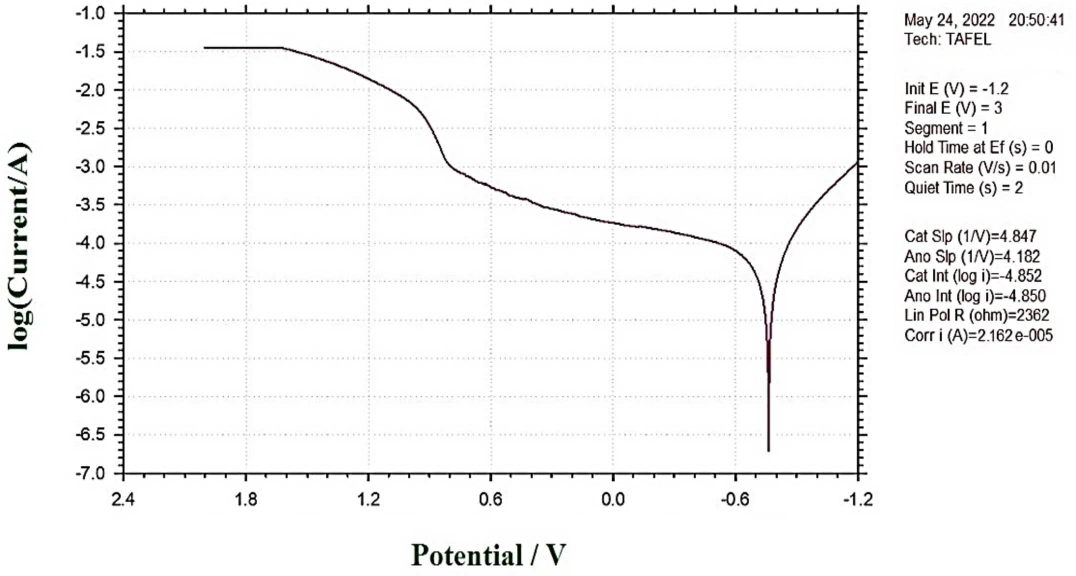
3.2. Corrosion results

The reinforced nanoparticles serve as physical barriers against corrosion attacks by filling in micron-sized cracks and holes, as well as protecting the surface, particularly for HA nanoparticle-reinforced Ag-based nanocomposite coating, thereby significantly enhancing corrosion resistance. The advantageous characteristics of the biological barrier of the coating regimes were enhanced with nano-sized fillers that had good barrier characteristics. the incorporation of HA nanoparticles into metallic coatings offers significant benefits in terms of reinforcement. [8].

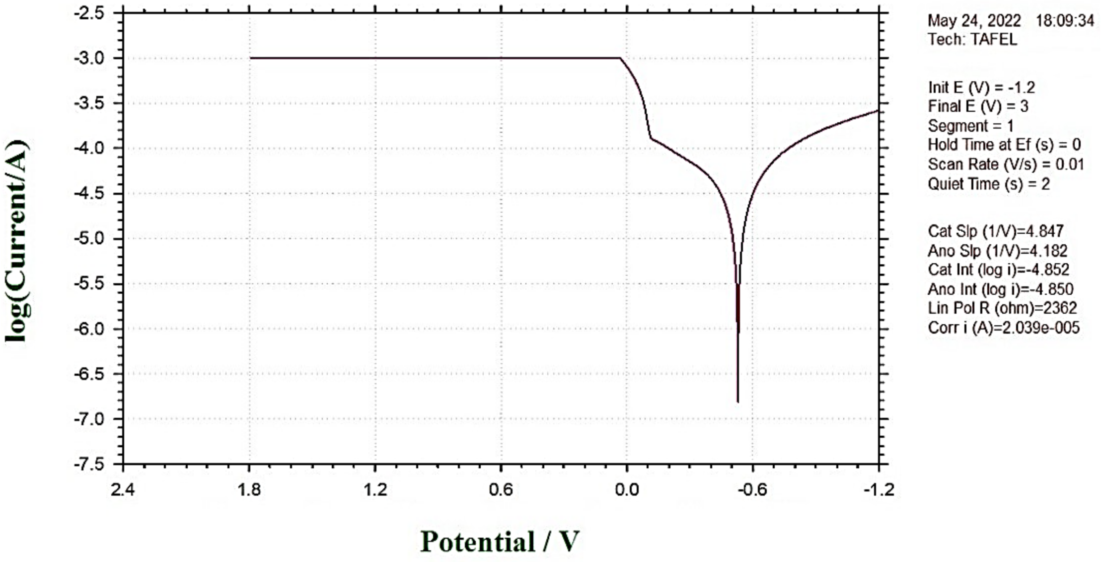
Figure 2 and Table 3 depict the factors of corrosion for the Ag-HA nanocomposite coating computed via Tafel extrapolation in Ringer's solution at 37 °C and the corrosion test instrument shown in Figure 3. Such factors comprise the Tafel slopes (bc and ba), current density of corrosion (I_{corr}), potential (E_{corr}) and rate of corrosion. The corrosion rate of the coated sample and electroless Ag-HA nano-composite coatings varied depending on the concentration of HA nanoparticles. The surface area exposed to corrosion was 1 cm, and it did not need to be covered with polymeric material during the corrosion examination. The corrosion rate decreased for the coatings from 5.954×10^{-1} mpy to 2.633×10^{-2} mpy in the presence of nano-HA. At 0.5%, the HA nanoparticles improved the coating performance and resulted in the best corrosion safeguard.

3.3. Ion release results

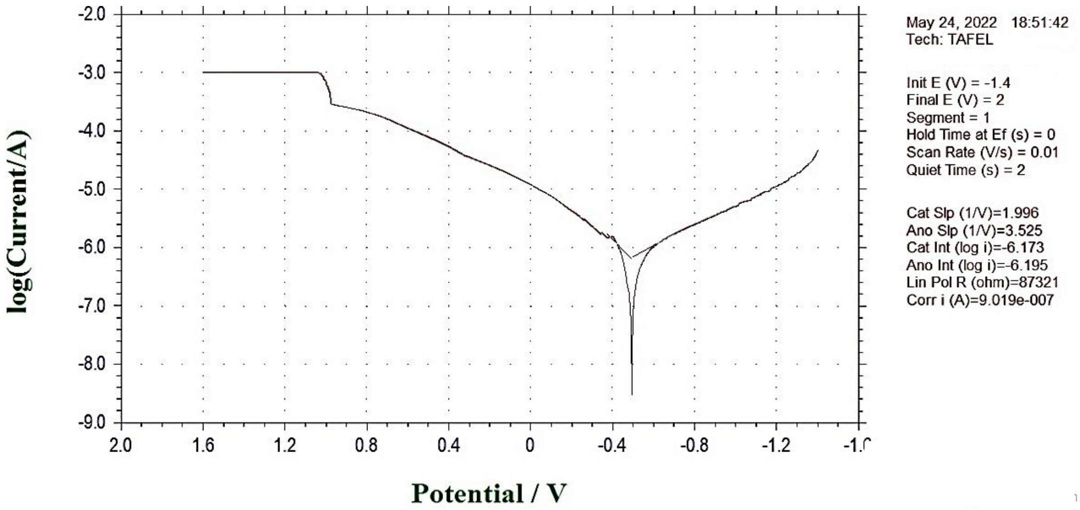
The (Ni and Cr) ion quantities that were released from 0.5 HA of implant sample in Ringer’s solution were measured. For the biomedical applications of the substrate coated with electroless Ag, the ion (Ni and Cr) content of the immersion test was analyzed for three and seven days, respectively, in Ringer's solution. The result of ion release from the 0.5 Ag-HA nanocomposite coating was approximately 0.26 percent nickel, which is within the permissible range for nickel in the human body. Cr was not released because a passive layer developed on its surface and was not destroyed by friction and micromovements in the immersion solution.



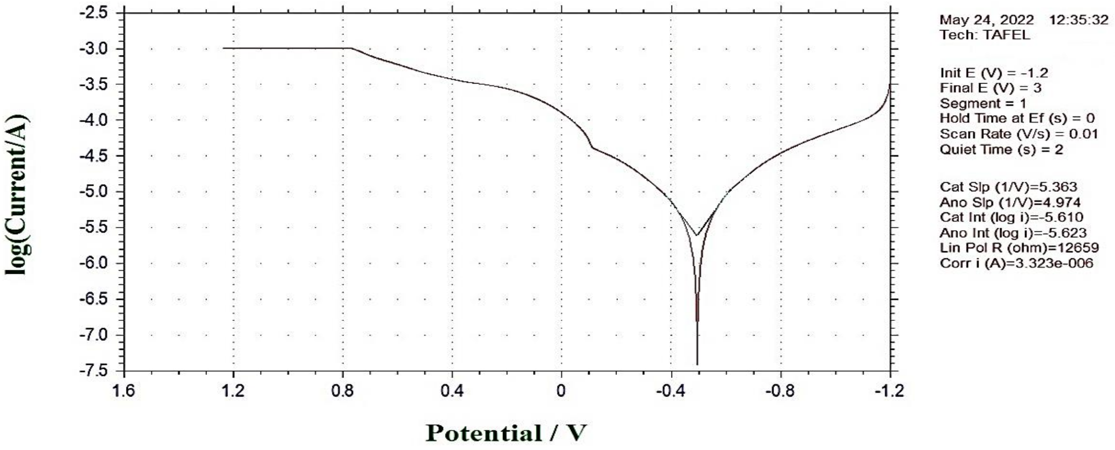
a. 316 L substrate without coating



b. Ag-0.1 wt % HA



c. Ag-0.3 wt % HA



d. Ag-0.5 wt % HA

Figure 2. The factors of corrosion for the Ag-HA nanocomposite coating computed via Tafel extrapolation in 500 ml Ringer's solution at 37 °C.

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

This work studied the effect of various concentrations (0.1, 0.3 and 0.5 g/L) of nano-HA particles on the mechanical (microhardness) and chemical properties (corrosion resistance and ion release) of Ag-HA nanocomposite coating. The following conclusions were drawn:

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. Thus, the corrosion rate decreased when the concentration of nano-HA particles increased.
2. The microhardness increased with increasing nano-HA concentration.
3. The resulting content of ions released for the substrate coated by electroless (Ag-HA) nanocomposite coating when analysing the element coating in Ringer’s solution was within the permissible limit in accordance with the amount of Ni permitted to exist inside the human body. Moreover, chromium element was not found.

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