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Combined laser/sol–gel synthesis of calcium silicate coating on Ti–6Al–4V substrates for improved cell integration

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Abstract

New studies have shown that tricalcium silicate powder is a bioactive material and can encourage bone–implant integration. This paper reports the synthesis of Ca_2SiO_4 coating on Ti–6Al–4V samples by laser irradiation under submerged conditions. The results of using a 160–1500 LDL 1.5 kW diode laser (rectangular spot = 2.5 mm × 3.5 mm, λ = 808 and 940 nm with equal intensities) is reported. A number of experiments were carried out varying laser parameters, such as scanning speed and laser power. Coatings are evaluated in terms of microstructure, elemental composition (XRD), SEM and wettability. The in vitro biocompatibility of the samples is investigated by monitoring 2T3 osteoblast cell growth on the samples.

Keywords: Laser surface treatment; High power diode laser; Tricalcium silicate; Bioglass; Biocompatibility; SEM; XRD; Wettability; Cell growth; 2T3 Osteoblast cell

1. Introduction

Titanium is biocompatible, corrosion resistant and tissue compatible, making it an excellent choice for bio-implants. It is ready to adsorb protein from biological fluids and creates a protein film. It also supports cell growth. Titanium and specially Ti–6Al–4V among its alloys are among the most commonly used materials in both dental and orthopaedic implantations [1–3].

Both pure titanium and Ti–6Al–4V are used in dental engineering as implants and dental prostheses. One big advantage in this field is that titanium is completely neutral in taste, which makes it the ideal choice for patients who show allergic or toxic reactions to other dental alloys.

A pure titanium surface can never be seen in the real world as a result of its high reactivity. It develops an oxide layer almost immediately [2]. The native oxide layer is thin and has an amorphous and porous structure. There is also the risk of viruses being carried by this layer. It was shown that shortly after implantation, titanium ions could be detected almost in all parts of organism; therefore, the oxide layer is not a real barrier [4].

Mosser et al. [5] studied the instant oxide layer of a titanium implant surface 5 years after implantation and they found that its thickness had increased from 5 nm (initial) to 200 nm indicating that the implant was continuously oxidizing in the organism and there was no protective layer to prevent further oxidization. It is also important that the oxide layer is porous and its quality does not improve as its thickness increases.

The above studies showed that the oxide layer appeared as a mediator between the implant and the organism instead of an insulator. However, the situation would be completely different, if there is a crystalline insulation layer on the implant surface. There are three possible methods to form a surface layer on an implant [4]:

- material deposition (positive material transport);
- material removal (negative material transport);
- material transformation without the deposition or removal (transport-free material process).

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Among surface coating methods on implants, plasma spray and sol–gel are the most widely used techniques. In plasma spraying, there is the risk of scaling and cracking as a result of the high temperature process, which can be considered as a disadvantage. Another possibility is the risk of scraped material being attached into the bone–implant interface. The critical stage in a sol–gel process is the heat treatment, since it affects the quality, compactness and structure of the surface layer [6].

Among laser deposition techniques Nd:YAG laser has been used to deposit hydroxyapatite (HA), which is one of the main inorganic chemical elements of bone, on titanium by using pulsed laser deposition [7]. Excimer laser was also reported to grow a HA coating on Ti–6Al–4V by using laser ablation [8].

Some new glasses and glass ceramics based on SiO_2, CaO and P_2O_5 with varying elemental compositions were found to be even better than HA materials in osseointegration. Joannia et al. have deposited thin films of bioactive glass-ceramics on a titanium substrate using a pulsed laser deposition technique. They have reported observing calcium phosphate precipitate on samples after immersing in simulated body fluid (SBF), suggesting the coating to be bioactive [9].

In another study on bioactive glass, Zhao and Chang synthesized tricalcium silicate (Ca_3SiO_5) powders by sol–gel process. Soaking the powders in simulated body fluid (SBF) for 10 days showed a dense hydroxyapatite (HA) layer formed on the surface indicating that the powder was bioactive [10].

In this paper, a combined laser/sol–gel technique is used to deposite a calcium silicate coating and determining its effect on osteoblast response.

2. Experimental procedure

Shot-blasted Ti–6Al–4V samples (aerospace industry grade) as rectangular sheets (60 mm × 50 mm × 10 mm) were used as the substrate. The calcium silicate powders were synthesized by sol–gel method by using $Ca(NO_3)_2{\cdot}4H_2O$ and TEOS (tetraethoxysilane) with an initial CaO/SiO_2 molar ratio of 3. Nitric acid was added as catalyst. The solution was prepared by adding 0.5 mol TEOS in 200 ml water under continuous stirring. Calculated amount of $Ca(NO_3)_2{\cdot}4H_2O$ was added to the solution and the solution was stirred for 1 h. Then, the solution was kept in an oven at 60 °C for 24 h until complete gelation occurred [10].

Experiments were carried out by using a 160–1500 LDL 1.5 kW diode laser (rectangular spot = 2.5 mm × 3.5 mm, λ = 808 and 940 nm with equal intensities). A thin layer of gel was applied on the substrate surface and then scanned by the laser beam. A number of experiments were carried out to obtain the optimum laser parameters. The best coating was made by applying a laser power of 120 W and a scanning speed of 1 mm/s.

Surface roughness measurements were obtained by using a laser surface profiler developed in house. The system uses the principal of optical triangulation to measure short distances with a resolution of one micron without surface contact. System handles the data by using a computer software and is capable of measuring Ra values on vertical and horizontal lines of the specified area on the sample.

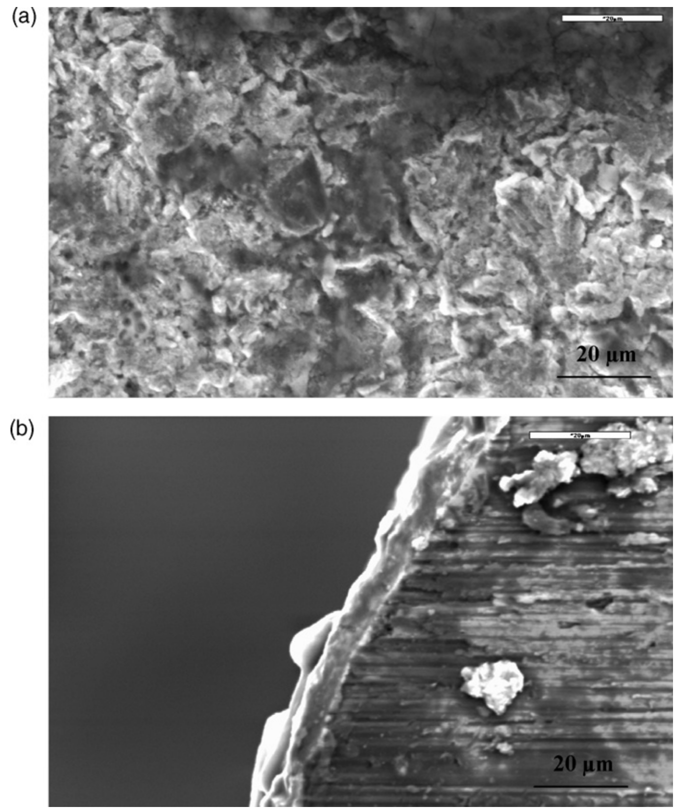

Fig. 1. SEM pictures: (a) cross-section and (b) top view of surface coating.

Contact angle measurement was carried out by using SBF in a FTA188: contact angle and surface tension analyzer instrument (Fig. 1). SBF is a protein-free fluid having an ion concentration nearly equal to human blood plasma (Na^+ 142.0 mM, K^+ 5.0 mM, Mg^{2+} 1.5 mM, Ca^{2+} 2.5 mM, Cl^- 148.8 mM, HCO_3^- 4.2 mM, HPO_4^{2-} 1.0 mM, SO_4^{2-} 0.5 mM). It was prepared by dissolving the above ionic species in deionised water and buffering at pH 7.4 using HCl or tris base ($H_2NC(CH_2OH)_3$) [11,12].

The in vitro test was carried out by osteoblast cell growth on samples and analysing the cell behaviour and attachment. 2T3 osteoblast cells were cultured on coated and non-coated samples and then the cell growth was measured by using MTT assay [13].

Among the existing methods to measure the cell viability, the reduction of tetrazolium salts is now recognized as a safe and accurate technique. In this test, the yellow tetrazolium salt (MTT: 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) is reduced in metabolically active cells to generate insoluble purple formazan crystals, which are solubilized by the addition of a detergent. This is a colorimetric measurement system which determines the reduction of a tetrazolium component (MTT) into an insoluble formazan product [13].

3. Results

3.1. SEM and XRD

SEM micrographs of the cross-section of coated samples (Fig. 1) revealed a thin layer coated on the surface. The