Bioactive and Antibacterial Coating on Titanium Alloy for Biomedical Application

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Abstract:- A multilayer hydroxyapatite/titanium (HA/Ti) coating was prepared on the Titanium alloy by magnetron sputtering. The composition, surface topography, microstructure, adhesion strength and electrochemical properties of the as-deposited coatings were characterized by SEM/EDS, AFM, XRD, EIS, etc. Hydraoxyapatite as a biocompatible material has excellent osteoconductivity and corrosion resistance. Titanium Alloy has an excellent corrosion resistance and high tensile strength and toughness even at extreme temperatures. This project investigates the result of an experimental study carried out to verify the chemical composition, to determine the surface characteristics, mechanical properties as well as observing the surface topography of coating of the composite material hydroxyapatite/Titanium coated Titanium Alloy. This composite material is a new biocompatible multi-layered coated Titanium alpha beta alloy, in which the multi-layered coating consisted of an underlying Ti bond coat, the alternating layer, and an HA top-layer. It has great application in biomedical fields such as in bone and teeth implanting.

Keywords:- Hydroxyapatite, Titanium, Topography, Composition, Corrosion resistance, Osceointegration, Biocompatible.

1. INTRODUCTION

There are always many accidents happening due to which a person might have a bone fracture or having missing teeth or any other reason for which an implant is necessary and for that there are many researches going on in the world for researching new biocompatible materials suitable for implants or a coating method suitable for implants. Biomaterials have been successfully developed and used to improve the quality of human life, not just for an aging population but also for younger people with heart problems. The success of such an implant largely depends on the selection of materials for their manufacture. Titanium alloys have been extensively used for the manufacturing of metal orthopaedic joint replacements and bone plate surgeries. Such alloys have very high tensile strength and toughness (even at extreme temperatures). These alloys also have a good yield strength and low elastic modulus, which is similar to that of bone. They are light in weight, have extraordinary corrosive resistence property and the ability to withstand extreme temperatures. But there are still many defects or disadvantages in using titanium alloys such as recently it has been noticed that most metallic materials, including Ti alloy, can undergo degradation in the long term. Many studies proved that Titanium alloy implant could cause health problems because of the release of aluminum (Al) and vanadium (V) ions into the human body's fluid system. Both V and Al ions are associated with long-term health problems, such as Alzheimer's, neuropathy, and Osteomalacia. In addition, alloy, as a bioinert material, exhibits poor osteoinductive properties. It cannot form effective

bone-bonding between the implant and the human tissue. Currently, these limitations have prompted many researchers to focus on solutions, leading to implant surface modification. Many studies have been made to develop hydroxyapatite (HA) coatings, due to its osteoconductivity and mechanical properties, on metallic substrates for dental and orthopaedic prostheses. Hydroxyapatite has a similar structure to the natural bone component. Hence, HAP coating allows for new surface properties such as osteointegration and biocompatibility, which lead to an improvement in implant functionality.

Many studies focus on the various methods used to obtain reliable HAP coatings, other active research investigate bioactivity, cytocompatibility, and antibacterial properties. Although the HAP coating should be compatible with the tissue surrounding the implant, it also should possess good mechanical properties, high bonding strength and corrosion resistance. To the best of our knowledge, few works have been done investigating the mechanical properties (the hardness and the elastic modulus) and adhesion behavior of HAP coating obtained by electrodeposition technique. Hence, a detailed mechanical and corrosion resistance analysis is indispensable to evaluate the reliability of the HAP deposited thin film. The aim of this work is to study the mechanical, surface and electrochemical characteristics of HAP coating deposited on Titanium Alloy.[9]

Hydroxyapatite is a naturally occuring form of the mineral calcium apatite-calcium, phophorous, and oxygen-that grows in hexagonal crystals. Pure hydroxyapatite is white in color. It makes up most of the human bone structure, builds tooth enamel and collects in tiny amounts in part of the brain. Hydroxyapatite is a rare material, in that it is a bioactive material, so it is one of the few lab-made materials that will help bones and teeth grow. Hydroxyapatite helps stimulate bone grownth, nano hydroxyapatite is most frequently used in surgeries involving bones and tooth enamel. Joint replacement implants can be coated with nano hydroxyapatite, so that the body is less likely to reject those implants, and the mineral coating encourages new bone growth around the implant, anchoring it more effectively.

2. COATING AND INSPECTION METHODS

A. Coating Method:-

RF Magnetron Sputtering Method:- A commercially pure Ti target was used, commercially available Titanium alloy plates were used as substrates. The Titanium alloy substrate surface was mechanically polished to a roughness of Ra=0.06μm. Prior to sputtering, the polished substrate surface was etched in 30% HNO_3 for 30 minutes at room temperature, followed by ultrasonic cleaning in acetone for 10 minutes. The sputter chamber was evacuated to a base pressure lower than 10^{-5} Torr, and then back-filled with high purity argon until working pressure of 10^{-2} Torr was obtained. Prior to deposition, the substrate surface was first sputter-cleaned for 10 minutes at 1 kV DC bias. The Ti and HA targets were in the side-by-side configuration.

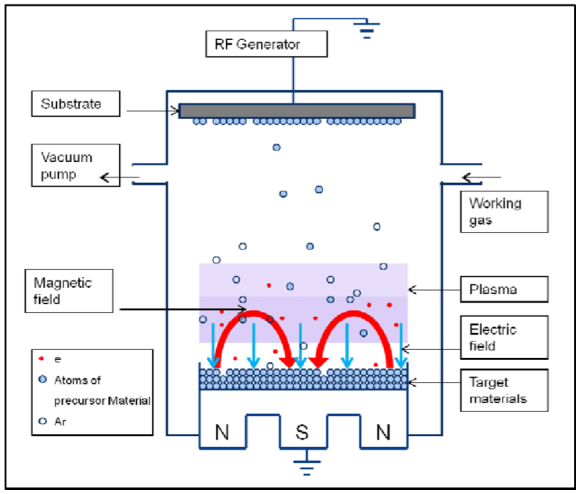

Fig:- RF magnetron sputtering method

The magnetron-assisted sputter deposition for the HA was performed in the RF mode (13.56 MHz)

and for the Ti in the DC mode. A thin Ti layer (about 0.3 μm) was first deposited as an initial bond coat (precoat) onto Titanium alloy substrates and then followed by alternating deposition which Ti gradually decreased and HA simultaneously increased by controlling the input power. The relative motion between the target and the substrate was created by the pallet rotating at 20 rpm. A variety of alternating layers were coated onto the substrate only when the substrate passed the target underneath. Finally a 2 μm thick HA was fast deposited on the alternating layer at 300 W RF discharge-powers.

B. Inspection Methods:-

I. Scanning Electron Microscopy:-

- Starting up the instrument

There are two things you will have to do before inserting the sample in the specimen chamber;

  - Turn on the computer screen and enter the access code.
  - Change the filament current to appropriate current, see instruction next to the SEM.
- Inserting the specimen
  - Vent the specimen chamber.
  - Put on gloves.
  - Mount the specimen on the specimen stage using tweezers.
  - Pump the specimen chamber.
  - Wait for adequate vacuum
  - Turn on the high tension.
- Recording an image
  - Center the beam at the crossover.
  - Start with a low magnification, focus the image and identify the specimen.
  - Center the beam again, this time using gun tilt without crossover
  - Adjust contrast and brightness.
  - Increase the magnification stepwise, focus after each step.
  - Correct for astigmatism.
  - Choose an appropriate magnification, make final adjustments (focus, astigmatism) and record an image (digital).

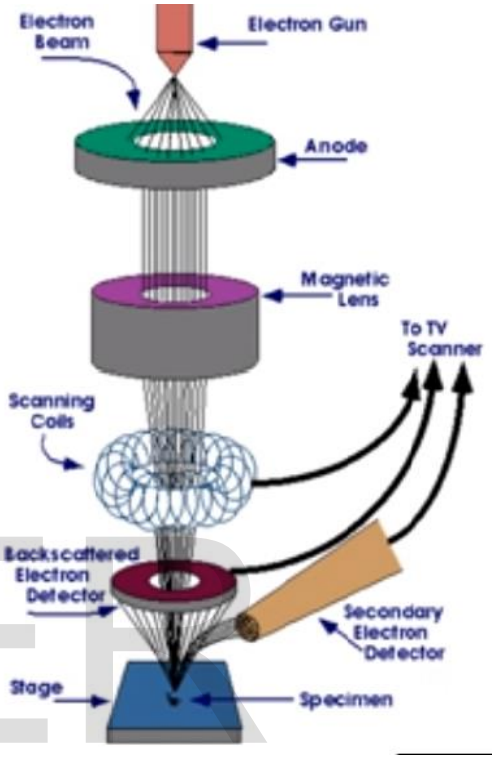

Fig:- Scanning Electron Microscope

II. X-ray Diffraction:- (Powder Method)

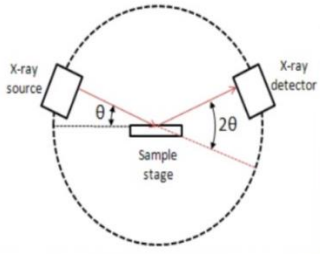

Fig:- Powder XRD Method

- Turn on the X-ray machine.
- The settings of the X-ray source power supply have to be manually set, and might need to be modified according to the results obtained.

- Check the calibration of the computerized goniometer by analyzing the position of peaks in a Silicone powder sample.
- Place the Si powder sample on a glass slide in the sample holder.
- Set the scan options in the Datascan software.
- After taking your scan, use MatLab software (or another software program of your choice) to locate the peaks.
- Compare the locations of these peaks to the standard values for Silicone powder.
- Determine any systematic errors of these differences in 2θ and determine their average value. Any offset determined from the calibration can be taken into account in subsequent scans of unknown samples.

III. Atomic Force Microscopy:-

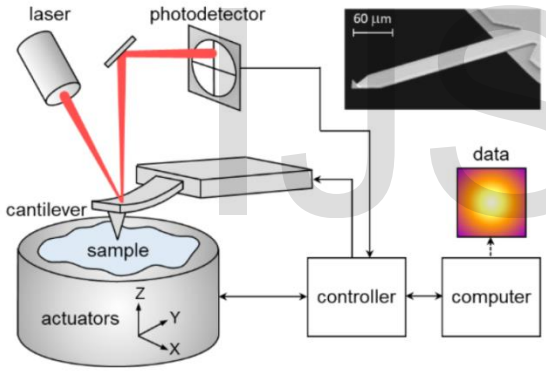

Fig:- Atomic Force Microscopy

The general approach to imaging is to:

- Set the overall output signal range and offset while in the z-mod regime,
- Stop the z-mod scan and engage the probe with the surface,
- Carefully adjust the cantilever deflection to give the desired bias point,
- Start the image scan.

Correct biasing is key to obtaining good images. The sensitivity should be greatest when the probe is engaged, and exerting a small force on the surface.

Use the stereo-microscope (at moderate magnification) and a fiber-light to observe the tip and position it as well as you can. Temporarily turning off the sensing laser will make it easier to see. You can move the sample "on the fly", as you're imaging.

IV. Energy Dispersive Spectroscopy:-

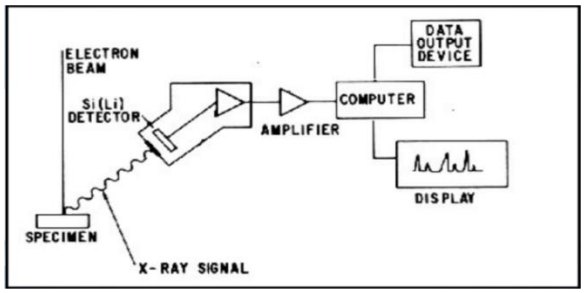

Fig:- EDS System Schematics

Energy dispersive X-ray spectroscopy (EDS) is a chemical microanalysis technique that, is typically performed in conjunction with an SEM. The EDS technique utilizes X-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analyzed volume on a micro- or nano-scale.

In an SEM, an electron beam is scanned across the sample surface and generates X-ray fluorescence from the atoms in its path. The energies of the X-ray photons are characteristic of the element which produced it. The EDS X-ray detector measures the number of emitted X-rays versus their energy. The energy of the X-ray is characteristic of the chemical element from which the X-ray was emitted.

By determining the energies of the X-rays emitted from the area being excited by the electron beam, the elements present in the sample can be determined. This mode of operation is called

qualitative analysis since only the types of elements in the sample are determined. The rate of detection of these characteristic X-rays can also be used to measure the amounts of elements present. This mode is called quantitative analysis. If the electron beam is swept over an area of the sample, then the EDS systems can also acquire X-ray maps showing spatial variation of elements in the sample.

V. Hardness Test:- (Brinell Hardness Tester)

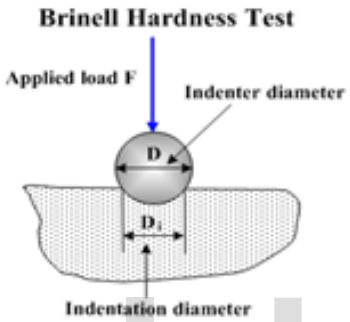

Fig:- Brinell Harness Test

- Insert ball of diameter 'D' in ball holder of the m/c,
- Make the specimen surface clean by removing dust, dirt, oil and grease etc.,
- Make contact between the specimen surface and the ball by rotating the jack adjusting wheel,
- Push the required button for loading,
- Pull the load release level and wait for minimum 15 second. The load will automatically apply gradually,
- Remove the specimen from support table and locate the indentation so made,
- View the indentation through microscope and measure the diameter ‘d’ by micrometer fitted on microscope.
- Repeat the entire operation for 3 times.
- Brinell Hardness Number can be obtained from tables 1 to 5 in IS:1500, knowing diameter of indentation, diameter of ball and load applied.

VI. Elastic Modulus:- (Universal Testing Machine)

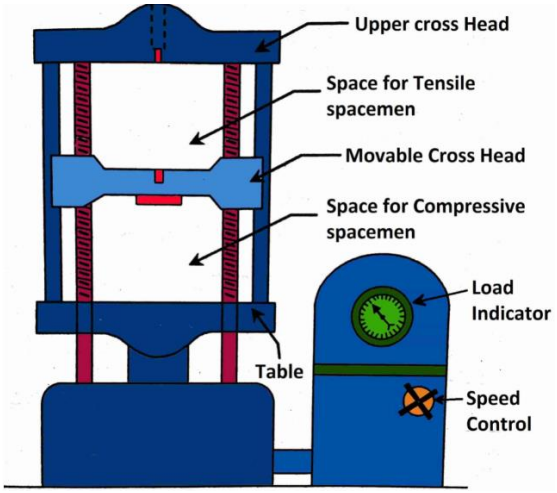

Fig:- Universal Testing Machine

- Adjust the supports alone the UTM bed so that they are symmetrically with respect to the length of the bed,
- Place the beam on the knife-edges on the blocks so as to project equally beyond each knife-edge. See that the load is applied at the centre of the beam,
- Note the initial reading of vernier scale,
- Apply a load and again nee the reading of the vernier scale,
- Go on taking reading applying load in steps each time till you have minimum 6 readings,
- Find the deflection (δ) in each time by subtracting the initial reading of vernier scale,
- Draw a graph between load (W) and deflection (δ). On the graph choose any two convenient points and between these points find the corresponding values of "W" and "δ". Putting these values in the relation find the value of E.
- Formula for Young’s Modulus of Elasticity is,

$$E = \frac{Wl^3}{48\delta I}$$

VII. Fatigue Test:- (Universal Tester)

- Measure the dimension of the test piece and inspect the surface roughness.

- Fix the test piece to the testing machine
- Set the test parameters and begin the test.
- Instructions on how to operate the testing machine is available on the machine manual.
- Test two specimens for each load value.
- Collate the results and record the testing parameters and testing conditions
- After obtaining the results for your load cases, plot stress against logN on a suitable graph paper and look for best fit lines and also determine the safe stress level if a fatigue life of 1,000,000 reversals had to be withstood.

Fig:- Universal Tester

VIII. Surface Roughness:- (Surface Profilometer)

Fig:- Surface Profilometer

- Since the individual roughness irregularities are too small to see with the naked eye and a roughness measuring instrument is required.
- A small stylus is drawn across the surface at a constant speed for a set distance.
- An electrical signal is obtained and amplified to produce a much-enlarged vertical magnification.
- This signal may be displayed on both graph and screen outputs, together with numerical values that characterize the surface texture.
- The ISO standard for roughness measurements is a 60° or 90° conical stylus with a spherical tip of 2µm radius. However, this is quite a delicate stylus, and needs an instrument with excellent mechanical properties to fully exploit it.

IX. Electrochemical Impedance Spectroscopy:-

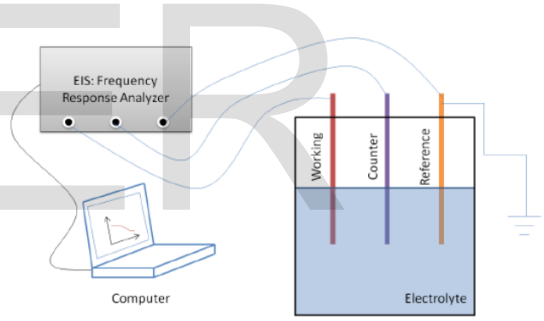

Fig:- Experimental EIS Setup using three electrode method

An electrochemical cell is used to house the chemical reaction and is electrically connected to the electrochemical spectrometer to obtain the electrical response of an electrolytic solution. EIS systems are operated using computer programs specifically designed for EIS testing. Therefore, prior to conducting an EIS experiment it is essential that all components of the system be attained.

Generally, EIS studies utilize a three electrode mode which is comprised of a working electrode (the sample material), a counter electrode

(commonly graphite or platinum), and a reference electrode. While electrode geometries may vary the general experimental setup remains similar to the procedure outlined below.

The three electrodes are mounted on an electrode stage and secured. The electrolytic solution is prepared and transferred to the sample container. A metallic sample container would provide additional pathways for electrons during experimentation leading to a reduction in the EIS current response as electrons move into the metal rather than the reference electrodes. Therefore, the sample container should be composed of an insulating material, such as glass or plastic, which will not interfere with the transfer of electrons during testing. The electrode mount is then placed on the sample container such that a portion of each electrode is submerged in the electrolytic solution.

Four leads are used to attach the three electrodes to the EIS frequency response analyzer. A working lead and a counter lead are used to carry current, whereas the working sense lead and reference leads are used to sense voltage. The working lead and working sense lead connect the exposed end of the working electrode to the EIS. The reference lead is attached to the reference electrode and the counter lead is connected to the counter electrode. The fourth lead is recommended to ground the system during testing. Once all leads are connected, the EIS system is setup and ready for testing.

X. Open Circuit Potential:-

Open circuit potential (OCP) refers to the difference that exists in electrical potential. It normally occurs between two device terminals when detached from a circuit involving no external load.

It is the potential in a working electrode comparative to the electrode in reference when there is no current or potential existing in the cell. Once a potential relative to the open circuit is made present, the entire system gauges the potential of the open circuit prior to turning on the cell. This is followed by the application of potential relative to the existing measurement.

Open Circuit Potential (OCP) is a passive experiment. By passive, the counter electrode (necessary to pass current through the cell) circuitry of the potentiostat is bypassed. In this mode, only the resting potential measured between reference and working electrode is measured.

This is not to say that the chemical system is at equilibrium. In fact, some systems may be far from equilibrium and their passive potential changes as a function of homogeneous reactions. What makes OCP unique is that is a purely electrolytic measurement, thermodynamically.

While measuring OCP is a benign task for a potentiostat, it can still be a useful experiment. Since, either by disconnecting the counter electrode or by placing a very high impedance resistor in its path as to prevent current passage, the OCP is simply the potential difference between working and reference electrode.

3. RESULT AND DISCUSSION

By examining and analysing the content in the research papers we come to the result that only using a Titanium alloy Material without coating is not suitable for the implants. A suitable coating material is required for isolating implant base material from the body to reduce or eliminate the adverse effect occured by only using the base material. Hydroxyapatite with Ca/P ratio of 1.67, possess the most similar chemical composition to the bone. So it is suitable as a coating material. The multilayered Hydraxyapatite and Titanium coating have high corrosion resistance, high adhesion strength and showed a better electrochemical behaviour than a monolithic Hydroxyapatite coating. The research works also showed that by

heat treated samples has higher corrosion resistance and improvement in nanomechanical and adhesion properties than the as deposited and uncoated samples.

4. CONCLUSION

By analyzing the various research works we come to conclusion that a multilayered Hydroxyapatite coating on the substrate material showed a high corrosion resistance, improved electrochemical behaviour and high adhesion strength and by heat treating the coated material the nanomehanical, adhesion and corrosion resistance properties improved further

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