

BIOACTIVE COATINGS ON 316L STAINLESS STEEL IMPLANTS

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Abstract

Bioactive coatings on metallic implants facilitate joining between the prosthesis and the osseous tissue, and increase the long-term stability and integrity of the implant. Literature suggests that current coating techniques provide inadequate adherence of the coating to the implants. A processing schedule was developed that minimizes reactions and produces thin coatings with the substrate. Hydroxyapatite and biphasic calcium phosphate (combination of hydroxyapatite and tri-calcium phosphate) coatings were carried out on 316L stainless steel implant material by a simple dip-coating method. Prior to the coating the substrate surfaces were passivated. The dip-coated implant materials were subsequently heat treated at appropriate temperatures for improving coating adhesion to the substrate. The coated implant materials have been characterized by X-ray diffraction, scanning electron microscopy and adhesion test. The results show that the dip coated hydroxyapatite and biphasic coatings of thickness of about 5-7 micron strongly attach to the 316L stainless steel substrates.

Introduction :

Bioactive hydroxyapatite has a substantial interest because of its chemical similarity to the calcium phosphate minerals in biological hard tissue, and its ability to form a strong chemical bond with bone¹. But the fracture toughness of the hydroxyapatite ceramics does not exceed the value of about 1 Mpa.m^{1/2}. Therefore, the hydroxyapatite ceramic materials cannot be used as heavy-loaded implants, such as artificial bone or teeth. Metallic implants (316L stainless steel, titanium, Ti-6Al-4V, etc.) are having high strength and fracture toughness, but their bonding ability to bone tissue is very low. In order to obtain bioactive and strong materials, the formation of hydroxyapatite on an implant with good mechanical properties is considered a good approach. Biphasic calcium phosphate coating is preferred when implant resorbability is desired.

Coatings of hydroxyapatite on metallic implants have been prepared by a variety of techniques, including plasma spraying, sol-gel, r.f sputtering, detonation gun coating, high velocity oxy-fuel coating, electrophoretic deposition, laser ablation, hydrothermal and biomimetic methods. At present, plasma spraying is the most commonly used method for preparation of the hydroxyapatite coatings. However, plasma-spraying method suffers with hydroxyapatite phase stability, lack of crystallinity and poor adhesion to the substrate. The electrophoretic methods have problems with poor adhesion and formation of other phases. The r.f sputtering suffers with amorphous nature of the coating material. This paper describes a simple dip-coating method, which produces a thin and adherent HA and BCP coatings on 316L stainless steel.

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Materials and Methods :

Dip coating solution was prepared by using hydroxyapatite/biphasic calcium phosphate, glycerin, polyethylene glycol, ethanol and distilled water. Hydroxyapatite and biphasic calcium phosphate ceramic powders were synthesized by microwave processing². The 316L stainless steel disc substrates obtain from commercial medical supplier. The ingredients of the dip-coating solution and their weight percentages are given below :

1. Hydroxyapatite (microwave synthesis) - 7.3%
2. Ethanol (99.9%pure, Changshu Yangyuan Chemical, China) - 66.2%
3. Polyethyleneglycol 600 PEG (E Merck, India) - 2.2%
4. Glycerine. (98%pure, Finar Lab-Reagents, India) - 10.2%
5. Distilled water - 14.1%

The method of preparation of HA dip-coating solution was shown in the processing flowchart in Fig. 1.

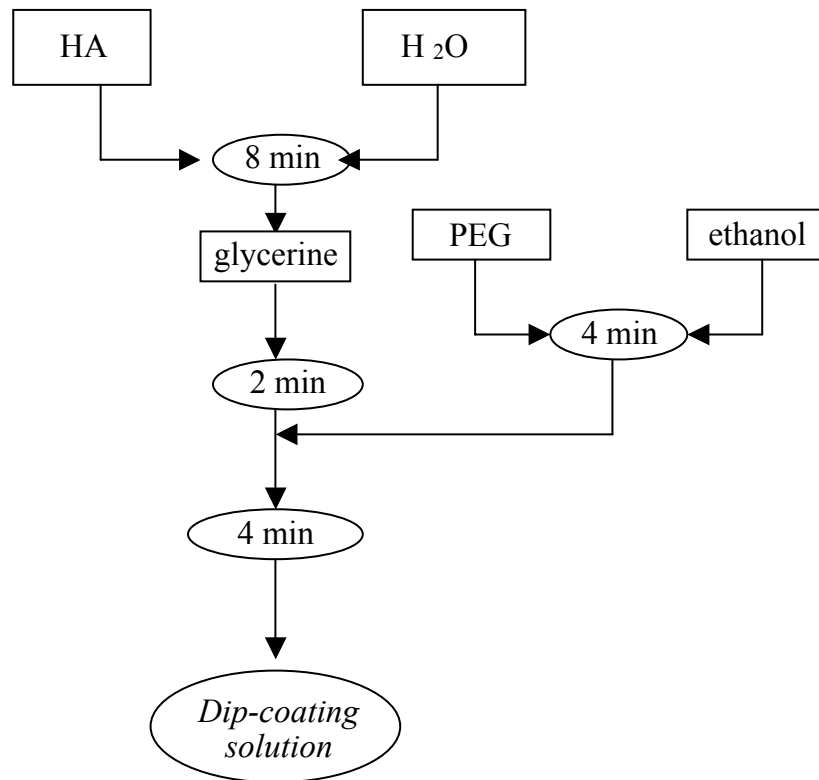


Fig. 1. Flowchart of the preparation of the Hydroxyapatite (HA) dip-coating solution.

The stainless steel substrate was annealed at 1080°C. After annealing the samples were subjected to surface passivation treatment, carried out in a solution of 20% HNO₃ for 15 min at 60°C. The 316L stainless steel disc samples were dipped into coating solution at 45° angles and withdrawn at a speed of 60-80mm/min. XRD of coated samples were performed by Shimadzu, X-ray diffractometer, using Cu K α radiation, for the

phase analysis. Scanning electron microscopy was done to examine the surface morphology, interfacial microstructure and to measure the thickness of the coatings. All samples were coated with a nanosize (5-20nm) gold film by sputtering. SEM examination was performed with a JEOL Scanning Electron Microscope (Model JSM-5300) with a beam voltage of 15 KeV. A qualitative adhesion test was carried out to measure the adhesion of a coating to the substrate. This test consists in determining whether or not the coating film peels off along with a strip of sticky tape pressed onto it and then pulled off. The 3M brand Scotch™ tape was used for the adhesion test.

Results and Discussion :

The XRD pattern of the hydroxyapatite coated 316L sample is shown in Fig.1. The XRD pattern clearly shows the major peaks of hydroxyapatite and stainless steel. Fig 3 is the XRD spectrum of biphasic calcium phosphate coated 316L sample. Fig 3 shows both hydroxyapatite and β -TCP peaks along with stainless steel substrate peaks. Scanning electron micrographs of HA and BCP coated stainless steel substrates are shown in figure 4 and 5 respectively. The surface morphology of the HA coating with the coating morphology appeared homogeneous and dense with some micro pores (Fig.4). The surface morphology of biphasic calcium phosphate coating as shown in fig 5 appeared homogeneous and rough. At higher magnification the coating surface showed some micro cracks due to shrinkage occurring during sintering process, this could supply points of “Mechanical Interlocking”²³ to promote osteointegration. These cracks do not influence the mechanical and adhesive properties of the coating, because they are not present in the cross section SEM micrograph as discussed below. The cross section micrographs of HA and BCP coating are shown in Fig 6 and Fig 7 respectively. The interface clearly gives an evidence of a well-deposited uniform thin film of well coatings. As expected, the coating covers entire surface of the substrate. A thickness of about 5-10 μ m is estimated for both HA and BCP coatings. The cross section examination reveals no detectable cracks; it is therefore reasonable to assume that the micro cracks observed on coating surface are limited in population and present on the surface. The XRD pattern of HA and BCP coated samples, after adhesion test are shown in Fig 8 and Fig 9 respectively. This indicates that the true bonding at the coating substrate interface should be stronger than that of high strength sticky tape.

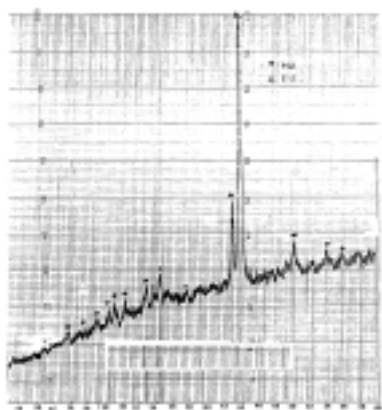


Fig. 2. XRD pattern of HA coated sample

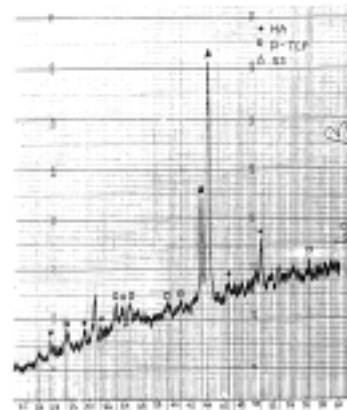


Fig. 3. XRD pattern of BCP coated sample

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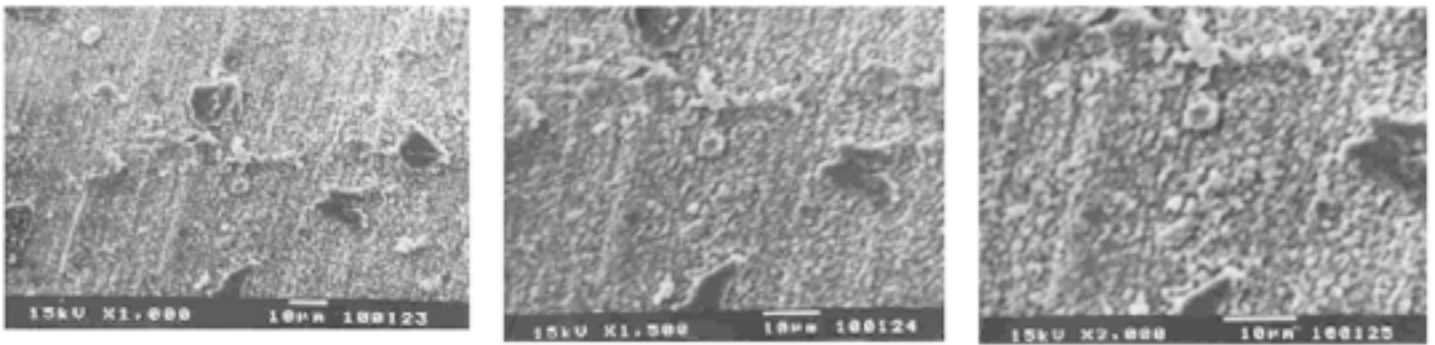


Fig. 4. Scanning electron micrographs of HA coated sample at 1000X, 1500X and 2500X

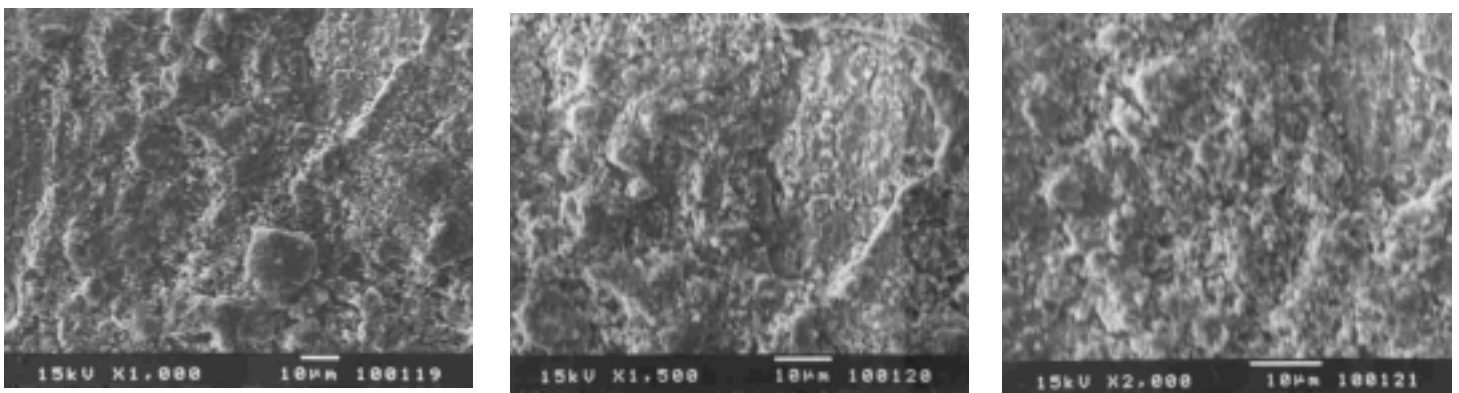


Fig. 5. Scanning electron micrographs of BCP coated sample at 1000X, 1500X and 2500X

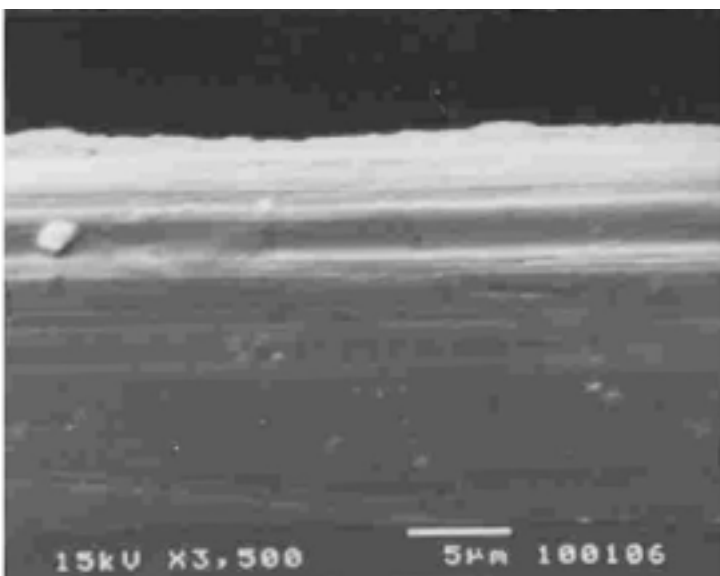


Fig. 6. Cross-section view of HA coated sample

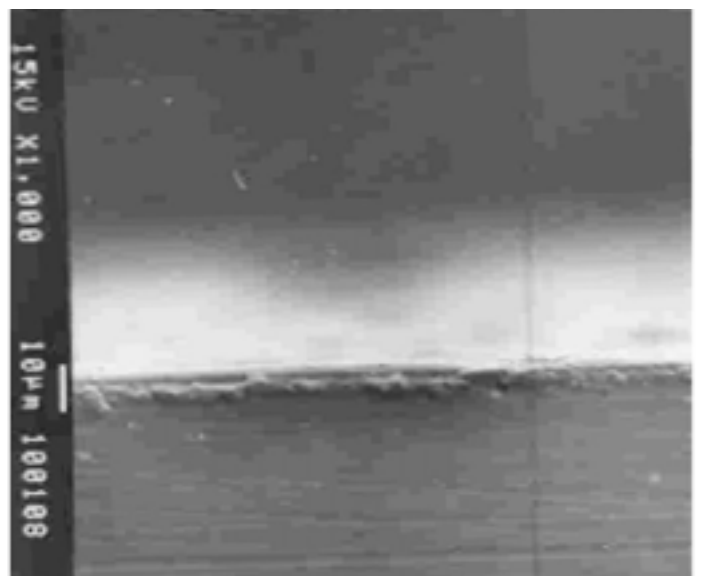


Fig. 7. Cross-section view of BCP coated sample

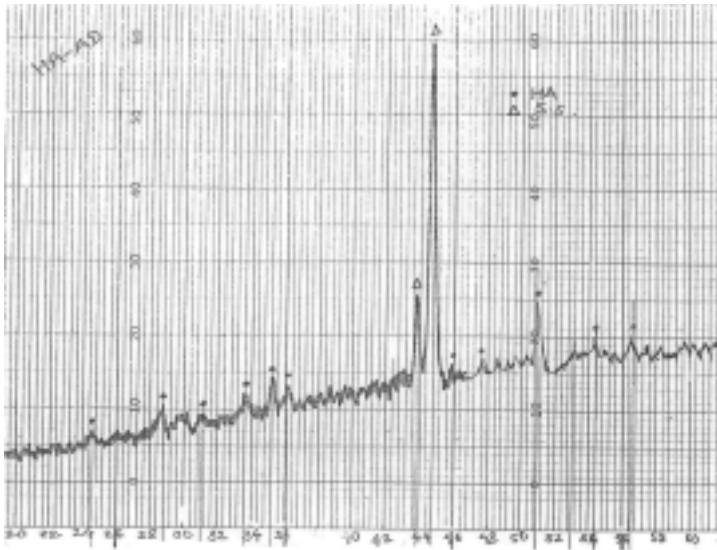


Fig. 8. XRD pattern of HA coated sample after adhesion test

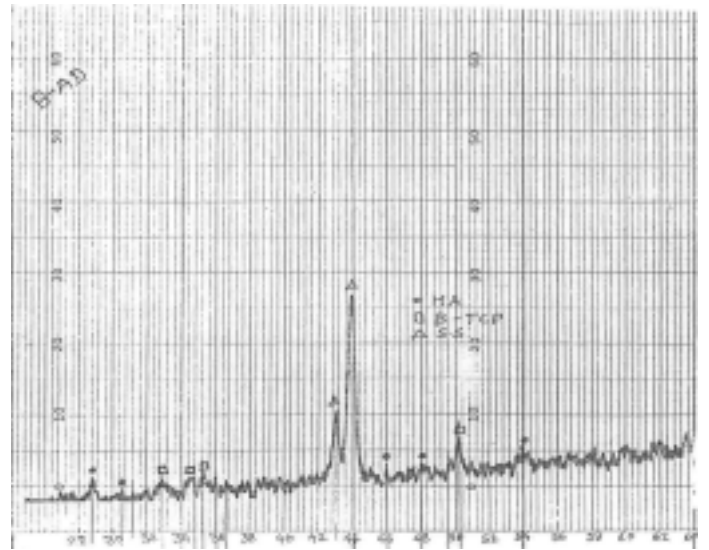


Fig. 9. XRD pattern of BCP coated sample after adhesion test

Conclusions :

- a) Dip coating is a simple method to produce hydroxyapatite or biphasic calcium phosphate coating on stainless steel substrates.
- b) The dense, fracture free coating can improve adhesion with the substrate and also acts as barrier layer between implant surface and body fluids.
- c) By dip-coating method, its possible to obtain a very thin coating of thickness 5-10 (m for both hydroxyapatite and biphasic calcium phosphate coatings on 316L stainless steel.

References :

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