MICROSCOPIC STUDIES OF CALCIUM SILICATE COATING ON TITANIUM ALLOY

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ABSTRACT
A methodology using biomimetic approach to produce bioactive coatings of hydroxyapatite on the surface of Titanium alloy substrate at ambient temperature has been reported. Coating of hydroxyapatite on titanium alloy at ambient temperature is known as biomimetic approach. 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 new generation of biomimetic coatings which are promising candidate for orthopaedic surgery. The surface morphology of the titanium alloy having a thin coating of Calcium silicate has been studied using scanning electron microscope (SEM) and atomic force microscope (AFM).

KEYWORDS: Calcium silicate gel, titanium alloy, SEM, AFM , biomimetic coatings

INTRODUCTION
Calcium silicate gel methodology has been established as simple and effective method to reduce the induction period for the formation of a well-defined apatite layer on the metallic surface. Calcium Silicate acts as a nucleating agent before soaking in SBF solution for the growth of apatite film on the surface of Titanium alloy (Xie J et al., 2008). Now day biomaterials research activities have drawn considerable attention due to its extensive application in the design of bone to achieve the excellent mechanical properties. Bone has some unusual properties, like it is stiff and tough, but lightweight material. These unusual properties arise due to its existence in nano composite form which contains 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 L., 2008). Presently, research activities in the field of bone tissue engineering have drawn wide attention and to the study these area, materials development are under progress using bone extra cellular matrix as a standard model. The compatibility of inorganic materials with living tissues and biological fluid is crucial in biomedical field. At present, most of the materials used in medical implants are biocompatible i.e. they do not interact with living systems. At present there are several biomaterials which are extensively used such as titanium substrates, silicon etc. Titanium substrates are used for tooth and bone implants (Vasheashta et al., 2005, NATO Science Series). Silicon is considered for production and maintenance of connective tissue in higher organisms. Porous silicate material is an excellent biomaterial with superb bio-stability and non-toxicity (Shi Xuenteao et al., 2008). Calcium silicate ceramics are bioactive and can be used as a new bioactive material in the field of biomedical applications. Porous structures of calcium silicate have been found to allow fast deposition of Hydroxyapatite layers or formation of apatite film with strong bonding to the surface and good osteo-integration (Narayan et al., 2004). Hydroxyapatite films evolved at physiological conditions exhibited the structure which are close resemble to those of bone mineral (Xu.Songfeng et al., 2008). Hydroxyapatite crystals have been deposited on titanium alloy substrate by sol gel method. Hydroxyapatite (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 Hydroxyapatite 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 hydroxyapatite 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 J.Z 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 hydroxyapatite 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. It is new generation of biomimetic coatings are promising for orthopaedic surgery.

Experimental
Materials processing
Commercial grade pure Titanium (Ti) substrate is used as a starting material which has chemical compositions 0.03% N, 0.10% C, 0.015% H, 0.18% O, 0.20% Fe and 0.5% by weight. The samples were cut into blocks having dimension 20 mm x 15mm x 5mm, which is used for the coating deposition. The surface was mechanically polished with emery papers continuously 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 stored in the desiccators to avoid any kind of contamination.

**Synthesis of calcium silicate**

Calcium Silicate was prepared by sol-gel method. Calcium silicate was obtained by reacting Calcium Oxide and Silica-gel. Sodium metasilicate was used as a Silica source. Concentrated Hydrochloric acid was used as a catalyst source to carry out the reaction. 50 gm of Sodium metasilicate was dissolved in 330 ml of distilled water at room temperature using magnetic stirring, giving a transparent clear viscous solution. To this solution 33.04 gm 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 solution 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-

**Hydrolysis**

\[
(1) \text{Na}_2\text{O}\cdot\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_3 + 2\text{NaOH}
\]

**Condensation**

\[
(2) \text{H}_2\text{SiO}_3 + 2\text{NaOH} + 2\text{HCl} \rightarrow 2\text{NaCl} + 2\text{H}_2\text{O}
\]

**Polymerization**

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 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-

\[
\text{H}_2\text{SiO}_3 + \text{CaO} \rightarrow \text{CaSiO}_3 + \text{H}_2\text{O}
\]

To get the crystalline powder of Calcium silicate, the washed resultant solution was dried at 150°C.

**Deposition of calcium silicate (CaS) gel by dip coating method**

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 in a laminar flow hood. 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.

**Results & 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 examined by Scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM).

**Scanning Electron Microscopy (SEM) Observation**

Figure 1 shows the SEM micrographs of calcium silicate coating over Ti-alloy substrate captured at 15 kV. The micrographs shows that coating is porous and uniform layer is deposited all over the metallic surface. At higher magnification there is presence of spheroid globules. The size of the individual globules ranges from 40 to 70µm. This reveals that most of the globules are in agglomerated form. Even at high magnification 8KX no cracks were observed in the coating. The examination of individual globules at higher magnification exhibited nanometric nuclei of calcium silicate crystal.

Fig. 1 SEM micrographs of calcium silicate coating over Ti-alloy substrate before soaking in SBF at 15 kv. (a) spheroid porous crack free type globules of CaS (b)showing porosity of CaS coating of round particular spot of (a)
Atomic Force Microscopy (AFM) Observation

Figure 2 SEM micrographs showing growth of particles in CaS coating on Ti-alloy substrate after soaking in simulated body fluid (SBF) for 72 hrs. [A] SEM micrographs showing porous type coating at 19 kv.[B] at 19 kv, and [D], [E], [F] at 14 kv SEM micrographs showing the growth of particles in the matrix of CaS coating.[C],[I] SEM micrographs showing porous, continuous & crack free coating on the Ti-alloy substrate [G],[H] SEM micrographs showing growth of particles in the matrices as lamellar structure. The surface of the coating is covered by a fresh layer consisting in forms of small granular structures of Ca-P (Hydroxyapatite). SEM micrographs reveal that apatite layer formed on the surface of calcium silicate after soaking in SBF solution is porous, continuous and crack free. The surface morphology of calcium silicate was investigated on high resolution scale with the help of Atomic Force Microscopy (AFM). It is a useful instrument to investigate in nano regime as well as it provides three dimensional information of surface topography of any specimens in ambient liquid or gas environments and over a large range of temperatures. Two AFM techniques, contact mode and Tapping Mode are very common used techniques for samples investigation. In contact mode, the microscope a sharp probe (tip) scanned across the sample surface in raster form while with constant contact in terms of force interactions with the surface. In Tapping Mode, the probe tip is only in intermittent contact with the sample while oscillating and lightly tapping the surface as it scans. Calcium Silicate coating over Ti substrate before soaking in simulated body fluid is shown in the Figure No. 3. The scan of the surface was done at lower scan contact mode in the area 100X100 micron meters². The Figure 3 (A, B, C) showing porous type topo microstructure of coating on the substrate. D showing crack free coating on the substrate, the difference in the colour contrast is due to height difference of the particles on the surface of coating. Figure, 3 (E, F) showing self assembly of particles of coating in one direction as like self assemblage in Lotus Leaf.
CONCLUSION
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 (CaSiO3) is a potential bioactive material that help to form and grow hydroxyapatite (HA) layer on CaS coated Ti substrate exposed to simulated body fluid. 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.

1. SEM results confirm that Hydroxyapatite coating is porous, continuous and crack free
2. AFM results reveal the ordered structure of CaS particles in the coating.
3. AFM microstructure of coating on Ti-alloy substrate at lower scan contact mode, Scan area 100x100 micron$^2$ showing porous type topo microstructure, crack free and self assembly of particles of coating in one direction.

REFERENCES