

A STUDY OF DIPPING TECHNIQUE TO DEPOSIT OF BIOCERAMICS ON STAINLESS STEEL 316L

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Abstract

The aim of this work was to evaluate the corrosion behavior of the uncoated and coated biomedical stainless steel 316L (st-st) and study the effect of bioceramics coating layer on the corrosion behavior in simulated body fluid solution. The dip coating technique is used to deposit three types of nanobioceramics powder including (HA, TiO₂, Al₂O₃), dip coating is used to achieve the coating at different deposition times including (10, 30, 60, 120 sec.), for each one of three types of nanobioceramics. A series of optical micrographs illustrate the microstructure of the uncoated and coated specimens, rough and porous surfaces gained from coating, the micro-topography of these small features (roughness and porosity) that obtained from coating might be factors in promoting osseointegration. The thicknesses were measured in order to found the effect of deposition time on dip coating, the results show that when increasing the deposition time the thickness of bioceramics deposition layer increase. Electrochemical potentiodynamic test were performed to determine the corrosion resistance of uncoated and all three types of ceramics coating, the result of Tafel slope values shows that corrosion resistance of the dip coated specimens higher than of uncoated st-st specimen, also the result shows I_{corr} and C.R of coated specimens decrease with increase in deposition time.

Keywords: Dip Coating, Bioceramics, Stainless steel 316L, Corrosion resistance.

List of symbol

st-st	stainless steel 316 L
SBF	simulated body fluid
E_{corr}	polarization potential
I_{corr}	current density
C.R	corrosion rate
HA	hydroxyapatite
TiO ₂	titanium dioxide
Al ₂ O ₃	alumina
PSZ	Partially stabilized Zirconia
PH	measure of the acidity or basicity mpymilliinch per year
EPD	Electrophoretic deposition P ₂ O ₅ Phosphorous Pentoxide
HCl	Hydrochloric Acid
NaCl	Sodium Chloride
KCl	Potassium Chloride
CaCl ₂	Calcium Chloride
NaHCO ₃	Sodium Bicarbonate
K ₂ HPO ₄ .3H ₂ O	Potassium Phosphate Dibasic Trihydrate
MgCl ₂ .6H ₂ O	Magnesium Dichloride Hexahydrate

1. LITERATURE REVIEW

Thair L. et al. Seventy-two commercially pure titanium implants (cpTi) were used in this study, (24) implants were coated with PSZ by EPD, and (24) by dipping method, the rest 24 implants were used as controls, they were inserted in the tibia of (32) New Zealand white rabbits & were followed for 2, & 6 weeks. Results revealed that bone-implant contact, increased with time & that implants coated with PSZ by dipping method have shown higher torque mean values than those coated by EPD method [1].

Tejpreet S. et al. In this study, HA and HA/TiO₂ bond were coated on st-st by using a flame spraying technique. The aim of this study is to evaluate in vitro corrosion behavior of coated specimens, the corrosion behavior of the uncoated and coated specimens was carried out in simulated body fluid (SBF) [2].

Bora M. et al. used Ti-6Al-4V substrate materials coated with HA by dip coating. The main inorganic phase of human bone is calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA). To achieve better biocompatibility with bone, metal implants made of Ti-6Al-4V are coated with bioceramics. Dip-coating techniques scarcely are used to apply HA onto metallic implants. Scanning electron microscopy and X-ray diffractometry have been used for sample characterization [3].

Lin C.K. et al. In this study, nano TiO_2 thick films were successfully deposited on st-st specimen by EPD process, and sintered at 600 and 700 °C [4].

2. PROBLEMS OF STAINLESS STEEL

Surgical grade type stainless steel 316L implant corrodes in human body environments, and release iron, chromium and nickel ions, these ions were found to be strong allergens and carcinogens. These attacks of localized corrosion and leaching of metallic ions from implants necessitates improvement in the corrosion resistance of st-st by modifying the surface.

3. THE RESEARCH OBJECT

- 1- Formation of coating layers from nano sized bioceramic particles which includes (HA, TiO_2 , Al_2O_3) deposit on st-st using dip coating technique.
- 2- Studying the microstructure of the coating layers, by characterizing it with optical microscope.
- 4- To increase corrosion resistance for the base st-st metal by coating it with (HA, TiO_2 , Al_2O_3).
- 5- Testing and measurement (coatings thickness in all bioceramics types that change depending on the deposition time, adhesive strength).

4. INTRODUCTION

The use of implant has expanded dramatically during the past decades owing to increase in the life expectancy, changing lifestyles and to improve implant technology [5]. Nowadays, corrosion is the major issues resulting in the damage of biomedical implants, the types of corrosion that occur to the currently used medical implant are pitting, crevice, galvanic, and corrosion fatigue. Any time, when the foreign material is placed inside the human body environments, the effect of this material on the body should be considered. When the metals

are placed inside the human body there are several causes that lead to corrode it, crevices formed between implants can reduce oxygen concentration, infectious microorganisms and all these contribute to the corrosion of the implants. Besides, corrosion and surface oxide film dissolution are the two mechanisms for introducing additional ions into the body. Extensive release of ions from metallic implants can result in adverse biological reactions and lead to mechanical failure of the implant [6]. To enhance the corrosion resistance and biocompatibility of the implant material like stainless steel, coating of bioactive materials is performed, the thin film coating of implant surfaces can be performed by various coating techniques [7,8].st-st is the common biomedical material used in medical implant such as orthopedic replacements,st-st implant corrodes in human body environments, and release iron, chromium and nickel ions, to reduce corrosion and achieve better biocompatibility, surface modification of stainless steel with protective bioceramic coating is considered advanced methods to improve the performance of orthopaedic implant, this bioceramic coating can be achieved by applying several coating techniques such as dip coating, electrophoretic deposition, electrochemical deposition, thermal spraying, sputter coating, pulsed laser deposition [6, 9].

Dip coating is an alternative method for prosthetic devices used in orthopedics it offers a number of advantages over other coating methods such as flexibility, control of coating morphology, chemistry and structure [10]. A step in improving the bone implants properties is the coating of metallic implants, having good mechanical properties, with thin biocompatible ceramic films, in order to improve the osseointegration] of these implants. The dip coating method is considered as the best processes of obtaining these ceramic coating [11].

Dip coating is used to modify the surface of the implant material and to create a new surface with totally different properties with respect to the substrate. When coated the metallic prostheses and implants by dip coating, with the bioceramics coating, display increased biocompatibility when placed inside the body environments, and these thin coating are also shown to impede the corrosion and undesired metal ion transfers from the implant itself [12].

5. EXPERIMENTAL WORK

5.1 Materials Preparation

The bioceramics materials used for coating are HA, TiO₂ and Al₂O₃ medical grade nano powders (particle size < 40 nm) were used as coating materials, the source of HA, TiO₂, Al₂O₃ nano powder are from Sky Spring Nanomaterial, Inc., USA. The substrate used for applying the coating was stainless steel 316L, Specimens were cut for use as a substrate for coating into the dimensions of (20 mm x 20 mm x 3 mm). The specimens were grinding using 220 grit polishing paper then followed by ultrasonic cleaning for 15 min. with distilled water and then washing in acetone for another 15 min.

5.2 Dip Coating Process

Dip coating system is self designed. It is so simple coating method as compared with other coating method. It consists of hot plate magnetic stirrer type (VS-130SH, Vision Scientific CO., LTD), stop watch and mercury thermometer to control the time and temperature, beaker of 50 or 100 ml, tongs to hold the specimen. The specimen to be coated is held by tongs to be immersed in suspension. The suspension for dip coating was prepared for three types of bioceramics by adding of P₂O₅ to the 50 ml of ethyl alcohol solvent to provide the gel, then 5g of bioceramic powder was added to the gel in a container to produce the final suspension which was kept on a stirrer and stirring was continued until a colloidal suspension was obtained. The solution was continuously stirred by a magnetic stirrer for 45 min. The suspensions were maintained at temperature 55 °C. The dipping process was performed for (10, 30, 60, 120 sec.). After the deposition, specimens were dried in air for 24 hr. After the specimens had been dried, sintering of the coated specimens was carried out for densification using carbonite furnace. The treatment was done under inert gas (argon) to prevent oxidation. All specimens were sintered at 500°C for one hr.

5.3 Characterization of coating

The uncoated and coated specimens were examined under the light optical microscope type (Scope Photo), to find out the microstructure of specimens. Measurement of thickness was performed for all the specimens coated by three types of coating using coating thickness gauge type (QuaNix1500 Germany). The test was carried out by holding the

instrument at right angles to the surface to be measured; the contact pin was placed on the surface and the small bottom is pushed. The thickness of the coating was indicated on the digital display.

5.4 Corrosion Test

The electrochemical corrosion behavior of the uncoated st-st specimen and coated with three types of bioceramics, were investigated by conducting the potentiodynamic polarization tests. The electrochemical corrosion test was carried out by using a potentiostat type (WENKING M. Lab.). SBF with chemical composition as shown in Table (1) at pH of 7.2 was used as the electrolyte for simulating human body fluid conditions. Electrochemical test system composed of potentiostat and glass cell and electrodes. Cylindrical glass container with one liter capacity was used with three electrodes: working electrode, counter electrode and reference electrode. The specimen was fixed on orifice with diameter (1cm) on the side of the cylindrical cell and the specimen was attached with solution through this orifice. The measurement of the current density I_{corr} and potential E_{corr} was done by analyzing the data values (current - voltage) using potentiostat software.

6. RESULTS AND DISCUSSION

6.1 Corrosion Behavior

The potentiodynamic scans of the st-st uncoated and coated with (HA, TiO_2 , Al_2O_3) by dipping are shown in Figures (1), (2) and (3) respectively. The results of these corrosion parameters are shown in Tables (2), (3) and (4). The result of Tafel slope values for all dip coated specimens also shows lower I_{corr} and C.R than those of uncoated specimen, also it can be observed that the I_{corr} and corrosion rates of coated specimens by dipping decreased with increase in deposition time (or coating thickness), until reaching the C.R values of (0.065, 0.179, 0.219) in specimens (HA, TiO_2 , Al_2O_3) respectively, these results indicate that all dip coated specimens can act as a protective layer on st-st and improve the overall corrosion performance. When comparing between three types of bioceramics (HA, TiO_2 , Al_2O_3) that were coated by dipping, it can also be observed that the parameters obtained for specimens coated with HA are lower than those of TiO_2 and Al_2O_3 .

6.2 Optical Microscope Observations

A series of optical micrographs illustrate the microstructure of uncoated and coated st-st, all optical micrographs were taken under magnification power of (10X). Uncoated st-st seem to have many scratches and rough in nature that is mainly due to the grinding process, as shown in Figure (4).

The surface of specimens that were coated with HA by dipping appears rough with cracking and clear porous surface, as shown in Figure (5), cracks were observed across the coating of HA which is probably due to thermal expansion mismatch of HA and st-st. Grooves and cracks were obvious on the surface of HA coating indicates the presence of rough surface, which might enhance osseointegration, this comes in agreement with the results of Albrektsson [13]. The specimen that was coated with TiO_2 by dipping shows rough and porous surface, the agglomeration of TiO_2 nano particles increases with increase in deposition time, as shown in Figure (6). The surface of specimens that were coated with Al_2O_3 by dipping appears rough and porous, but no cracking, with the large agglomeration of Al_2O_3 nano particles was observed in the specimen (D3) in Figure (7).

6.3 Effect of Deposition Time on Thickness: The results show that after increasing the deposition time of dip coating from (10, 30, 60 to 120 sec.) then the thickness of bioceramics deposition layer increases, as shown in Figure (4-34).

CONCLUSIONS

The following conclusions are reached:

- 1- It have been successfully deposited of bioceramics of (HA, TiO_2 , Al_2O_3) nano powder on st-st by dipping.
- 2- The corrosion parameters (corrosion rate and corrosion current density) are reduced by coating with the nano powder bioceramic (HA, TiO_2 , Al_2O_3) by dip coating, the corrosion parameters of coated st-st specimens by dipping decrease with increase in deposition time, and the specimens that were coated with HA by dipping in 120 sec. have the lower corrosion parameters, as compared with all other types of coating.
- 3- The microstructure of coated specimens for three types of bioceramics coating are rough, this might be factor in promoting the bone bonding ability.

4- The thickness of the coating layer of specimens coated by dipping increases with time.

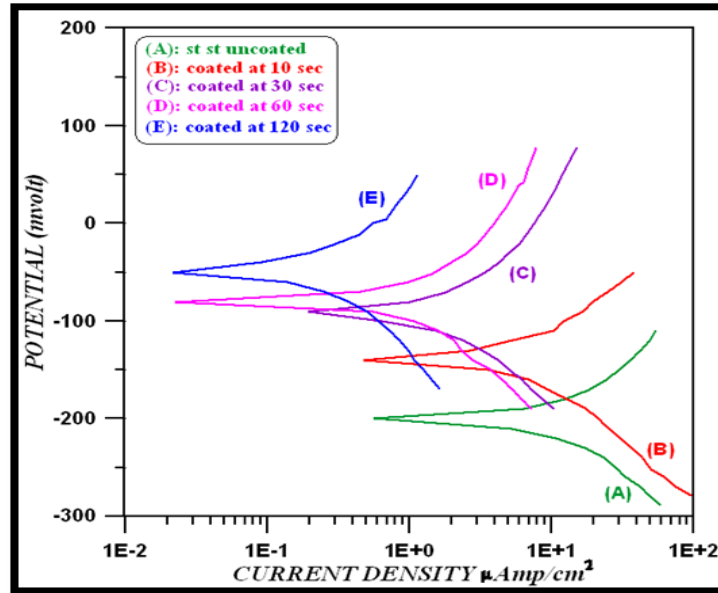


Figure (1): The polarization curves of st-st coated with HA by dipping.

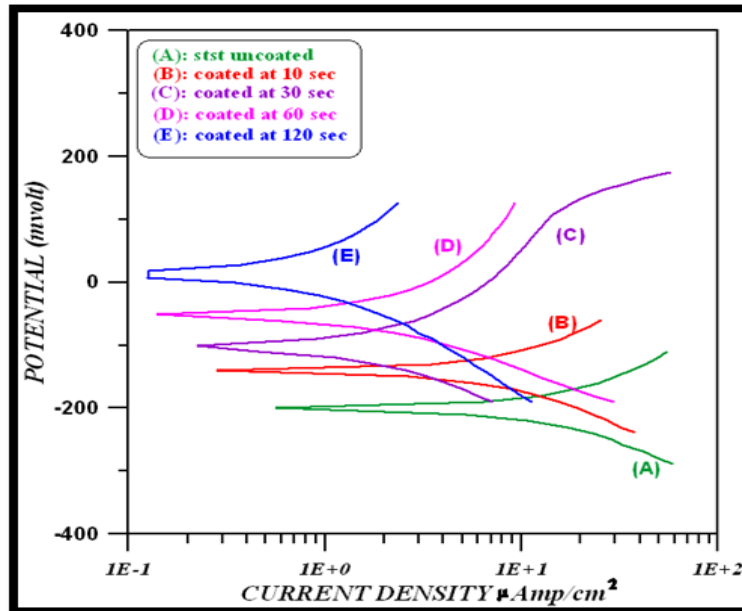


Figure (2): The polarization curves of st-st coated with TiO_2 by dipping.

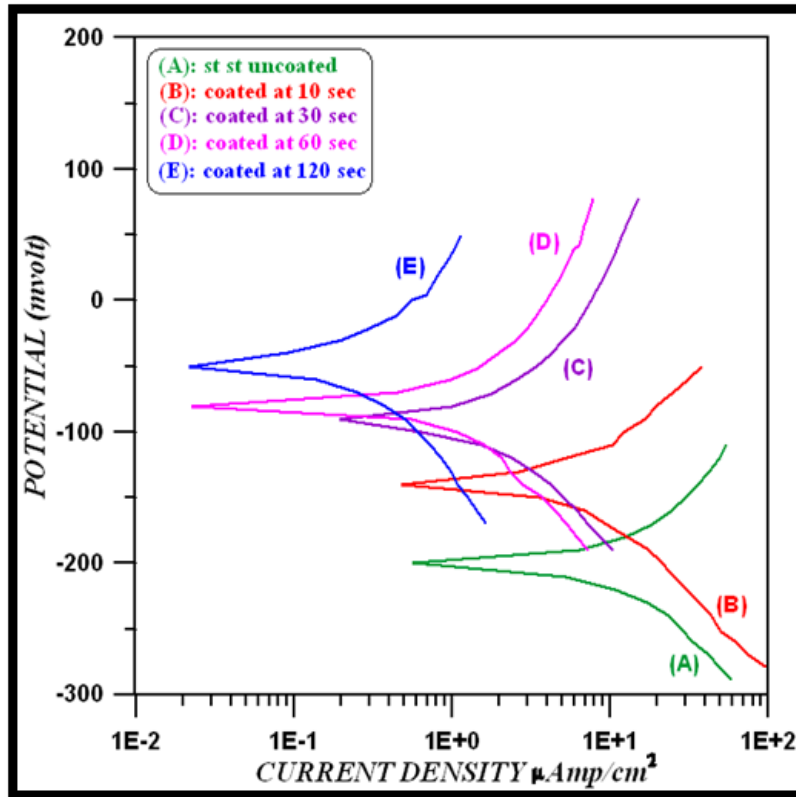


Figure (3): The polarization curves of st-st coated with Al_2O_3 by dipping.

Table (1) The chemical composition of simulated body fluid [14].

No.	Constituent	Weight (g/l)
1	NaCl	8.036
2	KCl	0.225
3	CaCl_2	0.293
4	NaHCO_3	0.352
5	$\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$	0.230
6	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.311
7	Na_2SO_4	0.072

Table (2): The corrosion parameters of the st-st uncoated and coated with HA by dipping.

Item	I_{corr} ($\mu\text{amp}/\text{cm}^2$)	E_{corr} (mV)	C.R (mpy)
st-st Uncoated	6	-198.7	2.628
Coated with HA at 10 sec.	3.5	-140	1.533
Coated with HA at 30 sec.	1	-90	0.438
Coated with HA at 60 sec.	0.63	-81	0.275
Coated with HA at 120 sec.	0.15	-50	0.065

Table (3): The parameters of the st-st uncoated and coated with TiO_2 by dipping.

Item	I_{corr} ($\mu\text{amp}/\text{cm}^2$)	E_{corr} (mV)	C.R (mpy)
st-st Uncoated	6	-198.7	2.628
Coated with TiO_2 at 10 sec.	3.5	-140	1.533
Coated with TiO_2 at 30 sec.	1.3	-100	0.569
Coated with TiO_2 at 60 sec.	0.9	-51	0.394
Coated with TiO_2 at 120 sec.	0.41	12	0.179

Table (4): The corrosion parameters of the st-st uncoated and coated with Al_2O_3 by dipping.

Item	I_{corr} ($\mu\text{amp}/\text{cm}^2$)	E_{corr} (mV)	C.R (mpy)
st-st Uncoated	6	-198.7	2.628
Coated with Al_2O_3 at 10 sec.	2	-160	0.876
Coated with Al_2O_3 at 30 sec.	1.8	-140	0.788
Coated with Al_2O_3 at 60 sec.	0.65	-110	0.284
Coated with Al_2O_3 at 120sec.	0.5	-80	0.219

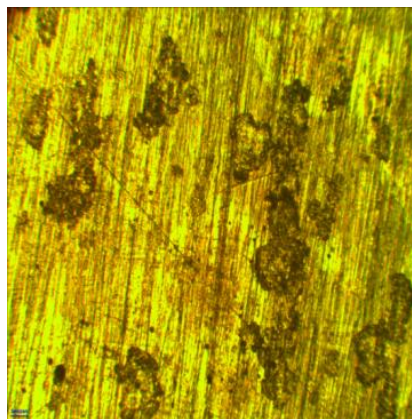
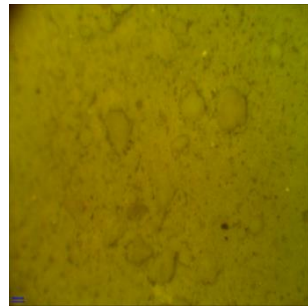


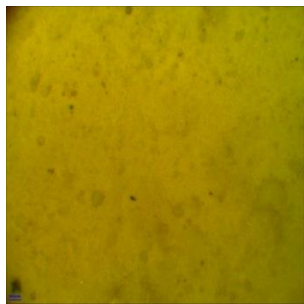
Figure (4): Optical micrograph view of st-st alloy uncoated, under magnification power of 10X.



(A1)



(B1)

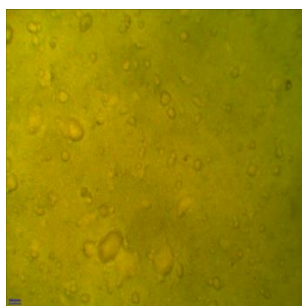


(C1)

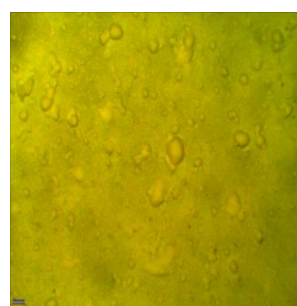


(D1)

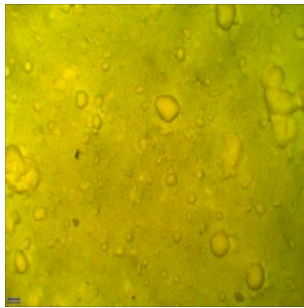
Figure (5): Optical micrograph view of st-st alloy coated with nano HA by dipping, under magnification power of 10X at different times: (A1) Coated at 10 sec. ; (B1) Coated at 30 sec. ; (C1) Coated at 60 sec. ; (D1) Coated at 120 sec.



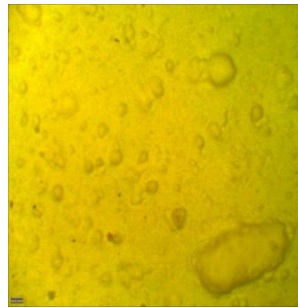
(A2)



(B2)

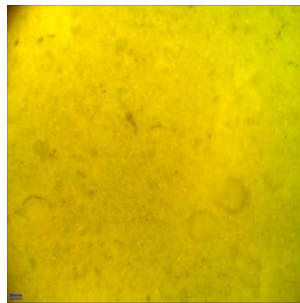


(C2)

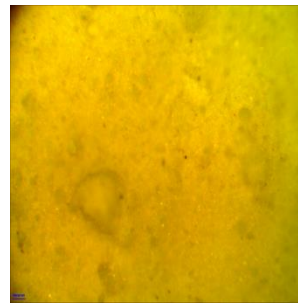


(D2)

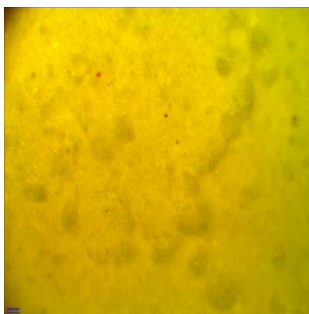
Figure (6): Optical micrograph view of st-st alloy coated with nano TiO_2 by dipping, under magnification power of 10X at different times: (A2) Coated at 10 sec. ; (B2) Coated at 30 sec.; (C2) Coated at 60 sec ; (D2) Coated at 120 sec.



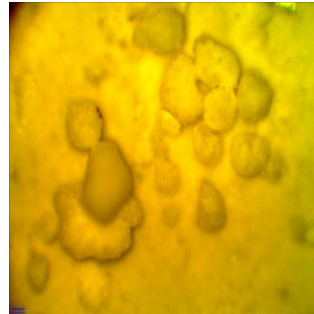
(A3)



(B3)



(C3)



(D3)

Figure (7): Optical micrograph view of st-st alloy coated with nano Al_2O_3 by dipping, under magnification power of 10X at different times: (A3) Coated at 10 sec. ; (B3) Coated at 30 sec.; (C3) Coated at 60 sec. ; (D3) Coated at 120 sec.

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