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Enhancement of Osseointegration and Antimicrobial Property of Titanium Alloy by the Application of Coating

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Abstract— The target is to develop implant material and investigate it by various inspection techniques so that it serves for much longer period or until lifetime without failure or revision surgery. Thus, development of appropriate material with high longevity, superior corrosion resistance in body environment, excellent combination of high strength and low Young´s modulus, high fatigue and wear resistance, excellent biocompatibility and be without cytotoxicity is highly essential. To avoid problems associated with Ti alloys and to enhance biocompatibility, Hydroxyapatite (HA)-Silver (Ag) composite coating is need to apply. Hydroxyapatite (HA) is a calcium phosphate, which has a high osseointegration due to its chemical similarity with bone mineral and Silver (Ag) is quite an attractive element for this purpose since it has broad antimicrobial spectrum. This project is focused on the Enhancement of osseointegration and antimicrobial property of Titanium alloy by the application of coating.

Index Terms— Titanium Alloy, Hydroxyapatite (HA), Osseointegration, Biocompatibility, Inspection Techniques, Cytotoxicity, Magnetron Sputtering.

INTRODUCTION

Bone and its few related components acts as utilitarianorgan. Long bones of the skeletonframework are prone to injury, and internal or external fixation is part of their treatment by the implants of biomaterials. Biomaterials are manufactured materials that are utilized to reestablish or replace the loss or failure of a biological structure. The materials used as implants are supposed to be highly non-toxic and ought to not cause any side-effectsor unfavorably susceptible responses within the human body. The Ti-6Al-7Nb alloy was specially created to replace the well-known Ti-6Al-4V alloy in biomedical applications due to supposed cytotoxicity of vanadium in the human body.In numerous of these combinations, non-toxic but heavy alloying elements like niobium, zirconium and tantalum are particularly employed. The superficial properties that are broadly wanted in surgical implants, such as Osseointegrationand bactericidal character, can not be provided by one material. Thus the composite coating is rising as a great alternative to improve required properties. Composite coating will help to improve the desired properties and biocompatibility of base metal and also makes it suitable for surgical implants. The new generation implants, aluminium and niobium alloy (Ti6Al7Nb) are characterized not only by high strength, low modulus and low density. They are also resistant to mechanical and biological corrosion, are characterised by high biocompatibility and low toxicity. Ti6Al7Nb has higher corrosion resistance and biotolerance in relation to Ti6Al7Nb. However the strength of Nb alloy is little less than Ti6Al7Nbbut it has all needed properties for biomedical implants. To avoid problems associated with Ti alloys and to enhance biocompatibility, Hydroxyapatite (HA) – Silver (Ag) composite coating is need to apply.

Hydroxyapatite (HA) is a calcium phosphate, which has a high osseointegration due to its chemical similarity with bone mineral. For this reason it has been widely used as a component for implant manufacture. Silver (Ag) is quite an attractive element for this purpose since it has broad antimicrobial spectrum. The combination of both bactericidal and osseointegration properties in HA-Ag composite coatings makes them attractive for potential use in the biomedical field. In the present work, a multilayer of HA-Ag is to deposited on a Ti6Al7Nb alloy; the effect of incorporation of the coating bilayer is being studied by different processes.

Substrate or Base Material- Low elastic modulus Titanium alloy (Ti6Al7Nb)
Coating Material - HA-Ag Composite
Coating Process - Magnetron Sputtering (MS)

BASE MATERIAL OR SUBSTRATE

For biomedical applications, titanium is favoured by low density, prevalent biocompatibility and elastic modulus lower than other metallic biomaterials such as precious metals, Co-Cr alloys and austenitic stainless steel. The early applications of elemental titanium as biomaterial date back to the nineteen fifties. In this way, the titanium workhorse Ti-6Al-4V alloy was embraced since the standard approach taken for the presentation of orthopedic materials has involved adaptation of existing materials. Recently, vanadium-free titanium alloys were created due to the potential cytotoxicity and adverse reaction of vanadium with the body tissues. In many of these alloys, non-toxic but heavy alloying elements like niobium, zirconium and tantalum are specifically used. A typical example is the Ti-6Al-7Nb alloy constructed by forging bulk material for hip prosthesis stems which was developed by Semlitsch et al. in the nineteen eighties.
The mostly used alloys in biomedical fields are Ti6Al4V and Ti6Al7Nb. All physical properties (Table 2) of the Ti6Al4V and Ti6Al7Nb are somewhat similar and do not show any major difference in the applications except for one major drawback of the alloy Ti6Al4V which is vanadium poisoning over long periods of time and also the cytotoxicity. Hence we've reached the conclusion that even though Ti6Al7Nb lacks a little bit in a couple of properties, it doesn't affect the durability or the performance of the implants and also overcomes the major drawback of the Ti6Al4V alloy.

Table 1. Property Comparison of Major Implant Alloys

Metals	Main alloying composition (wt%)	Mechanical properties*				
		YS (MPa)	UT (MPa)	YM (MPa)	Max elongation (%)	Hardness(MPa)
Stainless steel: 316L type	Fe; 16-18.5Cr; 10-14Ni; 2-3Mo; <2Mn; <1Si; <0.003C	206	689	193	45	95
CoCr alloys: CoCrWNi	Co; 19-21Cr; 14-16W; 9-11Ni	310	860	210	20	550-800
CoNiCrMo	Co; 33-37Ni; 19-21Cr; 9-10.5Mo	241	793	232	50	
Ti and its alloys: Pure Ti grade 4	Ti; 0.05N; 0.1C; 0.5Fe; 0.015H; 0.4O	485	550	110	15	250
Ti6Al4V	Ti; 5.5-6.75Al; 3.5-4.5V; 0.08C; 0.2O	862	931	116	10	3730
Ti6Al7Nb	Ti; 5.5-6.6Al; 6.5-7.5Nb; 0.08C; 0.2O	900	995	110	12	290
Degradable metals: Pure iron	99.8Fe	150	540	200	40	79
WE43 magnesium alloy	Mg; 3.7-4.3Y; 2.4-4.4Nd; 0.4-1Zr	150	250	44	4	105

From Above Property Table, suitable and high end qualities for implants and biomedical uses are displayed broadly by Ti alloys, hence we choose alloy metal of Ti group. There are two alloys in Ti alloy group which are majorly used for biomedical implants.

Table 2. Properties of Ti6Al7Nb and Ti6Al4V

Property	Mini. Value	Max. Value	Min. Value	Max. Value	Unit(S.I)
Density	4.51	4.53	4.429	4.512	Mg/m^3
Bulk Modulus	111	142	96.8	153	Gpa
Compressive Strength	1074	1086	848	1080	Mpa
Ductility	0.1	0.15	0.05	0.18	
Elastic Limit	895	905	786	910	Mpa
Fracture Toughness	68	75	84	107	$MPa.m^{1/2}$
Hardness	2700	2900	3370	3730	Mpa
Tensile Strength	995	1005	862	1200	Mpa
Youngs Modulus	100	110	110	119	Gpa
Maximum Service Temp.	600	650	620	690	K

Graph, Shows nearly equal weight loss during wear sliding against abrasive paper.

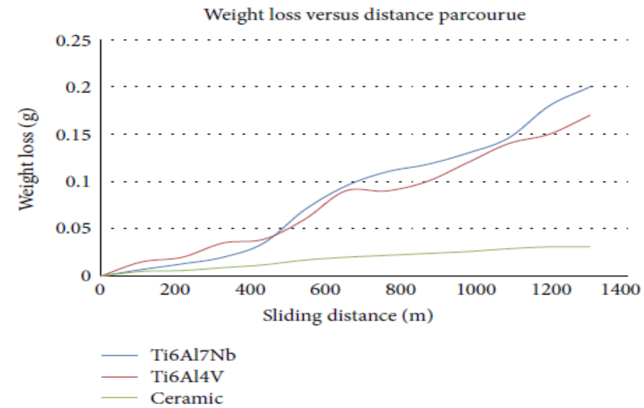

Fig. 1 Weight loss of Ti alloys during wear sliding against abrasive paper

EXPERIMENTAL WORK

Coating Process-

A magnetron is placed near the target in sputtering processes. Then, in the vacuum chamber, an inert gas is introduced, which is accelerated by a high voltage being applied between the target and the substrate in the direction of the magnetron, producing the release of atomic size particles from the target. These particles are projected as a result of the kinetic energy transmitted by gas ions whose have reached the target going to the substrate and creating a solid thin-film. Being a clear depositon process, sputtering permits a better densifcation, and reduce residual stresses on the substrate as deposition occurs at low or medium temperature. Also gives high homogeneity, compaction and purity.

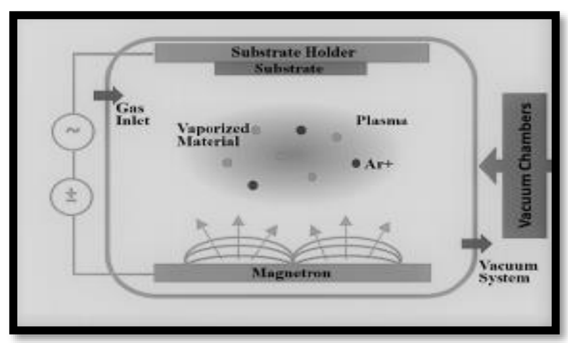

Fig. 2 Magnetron Sputtering Process

Various Techniques to Inspect Coating Material-Surface Characteristics Test

1. **SEM (Scanning Electron Microscopy)-**

SEM is a method for high resolution surface imaging. The SEM uses electrons for imaging, much as light microscopy uses visible light. The advantages of SEM over lightmicroscopy include greater magnification (up to 100,000X) and much greater depth of field. Different elements and surface topography emit different amounts of electrons; the varying amount of electrons are responsible for the contrast in the electron micrograph (picture) which is representative of surface topography and composition.

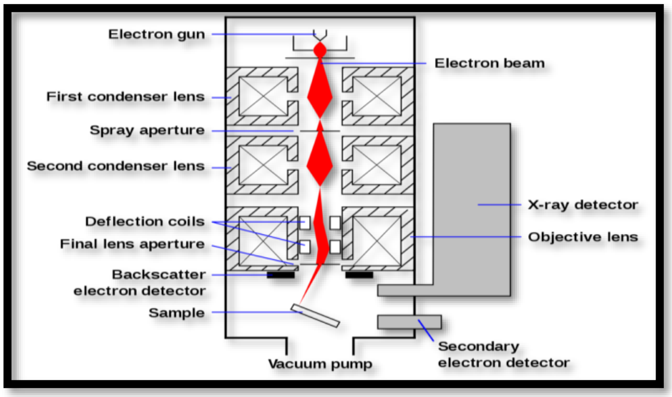

Fig. 3 SEM (Scanning Electron Microscopy)

2. XRD (X-ray Powder Diffraction)-

X-ray Diffraction (XRD) is a nondestructive technique for characterizing crystalline materials. In XRD analysis a collimated X-ray beam of known wavelength hits the test sample. The crystalline parts of the materials exhibit three dimensional long range order of repeat arrangements of atoms (unit cells). The 3D unit cell ordering forms crystal lattices that diffract X-rays. X-ray diffraction occurs at specific angles with respect to the lattices spacing defined by Bragg Law and the result of an x-ray diffraction analysis is a diffractogram a plot of diffraction peak intensities versus the angles of diffraction. The lattice spacing and crystal structure parameters can be determined from the plot. The response of amorphous, not ordered materials or domains in XRD is characterized by broad low intensity signals. If the material is completely amorphous no peaks will be observed in XRD. XRD is unique in providing a wide variety of information on crystal structures, crystalline phases, preferred crystalorientations (texture), and other structural parameters such as crystallite size, percent crystallinity, strain, stress, and crystal defects.

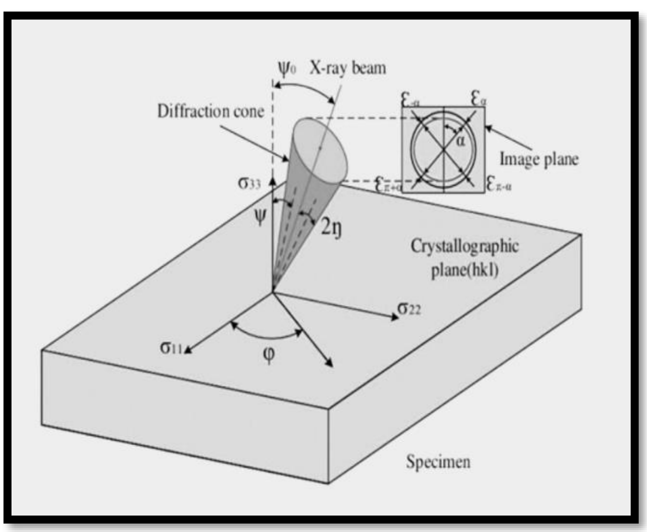

Fig. 4 XRD (X-ray Powder Diffraction

3. EDS (Energy-dispersive X-ray spectroscopy)-

Energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. Energy dispersive spectroscopy (EDS) measures the number of x- rays produced by a solid sample when irradiated by electrons versus the energy of these x-rays. The EDS technique identifies and quantifies the element constituents of the sample.

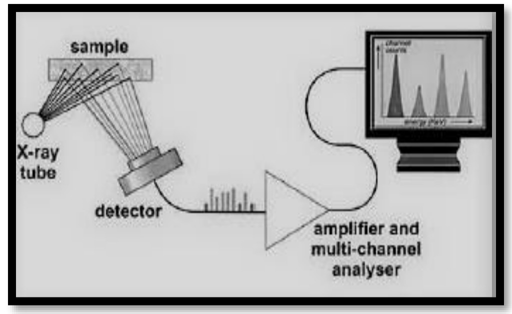

Fig. 5 EDS (Energy-dispersive X-ray spectroscopy)

4. Surface Roughness

The roughness of a surface has most commonly been measured by an instrument in which a stylus travels across the surface, the movement of the stylus is amplified and the signal recorded. The result is generally expressed as Ra or average roughness and is the arithmetic average value of the deviation of the trace above and below the centre line. The value of Ra normally measured in micrometer. Surface roughness is a measure of the texture of a surface. If these deviations are great, the surface is rough, if they are small, the surface is smooth. Roughness is typically considered to be high-frequency, short wavelength component of a measured surface. In practice, it is often to know both the amplitude and frequency to ensure that a surface is fit for purpose.

Mechanical Test

1. Hardness Test

Hardness Test by Vickers Test- The Vickers Hardness Test can be performed on both the micro and macro hardness scales with a maximum test load of 50 kilograms. This type of hardness test is also performed by applying controlled force for a specific amount of time to an indenter, which in this case is a square-based diamond pyramid. The impression measurement and test load are used in the appropriate formula to calculate the Vickers hardness value. Like Brinell and Knoop, this method has one scale that covers its entire hardness range.

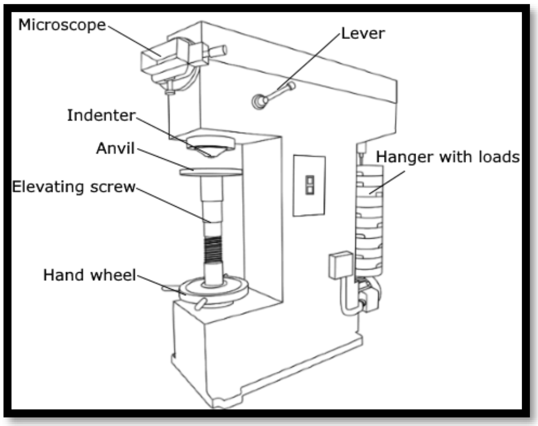

Fig. 6 Hardness Test

2. Elastic Modulus Test

Modulus of Elasticity, also known as Elastic Modulus or simply Modulus, is the measurement of a material elasticity. Elastic modulus quantifies a material resistance to nonpermanent, or elastic, deformation. When under stress, materials will first exhibit elastic properties: the stress causes them to deform, but the material will return to its previous state after the stress is removed. After passing through the elastic region and through their yield point materials enter a plastic region, where they exhibit permanent deformation even after the tensile stress is removed**.**

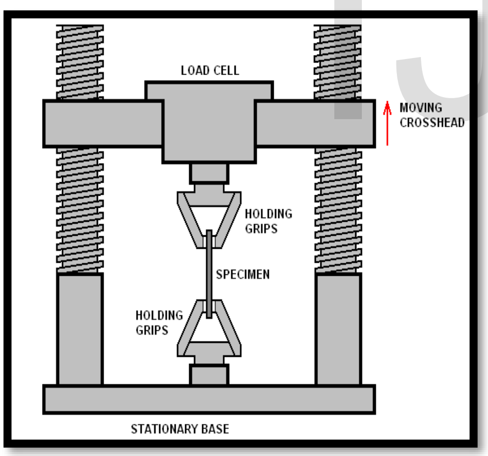

Fig. 7Elastic Modulus Test

3. Fracture Toughness

In this test force is applied to a pre-rack specimen. The intention of a fracture toughness test is to measure the resistance of a material to the presence of flaw in terms of the load required to cause brittle or ductile crack extention (or to reach maximum load condition) in a standard specimen containing a fatigue pre-crack.

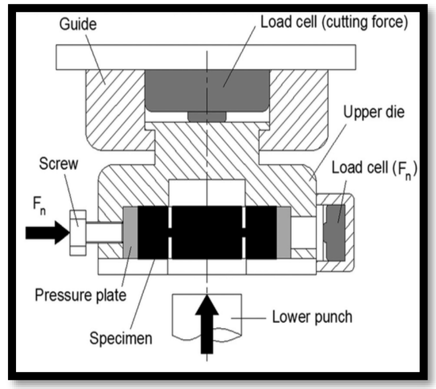

Fig. 8 Fracture Toughness

Electrochemical Test-

1. Open Circuit Potential (OCP)-

It is the potential where no current is flowing, because the circuit is open. Between two metals in the same solution the OCP is the highest potential difference possible without applying a potential from the outside. Measuring the OCP is also non-invasive, because no current is flowing. For most applications the OCP and other potentials will be measured versus a reference electrode. Due to the fact that potentials are additive, one can easily calculate what the potentials would be versus other reference electrodes. All metals with a positive standard potential versus SHE are noble metals. They are resistant to acid corrosion, because to corrode the protons of the acid need to be reduced to hydrogen and for that to happens the potential of the metal would need to be lower (more cathodic) than the potential of the proton reduction.

2. Electrochemical Impedance Spectroscopy (EIS)-

EIS is an electrochemical techniques to measure the impedance of a system in dependence of the AC potentials frequency. EIS is one of the most complex techniques in electrochemical research. EIS is very surface sensitive, which makes many changes visible that other techniques donâ€™t see, for example changes in polymer layers due to swelling, surface changes due to protein adsorption or penetration of corrosion protection layers. EIS is an the evaluation of electron transfer properties of the modified surfaces and in understanding of chemical transformation.

Conclusion-

The new generation implants, made of aluminium and niobium alloy (Ti6Al7Nb), are characterized not only by high strength, low modulus and low density but also by their high biocompatibility and low toxicity. The implants are resistant to mechanical and biological corrosion, making the alloy suitable for biomedical application. The composite coating helps in improving desired properties like biocompatibility of base metal and the combination of bactericidal and osseointegration properties in HA-Ag composite coatings makes them attractive for potential use in the biomedical field like surgical implants. This was also reinforced by cytotoxicity test which confirmed that the applied surface modification does not affect cell growth. The target of this project is development of implants that can serve for much longer period than currently available alloys do, or until lifetime without failure or revision surgery. Thus, development of appropriate material with high longevity, superior corrosion resistance in body environment, excellent combination of high strength and low young modulus, high fatigue and wear resistance, high ductility, excellent biocompatibility and be without cytotoxicity.

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