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Electrophoretic Deposition of Calcium Phosphate Ceramics over Duplex Stainless Steel (S2205) and its Characterization

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Abstract *Bio materials are the emerging field in the world of science and innovation. Austenitic stainless steels and titanium alloys are widely used for orthopedic applications. However, a long time exposure leads to dissolution of alloying elements in to the body fluids causing allergic issues. In this work, bioactive HAp is coated over duplex stainless steel for fast recovery of the patient reducing the problem like allergy. Parameters like voltage and coating time are varied for electrophoretic deposition and deposited samples were characterized using scanning electron microscope coupled with spectroscopy. The various morphologies of HAp and TCP crystals were observed and the formation of calcium deficient HAp was confirmed by EDS analysis. It is also observed that, increasing the coating time leads to the formation of thicker coating with poor adherency.*

Key Words: *Electrophoretic deposition, HAP, TCP, Duplex Stainless Steel*

1. INTRODUCTION

This paper deals with the coating of bioactive ceramics over duplex stainless steel and their characterizations. The requirement of materials particularly in orthopedic applications are demanding high corrosion resistant materials with good bio compatibility. Several coatings are made majorly in materials like Ti alloys and Austenitic Stainless Steels. In general, Ca-P are the inorganic constituent in most of the hard tissues. In humans, carbonated hydroxyapatite is present in teeth, bones, etc. Ca-P compounds are also formed in earth due to mineral deposition under severe atmospheric condition, but the Ca-P compound formed in human bones and teeth are nanocrystals that formed under normal atmospheric condition (Growth of teeth). This mechanism of crystal formation in living organisms is termed as Biomineralization. When this crystal growth becomes abnormal in living organisms it is called as Pathological Crystallization which leads to formation stones, atherosclerosis. There are several combinations of Ca-P compounds are available out of which, compounds having Ca/P ratio ranging from 1.45 to 1.90 are used for applications. This Ca-P is to be monitored carefully. Ca/P ratio of 1.66 is mostly appreciable for implants in living organisms.

In electrophoretic deposition, Ca and P are added as separate compounds of Ca and P in the electrolytic solution. During processing period, this compound dissociates and forms Ca and P ions which will combine and form Ca-P compounds with Ca/P ratio that depends on the parameters like pH of the solution, voltage, concentration of precursors added. The objective of this work is to coat HAP and TCP over duplex stainless steel, study their morphological characterization, adherency and composition using techniques like SEM, EDS, Tape test.

2. MATERIALS AND METHODS

The HAp and TCP coatings are electrodeposited over 2205 steel with varying voltage and time. Duplex stainless steel samples of diameter 1" and thickness of 1 cm is taken for coating. The steel is degreased, polished with emery sheet (up to 1500) to get rough surface and inhibited in HCl for 30 minutes. After inhibition, samples are cleaned in running water followed by acetone.

The electrolytic solution is prepared for coating TCP and HAp in the composition mentioned below.

a) Electrolytic solution for coating of TCP:

3.16g of Tricalciumphosphate + 4g of EDTA for a standard solution of 100ml.

b) Electrolytic solution for coating of HAp:

The electrolyte solution contained 0.6 mM Ca $(NO_3)_2 \cdot H_2O$ (analytical grade) and 0.36 mM $NH_4H_2PO_4$ (analytical grade) with Ca/P ratio being 1.67 in DI water. 0.1 M $NaNO_3$ was also added in order to improve the conductivity of the electrolyte.

Once the solution is prepared, electro deposition unit is set up and the coating is carried out with voltage and time as varying parameters. A Pt plate was used as counter electrode (anode) and duplex stainless steel was used as working electrode.

a) Electro deposition of hydroxyapatite:
Voltage = 7.5V, 10V, 12.5V and 15V
Coating time = 7.5 min, 10 min, 12.5 min, 15 min, 30 min, 60 min, 120 min

b) Electrophoretic Coating of TCP:
Voltage = 10V, 12.5V and 15V
Coating time = 7.5 min, 10 min, 12.5 min, 15 min

Once the coating is made, to study the adherency of the coating, tape test is made. Followed by tape test, EDX analysis is made to study the elemental composition to verify whether the required Ca/P ratio was obtained. Studying of

coating morphology is very important, which is done by SEM analysis.

3. RESULTS AND DISCUSSIONS

The characterization was made for both base metal and coated samples and the obtained results are discussed below.

3.1. Base Material Characterization:

The microstructure, phase fraction, mechanical properties of the duplex stainless steel was studied before coating the bioactive ceramics. The microstructure reveals homogeneously distributed austenite (Bright phase) in ferrite matrix (Dark phase). Phase fraction analysis was made through Ferritoscope and it is observed that the steel contains 49% ferrite. The mechanical test results shows an ultimate tensile strength of 748.13 MPa, yield strength of 536.70 MPa, with elongation of 37%. The obtained value is higher than the ASTM standard value of UTS 680 MPa (min) and YS 520 MPa (min). The ultimate tensile strength and yield strength of the steel is enhanced due to formation of homogeneous microstructure. The hardness of the produced DSS was found to be 229 BHN. The hardness of the material has met with the standard value of 225 BHN (Min) for the grade 4A. Charpy impact strength of the duplex stainless steel is 170 MPa that agree with the standard values (150 MPa (min)).

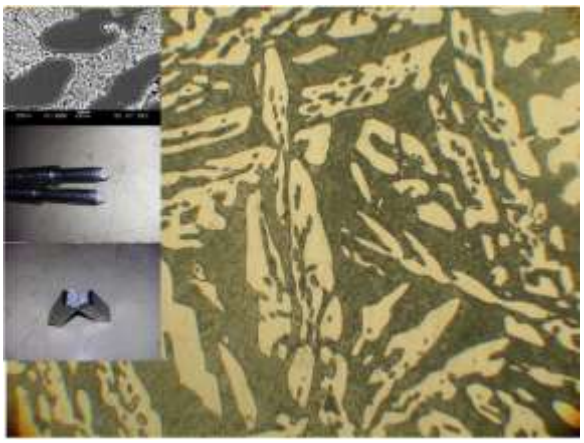

Fig. 1: Microstructure of Duplex Stainless Steel Grade 4A

3.2. Characterization of the HAP Coated Samples:

1. Visual Observation:

The coating of hydroxyapatite was done in the calcium phosphate electrolyte with pH maintained at 7 and at room temperature. During coating process various visual changes were observed. During trial coating of HAp, the electrolytic solution changed its color from white to yellowish color. This color change indicated some reactions taking place inside the electrolytic solution.

When the coating time was increased to 120 min, the color change was observed again from white to transparent yellow color indicating that the Ca and P ions present in the solution were reacting and also the coated sample observed has a brownish coating. Where the coating was already completed at some particular time and the coating was removed due to excessive exposure of the material in the electrolytic solution.

In coating of HAp with varying voltage from 10V to 15V, the development of HAp particles over the duplex stainless steel substrate was keenly observed. At 10V the base layer of the coating was formed, with increase in voltage to 12.5V, network like structure with large number of pores was observed. When the voltage is further increased to 15V, the HAp particles started growing over the network and completely covered the network like growth and formed a completely coated layer with very less pores as shown in Fig.2

2. Tape test:

Samples coated at 10V with coating time 7.5 minute and 10 minute showed good adhesion than that of the other two coatings.

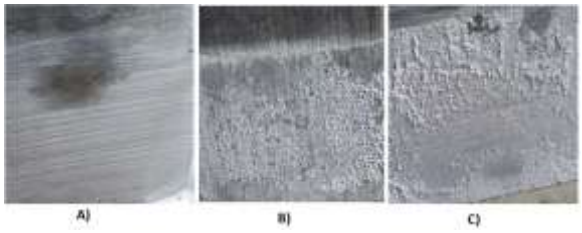

Fig. 2: A) At 10V Formation of base layer over the substrate which is adherent, uniform and homogeneous B) at 12.5V Homogeneous distribution of micro pores with relatively less adherency than A) is observed C) at 15V Uniform coating with less micro pores was formed but with poor adherency.

3. EDS Analysis:

EDS analysis indicates the formation of the calcium deficient hydroxyapatite with Ca/P = 0.785

4. SEM Analysis:

The first experiment was carried out at the voltage of 10V and coating time ranging from 7.5 Mins to 15 Mins. Current density of the coating was 12.5 mA/cm^2. The second experiment was carried out at voltage range of 7.5V to 12.5V. The coating time was maintained as 10 Min and the varying current densities of 7.85 mA/cm^2 for 7.5V, 12.5 mA/cm^2 for 10V and 14.58 mA/cm^2 for 12.5V.

The SEM analysis of the coated samples are made and are shown below.

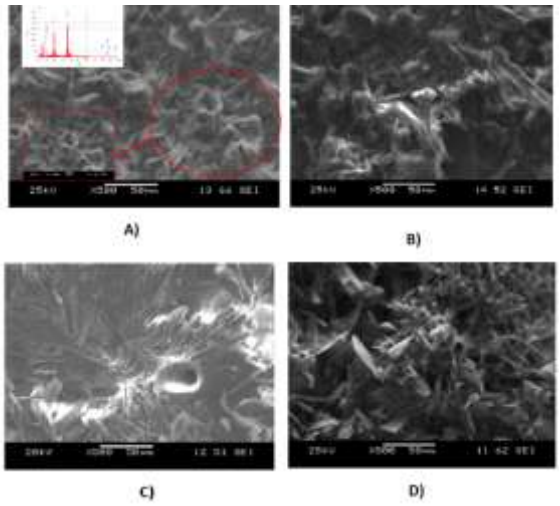

Fig 3: SEM images of electrolytic coated DSS with varying time A) for 7.5 Min, formation of short strings are observed B) for 10 Min, formation of flaky structure was observed with some round particles C) for 12.5 Min, large flakes are formed with a common point as a origin for various flaks D) for 15 Min, broken flake structure is obtained due to exposure of the sample in the electrolytic solution for excessive time.

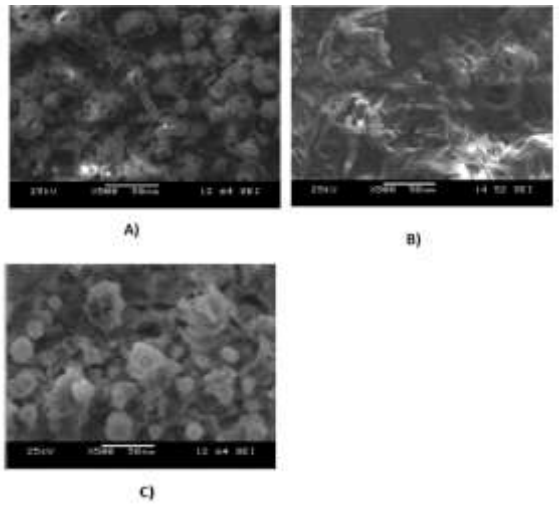

Fig 4: SEM images of electrolytic coated DSS with varying voltage A) for 7.5V, formation of short tubular structures are observed with micro pores B) for 10V, formation of flaky structure was observed with some round particles C) for 12.5V, large tubes are formed.

3.3. Characterization of the TCP Coated Samples:

1. Tape test:

Samples coated at 10V with coating time 10 minute showed good adhesion than that of the other two coatings.

2. EDS Analysis:

The result of TCP coated sample with Ca/P ratio of 1.935. Where the Ca/P ratio of TCP which is acceptable.

3. SEM Analysis:

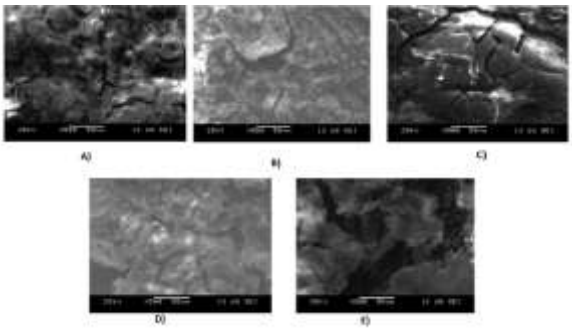

Fig 5: SEM images of electrolytic coated DSS with varying coating time A) for 5 min, formation of short fibrous structures are observed with micro pores B) for 7.5 min, formation of large flaky structure was observed C) for 10 min, rods are formed with some cleavages and also some micro particles of rounded shapes D) Flakes are formed with large pores and cracks formed due to hydrogen evolution E) Rod like structures with flakes at the top are observed resembling celosia structure.

Coating of TCP was carried out on duplex stainless steel and the results are obtained as follows. The first experiment was carried out at the voltage of 10V and coating time ranging from 5 Mins to 15 Mins. Current density of the coating was 11.47 mA/cm^2. Fig 6. reveals the SEM images of electrolytic coated DSS with varying voltage where A) shows the coating morphology at 10V, enclosing the formation of short rods like structures are observed with micro cracks B) indicates the coating at 12.5V, revealing the formation of rounded structure was observed but some of the particles started to break down from the surface due to high voltage and C) shows the coating at 15V, revealing large tubes are formed with some micro particles of rounded and rod shapes are observed.

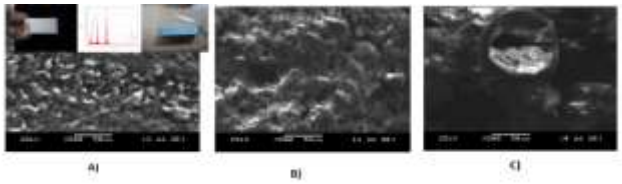

Fig 6: SEM images of electrolytic coated DSS with varying voltage

3.4. Growth Mechanism observed:

From the SEM analysis, three kinds of growth modes are observed namely, Frank-van-der-Marwe mode, Stranski-Krastanow mode, and Volmer-Weber mode. Where, Frank-van-der-Marwe mode is layer by layer growth mode. In this growth mode, the absorbate surface and absorbate-absorbate interactions are balanced. This type of growth

requires lattice matching and hence considered as ideal growth mechanism as shown below in Fig. 7. A.
Fig. 7. B shows, Stranski-Krastanow mode of growth where, layer plus island growth occurs. In this growth mode, the absorbate-surface interactions are stronger than absorbate-absorbate interactions. In this mode, thin films grow epitaxial at the crystal surface or interface. This process is a two-step process, in which initially complete films of absorbate, up to several monolayers thick, grown by layer by layer fashion on a crystal substrate. Beyond critical layer thickness, which depends on the strain and the chemical potential of the deposited film, growth continuous through the nucleation and coalescence of absorbate islands?

In Volmer-Weber growth mode, adatom-adatom interactions are stronger than those of the adatom with the surface, leading to formation of three dimensional adatom clusters or islands. Growth of these clusters, along with coarsening, will cause rough multi-layer films to grow on the substrate surface as shown in Fig. 7. C.

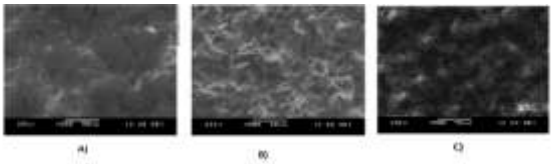

Fig.7: SEM images of the obtained structures showing three different modes of particle growth.

A) Frank-van-der-Marwe Mode, observed in TCP coated sample at 7.5 min, and 10V
B) Stranski-Krastanow Mode, observed in HAp coating at 7.5 min, and 10V
C) Volmer-Weber Mode, observed in HAp coated sample at 10 min, and 7.5V

4. CONCLUSION

HAp and TCP are successfully coated over the produced DSS samples and observed that the coating are very adherent at the following parameters. For HAp coating, 7.5 V and 10 V with 10 min coating time showed good adherency. Whereas for TCP coating, 10 V with 10 min coating time gave good adherency. Growth of HAp and TCP particles over the surface during the coating process was analyzed and reported. Crystallographic growth of calcium phosphates were discussed. It was observed that, Volmer-Weber method was predominating in HAp coated samples and Frank-van-der-Marwe mode predominates in the growth of TCP particles.

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