

XRD analysis of calcium silicate coating on titanium alloy

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Abstract

Application of calcium silicate gel is an effective and simple method in forming a well-defined apatite layer over a metallic surface. This paper describes a method to produce bioactive coatings on the surface of titanium alloy substrate. It is a biomimetic approach for coating hydroxyapatite on titanium alloy at ambient temperature. In the present study, coating is obtained by the use of CaO-SiO₂ based glass as a possible source of nucleating agent of apatite formation. Ca-P is known to be one of the precursors during the bone mineralization process thereby it is of promising approach of biomimetic coatings for orthopaedic surgery. XRD results confirm the different phases are present in the coating. Scratch test results reveal the required adhesion strength of coating on titanium alloy.

Keywords: Calcium silicate gel, titanium alloy, XRD tests, biomimetic coatings.

Introduction

Biomaterial research activities have attracted the study of bone, due to its intricate design for which bone shows excellent mechanical properties. Bone is stiff and tough but lightweight material. This unusual combination of properties has been resulted from its nano composite structure of approximately equal volumes of mineral and hydrated organic materials. The biomimetic process allows the formation of apatite film after immersion in simulated body fluid (SBF) solution on calcium silicate coated metal implant. Films deposited onto the surface of metal implant exhibited chemical composition closely to bone (Oyen Michelle, 2008). Presently, research interest also catches the attention on thin coating or scaffolds for bone tissue engineering. However, biomimetic field research on bone extra cellular matrix is taken as a model for materials development. The compatibility of inorganic materials with living tissues and biological fluid is crucial in biomedical applications. At present, most of the materials used in medical implants are bio-inert *i.e.*, they do not interact with living systems. This is ideal mechanical substitutes for replaced body parts, such as artificial hips. Titanium substrates have been used till now for tooth and bone implants (Vasheashta *et al.*, 2005). Silicon is considered to be an essential structural element and plays important role for production and maintenance of connective tissue in higher organisms. Porous silicate material has been shown to be an excellent biomaterial with amazing bio-stability and non-toxicity (Shi Xuentao *et al.*, 2008). Calcium silicate ceramics can be used as a bioactive material in the field of biomedical applications. Porous structures of calcium silicate have been found to allow fast deposition of hydroxyapatite (HA) layers or formation of apatite film with strong bonds to the surface and good osteo-integration (Narayan *et al.*, 2004). HA evolved at physiological conditions exhibited structures closely resembling those of bone mineral (Xu Songfeng *et al.*, 2008). HA crystals have been deposited on titanium alloy substrate by sol-gel method. HA has been widely used in bone implant in biomedical field because of their

favourable biocompatibility and osteoinductive properties. Many studies have been conducted using HA coatings on metal implants to combine the biocompatibility of ceramics. HA plasma-sprayed coating on titanium alloy substrate is successfully used for joint reconstruction. However, the plasma-spraying technique presents some drawbacks. It is not possible to evenly deposit HA coating on porous implants and not possible to deposit HA at high temperature because they decompose at high temperature (Barrere *et al.*, 2001). Titanium and its alloy are widely used as orthopaedic and dental implant materials due to their good biocompatibility and corrosion durability. However, bone does not bond directly to these materials as they get encapsulated by fibrous tissue after implantation, which isolates them from the surrounding bone (Saiz & Tomsia, 2008). HA coating by plasma spraying is limited due its high processing temperature as mentioned earlier. Moreover, this process cannot provide uniform coatings on porous metal surfaces and often closes the minute but essential surface features (Shi *et al.*, 2008). Biomimetic process is one of the most promising techniques for producing a coating at ambient temperature, overcoming the drawbacks of plasma-spraying (Bharati *et al.*, 2005).

This paper investigates a biomimetic approach for coating HA on titanium alloy substrates by using a calcium silicate based glass as a source of nucleating agent for apatite formation on the surface at ambient temperature.

Experimental

Materials processing

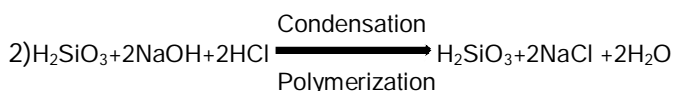
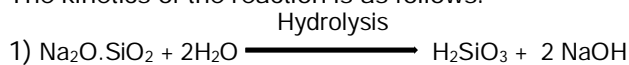
Commercial grade purity Titanium (Ti) substrates having chemical compositions 0.03% N, 0.10% C, 0.015% H, 0.18% O, 0.20% Fe and 0.5% others by weight. The samples were cut into blocks measuring the size 20 mm x 15mm x 5mm, for the coating deposition. The surface was mechanically polished with emery papers consecutively with grit sizes up to 1200 in steps. The surface was then washed with ethanol, for half an hour and then the substrate was dried at 45°C. The

samples were kept in the desiccators until application of the coatings.

Synthesis of calcium silicate

Calcium silicate was prepared by gel method. Calcium silicate was obtained by reacting calcium oxide and silica-gel. Sodium metasilicate was used as a silica source. Conc. HCl was used as a catalyst source to carry out the reaction. 50 gms of sodium metasilicate was dissolved in 330 ml of distilled water at room temperature with magnetic stirring, giving a transparent clear viscous solution. To this solution 33.04 gms of conc. HCl was quickly added with vigorous glass rod stirring to get a white viscous gel. The white gel obtained was further stirred with rotors for 24 hours. Condensation polymerization took place to form a silicic acid. The solution pH=7.2 were maintained. The resulting gel was washed twice with single distilled water and ethanol to remove sodium chloride formed during the reaction. Ethanol was used to maintain the porosity and viscosity of the silica gel.

The kinetics of the reaction is as follows:



Now in the silica gel solution, 30 gm of calcium oxide was mixed with rotor (stirring). In the resulting solution 30 gm of conc HCl was added quickly for maintain the pH (because reactants calcium hydroxide and sodium silicate are very alkaline) with vigorous stirring for again 24 hours. A white gel of calcium silicate was obtained which was washed with single distilled water twice.

The kinetics of the reaction is as follows:



To get the crystalline powder of calcium silicate, the washed resultant solution was dried at 150°C. The dried calcium silicate gel was confirmed experimentally by XRD analysis.

Deposition of calcium silicate gel by dip coating method

Total immersion dip coating method is generally used for the deposition of calcium silicate gel coatings onto the substrates surface. The substrates were coated by dipping it into calcium silicate gel. The gel was flown out at constant rate after film deposition. The thickness coating depends upon the viscosity of gel and dipped time. The coatings were air-dried in a laminar flow hood in a clean room. The air dried sample was further dried at 110°C to remove the water molecules from the coating. The heat treatment at 750°C was given to the coated sample for 45 minutes. This heat treated coated sample was then soaked into stimulated body fluid for 72 hours at normal room temperature. Drying the gel by means of low temperature treatments to high temperature (25-100 °C), it is possible to obtain porous solid matrices called xerogels. It is important to remember that morphology

and thickness of the coatings depend upon viscosity of gel, aging of gel, withdrawal rate of sample and sintering temperature.

The coating process usually consists of 4 steps: (1) The desired colloidal particles once dispersed in a liquid to form a sol. (2) The deposition of sol solution produces the coatings on the substrates by dipping. (3) The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network. (4) The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

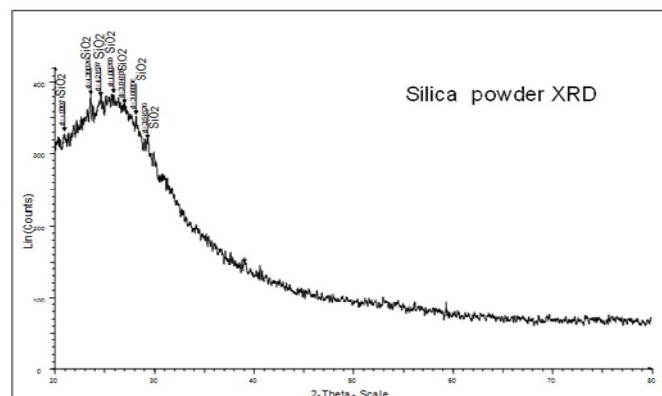
Results and discussion

Calcium silicate coating was developed on the titanium substrate by dip coating method and subsequent heat treatment of the substrate stabilises the CAS coating on the substrate by diffusion bonding. Further, via biomimetic process apatite layer was formed on the surface on the CAS coated titanium substrate. The experimental observations were studied by X-ray diffractometer (XRD). Coating hardness and coating strength were measured by the scratch test method.

X-Ray diffraction analysis

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal informations about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for

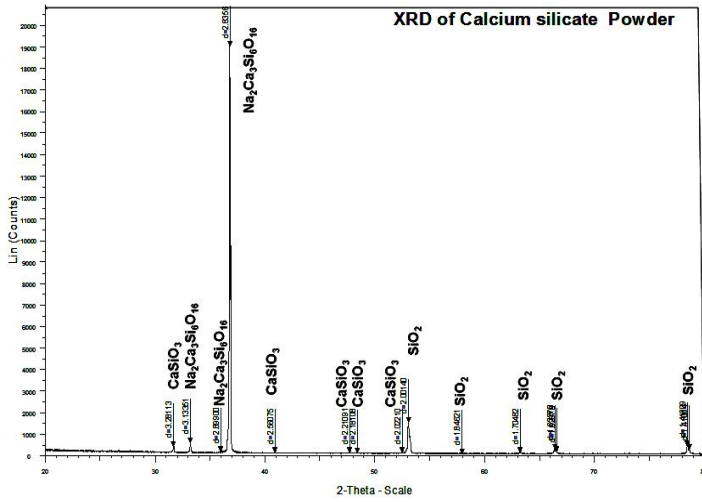
Fig. 1. X-ray diffraction pattern of Silica powder



Diffraction Data.

X-Ray diffraction analysis was performed using a flat camera and 40keV Cu- α ($\lambda = 1.54\text{\AA}$) radiation. The samples were scanned from 20° to 80° at 2 θ with a scan speed of 0.02°/sec. The formation of silica gel powder and Calcium Silicate powder was confirmed by X-ray diffraction technique. Fig.1 shows X-Ray diffraction

Fig.2. XRD spectra of mesoporous Calcium Silicate powder calcined at 110°C collected with a Cu-Kα X-ray source



pattern of the silica gel powder obtained from acidic hydrolysis of sodium silicate dried at 110°C. All exhibit XRD pattern with a very intense diffraction peak of mesoporous silica. The pattern shows the amorphous type characteristics of silica gel. The 'd-values' in marked positions are representing according to that of silica powder diffraction file. Fig.2 shows presence of calcium silicate phase along with sodium calcium silicate and silica phase. Fig.3 shows thin film X-Ray diffraction pattern of the calcium silicate coating sintered at 750°C before soaking in SBF solution. Fig.4. of X-ray Diffraction pattern of thin film shows different phases are present in the coating along with the phase of Calcium silicate. Complicated phases of sodium titanium chloride (NTC)

Fig. 3. XRD patterns for the porous coating of CaS obtained from reacting calcium oxide silica on Ti-alloy substrate collected with a Cu-Kα X-ray source

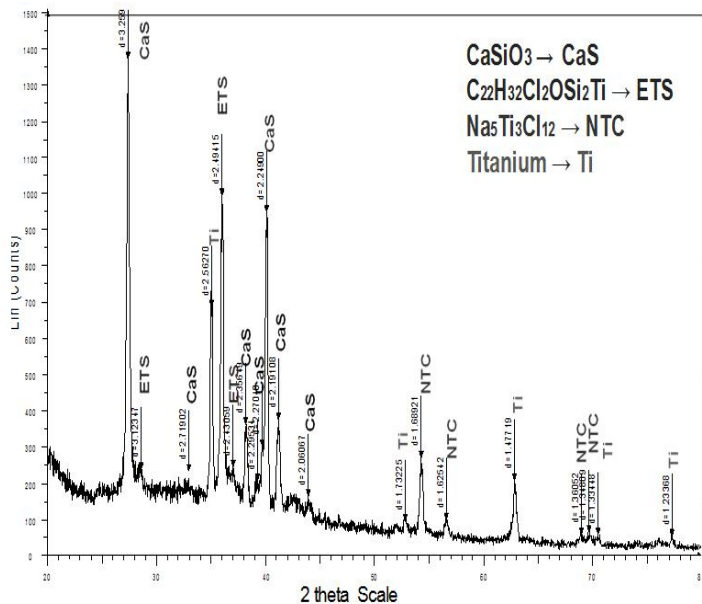
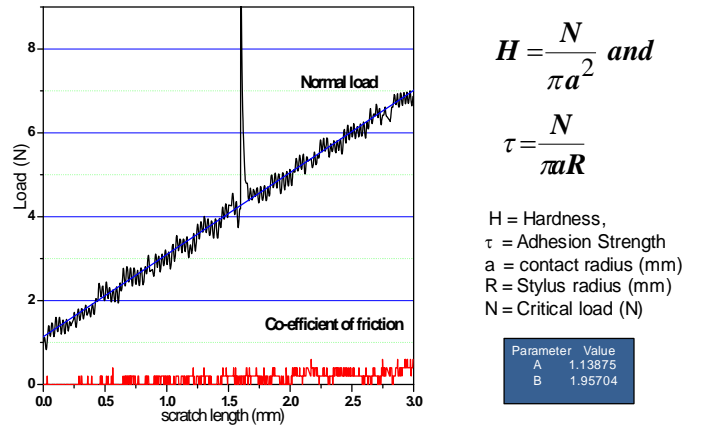


Fig.4. Comparison test of Load (N) versus Scratch length (mm)



and ethyl chloro titanium silicate (ETS) were marked in the coating.

The ETS and NTC phases are related to that of silicate structure which is originated during silanol condensation reactions. Silanols are compounds containing the Si-OH group and are thus analogous to the much better-known as alcohol group. The hydrolysis of the silicate groups and condensation of the resulting hydroxyl groups which might have reacted with NaCl and reminiscent of alcohol lead to form ETS and NTC phases in complicated reaction steps and have had formed after the heat treatment stage of the CAS coating with the Titanium substrate. But at this stage, formation of ETS and NTS in the complicated chemical process of reaction stages will not be discussed here keeping in mind about aim of present thesis work. However, it is important to remember that CAS coating has been bounded with titanium substrate by diffusion process, via, intermetallic diffusion bond (Bharati *et al.*, 2005).

Hardness testing

Scratch testers are dedicated instruments for characterizing the surface mechanical properties of thin films and coatings, e.g. adhesion, fracture and deformation. The scratch tester's ability to characterize the film-substrate system and to quantify parameters such as friction and adhesive strength, using a variety of complementary methods, makes it an invaluable tool for research and development.

This technique involves generating a controlled scratch with a sharp tip on a selected area. The tip material (commonly diamond or hard metal, Tungsten carbide) is drawn across the coated surface under constant, incremental or a progressive load. Scratch test was done to measure the strength of bonding between the substrate and the coating. The scratch test method consists of the generation of scratches with a spherical stylus (generally Rockwell C diamond, tip radius 200 micrometer, tip materials) that is drawn at a constant speed across the coating substrate system to be tested under a progressive loading at a fixed rate (loading rate, dl/dt=30N/m) this test is basically a comparison test.

From scratch test method, Coating Hardness and Adhesion strength was found to be $H = 26.5$ MPa, and $\tau = 132.7$ MPa Fig. 5. Showing the optical microscopy of scratch produced by scratch test by Rockwell C diamond, tip radius 200 micrometer. The optical microscopy analysis was done after scratch hardness shown that the coating could not be removed completely even after scratch produced in the coating. It shows that coating adhesion Scratch tests results shows good adhesion strength and scratch hardness of coating on the metal implant.

Calcium silicate gel methodology proved to be a very effective and simple method to reduce the induction period for the formation of a well-defined apatite layer on the metallic surface (Bharati et al., 2005). Calcium silicate (CaSiO_3) is a potential bioactive material that help to form and grow hydroxyapatite (HA) layer on CAS coated Ti substrate exposed to simulated body fluid.

Conclusion

XRD results confirm the different phases are present in the coating before soaking in SBF solution. Scratch tests results shows good adhesion strength ($\tau = 132.7$ MPa) and scratch hardness ($H = 26.5$ MPa) of coating on the metal implant. Calcium silicate is a good nucleating agent for the formation of hydroxyapatite film on the metal implant. The formation of the HA layer is an essential requirement for an artificial bioactive material to be used as bone substitute. This finding opens up a wide field for biomedical applications in bone implant.

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