

Interaction of hydroxylated PACVD silica coatings on titanium with simulated body fluid

Hailong Zhang^a, Darren Simpson^b, Sunil Kumar^c, Roger St. C. Smart^{b,*}

^a Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

^b ACeSSS (Applied Centre for Structural and Synchrotron Studies), University of South Australia, Mawson Lakes, Adelaide, SA 5095, Australia

^c Ian Wark Research Institute, University of South Australia, Mawson Lakes, Adelaide, SA 5095, Australia

Received 20 March 2006; received in revised form 31 July 2006; accepted 31 July 2006

Available online 14 August 2006

Abstract

Nano-film coatings of hydroxylated silica reacted at low-temperature (<100 °C) with titanium substrates by a plasma assisted chemical vapour deposition (PACVD) technique have been studied for their interaction with simulated body fluid (SBF; the inorganic component of human blood plasma) with the aim of growing calcium hydroxy phosphate (CHP) bioactive overlayers. This layer is the precursor to formation of crystalline calcium hydroxyapatite (HA), a growth component of bone and teeth. The *in situ* plasma method produces 50–100 nm thick silica films with hydroxylated surfaces using a sequence of dry air; tetraethoxysilane (TEOS) vapour mixture with air; and 30% H₂O₂ solution. Two types of hydroxylated silica coatings were deposited and studied: Type I coatings, deposited using high TEOS/air ratio and high deposition rates, were observed to be unstable upon interaction with simulated body fluid tending to detach from the substrate in SBF solution; Type II coatings, deposited using low TEOS/air ratio and low deposition rates, produced functionally graded, strongly adherent films which exhibited chemical and mechanical stability and the growth of CHP and HA upon interaction with amine-free SBF. The interaction of Type II coatings with amine-stabilized SBF as used by other researchers did not result in the formation of the CHP layer. The results show that control of the TEOS/air ratio and rate of deposition (operating pressure) is essential for production of the functionally graded, strongly adherent oxide/silicate/silica layer and that hydroxylation of the silica surface strongly promotes CHP and HA growth. The study shows that the surface chemistry of the PACVD silica films and their behaviour in SBF are different from those of silica gels produced by hydrolysis and polycondensation of alkoxide precursors and from bioglass formulations.

The results are also cautionary in that it is possible to produce PACVD silica films without the formation of the graded interlayers and consequently with poor adhesion to the substrate. It is clearly essential to maintain control of the TEOS/air ratio and low deposition rates to produce the required sequence of reactions in the metal oxide/silicate layer and in the surface hydroxylation of the silica film without incorporation of hydrocarbons and molecular water.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Thin-film coatings; Hydroxylated silica; Calcium hydroxy phosphate; Bioactive coatings; PACVD

1. Introduction

In general, most of the artificial materials implanted into bone defects are surrounded by fibrous tissue, thus isolating them from the bone environment. However, some bioactive materials, such as many silica-containing glasses and glass-ceramics successfully used as middle ear implants, vertebral prostheses, bone fillers, etc. have been found to bond to living bone through a bonelike hydroxyapatite (HA) layer on their surface in the body

environment [1–4]. Many investigations have indicated that it is hydroxylated silica formed on these bioceramic surfaces in the body that plays an important role in forming a biologically active bonelike HA layer [5,6].

Hydrated silica is labile, acidic and feasibly catalytic in bone growth according to Williams [7]. It has been reported that pure silica gel produced by hydrolysis and polycondensation of tetraethoxysilane (TEOS) in aqueous solutions containing polyethylene glycol causes the formation of HA on hydrated silica surface as the gel is soaked in simulated body fluid (SBF) [8]. These authors suggested that hydroxylated silica gel is highly catalytic for calcium hydroxy phosphate (CHP) nucleation on its surface in SBF. In the physiological body fluid (pH 7.4), a

* Corresponding author. Tel.: +61 8 83023353.

E-mail address: Roger.Smart@unisa.edu.au (R.St.C. Smart).

negatively charged silanol surface initially attracts calcium ions. This is followed by electrostatic interaction and hydrogen bonding ($\text{OH}-\text{PO}_4^{3-}$) that brings phosphate anionic groups adjacent to Ca^{2+} ions. Near the silica gel surface, the accumulation of calcium ions and phosphate anionic groups enhances a precipitation reaction. A sufficient concentration of acidic silanol groups at the surface then induces CHP formation. Subsequent crystallization of the initially largely amorphous CHP produces crystalline HA formation.

More recently, Patel et al. [9] have developed a phase pure HA and silicon substituted (0.8 wt.%) coprecipitated HA in granular form. These preparations were implanted in the femoral chondyte of rabbits for 23 days with good bio-acceptance and new bone formation both on the surfaces and between the granules of both HA and HA/Si. The quantitative histomorphometric results, however, showed that there was much higher bone ingrowth for the HA/Si (i.e. $37.5 \pm 5.9\%$ cf. $22.0 \pm 6.5\%$) and that the bone/implant coverage was also greater (i.e. $59.8 \pm 7.3\%$ cf. $47.1 \pm 3.6\%$) [9].

In clinical applications requiring bone growth and bonding, bio-inertness of metals and brittleness of calcined silica gel coatings are major problems. The discontinuous, unreacted interface at the metal oxide/silica boundary separates relatively easily under shear. We have shown that plasma-deposited nano-film coatings of silica on metallic substrates, however, achieve improved performance, mechanical strength and adhesion [10,11]. The reason for these improvements is the formation of a functionally graded, nano-composite interfacial layer 50–100 nm thick across the metal/metal oxide/metal silicate/silica transition with nanoparticles of each phase embedded in adjacent layers. This reaction layer is formed by the plasma products, particularly SiO^- , SiOH^- , O^- ions, and SiO radicals, during plasma assisted chemical vapour deposition (PACVD) of TEOS vapour [10,11]. Hydroxylation of the silica surface to give bioactivity, combined with the high mechanical strength, should achieve improved performance in physiological and implant applications.

There are several advantages of this PACVD plasma method when compared with alternative methods of treating titanium surfaces to induce HA growth. The functionally graded layer is highly adherent. Testing at Lawrence Berkeley Labs, USA [12] did not produce detachment of the nano-film at 27 MPa and nano-indentation at 500 g produced no spalling of the layer. The process does not induce a mechanically and chemically weak interlayer between the metal and the HA as found with alkaline reaction (e.g. [13]) and oxidation pretreatment (e.g. [14]). Some of these alternatives have been reviewed in reference [10]. The process can be carried out in a single step without solution immersion before CHP and HA growth in SBF. The plasma reaction has been kept as simple as possible both in reagents and methodology. The process does not require high-temperature deposition or reaction treatment, reducing damage to the underlying surface of the metal. Since both the PACVD and SBF deposition processes are non-line-of-sight in nature, this method possesses the advantage of continuously coating complex, three-dimensional biomaterials/devices. The thinness of the deposited PACVD composite layer ($\sim 1 \mu\text{m}$) allows finely

structured implants, such as cranio-facial and orthopaedics screws to be coated without compromising their essential design features. PACVD silica-coated titanium screws, produced by this method, have been used for two sets of dental implant trials in the mandible of sheep, indicating enhanced bone growth (bone-implant contact increase of about 50%) as compared to uncoated implants [15], a result similar to that of Patel et al. [9]. The presence of silicates and silica in the graded layer apparently confers additional availability of hydroxylated species catalytic in bone growth [7,9].

Previous experiments with these PACVD coatings in our laboratory have suggested that the formation of this graded, composite structure is dependent on the conditions of plasma deposition, particularly TEOS/air ratio, rate of deposition (operating pressure) and plasma power. The consequences of different surface structure and composition in chemical stability (particularly interfacial hydrolysis), mechanical strength (particularly adhesion) and bioactivity have not been investigated. In this study, we have investigated the effect of TEOS/air ratio on the growth and structural and compositional characteristics of hydroxylated silica coatings deposited by the low-temperature PACVD process onto titanium, a material commonly used for medical and dental implants. The results show that control of the TEOS/air ratio and rate of deposition (operating pressure) is essential for production of the functionally graded, strongly adherent oxide/silicate/silica. High TEOS/air ratio or rate of deposition can produce unstable coatings. Additionally, an *in situ* plasma method for hydroxylation of the stable, graded PACVD silica coatings inducing CHP-based bioactive layers in interaction with SBF has been tested. The study shows that the surface chemistry of the PACVD silica films and their behaviour in SBF are different from those of silica gels produced by hydrolysis and polycondensation of alkoxide precursors (e.g. [8]) and from bioglass formulations.

2. Experimental

2.1. Materials

Titanium sheet (99.7% purity) and tetraethoxysilane (98% purity) were purchased from Aldrich Chemical Co. and hydrogen peroxide (H_2O_2) 30% (Univar) analytical reagent was obtained from APS Finechem (Australia). The titanium substrates were prepared by cutting the 0.25 mm thick sheet into $10 \text{ mm} \times 10 \text{ mm}$ pieces. Prior to plasma deposition, the metal pieces were rinsed in 5 wt.% KOH solution followed by a Milli-Q water wash, then immersed in a warm solution containing 1.6 wt.% HF, 33 wt.% HNO_3 for 2–3 min followed by copious Milli-Q water rinse. This is a standard method for chemical cleaning of titanium surfaces [16].

2.2. Experimental techniques

2.2.1. Plasma assisted chemical vapour deposition

The technique of plasma assisted chemical vapour deposition was employed for preparing thin-film coatings of hydroxylated silica onto Ti substrates. The schematics of the PACVD appara-

Download English Version:

<https://daneshyari.com/en/article/597922>

Download Persian Version:

<https://daneshyari.com/article/597922>

[Daneshyari.com](https://daneshyari.com)