Characterisation of bioactive glass coatings on titanium substrates produced using a CO_2 laser

N. MORITZ[1,2,*], E. VEDEL[3], H. YLÄNEN[3], M. JOKINEN[1,2], M. HUPA[3], A. YLI-URPO[1]
[1]*Institute of Dentistry/Biomaterials Research,* [2]*Turku Centre for Biomaterials, University of Turku, Itäinen Pitkäkatu 4B, FIN-20520, Turku, Finland and* [3]*Process Chemistry Group, Åbo Akademi University, Piispankatu 8, FIN-20500, Turku, Finland*
E-mail: niko.moritz@utu.fi

Titanium and its alloys are widely used in load-bearing bioinert implants. Bioactive glasses (BAGs) form a chemical bond with bone, but they are not suitable for load-bearing applications. Creating a BAG coating on a titanium implant could combine the best properties of both materials. The results tend to be poor when conventional firing methods are applied to coat titanium with BAG. A local application of heat to melt the glass can be achieved by a CO_2 laser. A new method is introduced to create BAG coatings on titanium locally in a controlled manner, with a focused CO_2 laser beam. The coatings produced by this method precipitate calcium phosphate *in vitro*. Processing parameters (number of coated layers, laser power, and processing atmosphere) providing a firm attachment of the glass and good *in vitro* bioactivity were identified. XRD analysis showed no crystallisation of the glass due to processing with the laser. EDXA indicated the formation of a calcium phosphate layer, which FTIR suggested to be a hydroxyapatite. The results show CO_2 laser processing to be a promising technique for the manufacture of 30–40 μm BAG coatings on titanium.

1. Introduction

Biomaterials used in orthopaedics and dentistry are bioinert when harmful interactions are not occurring between the living body and the implant. Titanium and its alloys are among the most widely used bioinert materials. The well-known biocompatibility of titanium is attributed to its ability to form a thin oxide surface layer. However, in many clinical situations good biocompatibility of titanium is not sufficient for proper fixation of the implant, even when the implant is designed to allow bone ingrowth and mechanical interlocking with bone.

In the early 1970s, Hench *et al*. introduced the concept of a bioactive glass [1]. Here, bioactivity is considered as the ability of a bioactive glass to form a firm chemical bond with bone [2, 3]. This mechanism of bone bonding is thought to lie in the ability of a bioactive glass to release and attract ions of calcium and phosphorus from the body fluid, leading to the formation of an amorphous hydroxyapatite at the surface of the glass [3]. The hydroxyapatite crystallises and, through interaction with organic components, becomes integrated into the host bone tissue. Thus, the formation of calcium phosphate and hydroxyapatite on the surface of a bioactive glass *in vitro* can be used as an indicator of the bioactive properties of the glass in terms of bone-bonding [4]. The bioactivity of a glass depends on a combination of different properties including the chemical composition, morphology of the reacted surface [5, 6], surface charge [7], etc.

The release of ions from the bulk glass leads in the long run to resorbtion of the glass. In some clinical applications, bioactive glass can be used as a filler. However, bioactive glass, as such, is hardly an option for implants [8]: it is brittle, it does not withstand bending and tension, and it resorbs away.

One way to combine the superior properties of titanium and bioactive glasses in implants would be to create a bioactive glass coating on the surface of the titanium implant [9]. There are a number of coating techniques available, such as enamelling, glazing, flame spray coating, rapid immersion coating, ablating/sputtering, etc. Each of these techniques has its limitations when applied to coat medical implants with bioactive glass.

Conventional methods involving time-consuming heat treatments often lead to the diffusion of unwanted ions through the coating, resulting in a decrease or loss of bioactivity. The difference in the thermal expansion coefficients of a titanium substrate and a bioactive glass coating may result in detachment of the coating from the substrate. Even a short-term reheating of the glass during the coating procedure may lead to phase separation or crystallisation of the amorphous glass, which also may

*Author to whom all correspondence should be addressed.

have a negative effect on the bioactivity [10]. Moreover, the extensive oxidation of the titanium surface due to the heat-treatment also contributes to poor attachment of the coating [11].

Application of a base coating and/or successive coatings of different chemical compositions might reduce the mismatch of the thermal expansion coefficients, but ion diffusion from the base coating might be a problem [10].

Bioactive glasses suitable for repeated heat-treatment were developed at Åbo Akademi University [12]. A focused CO_2 laser beam can be applied to melt these glasses and create a bioactive glass coating on a titanium substrate. When the beam is scanned over the surface, heat-treatment occurs locally and rapidly, primarily affecting the glass layer [13, 14]. Thus, the harmful effect of oxidation of the substrate is lesser than in the conventional treatments of enamelling, glazing, etc. Moreover, with the laser-treatment the glass coating is not uniform but comprises separate but interconnected droplets that are firmly attached to the titanium. The mechanical attachment of such a coating to the substrate is believed to be better than that of a uniform coating, as stresses are smaller.

Since bioactive glass resorbs in the body, the coatings will not remain on the titanium permanently. Thus, their main purpose would be to improve the incorporation of the implants at the early stages of the fixation by promoting bone ingrowth thus allowing faster mechanical interlocking of the implant in the host bone. In this respect, a further advantage of using a focused laser beam for creating the coatings is the possibility to do it locally, exactly at the spot on an implant surface, where the implant design would benefit most from the introduction of bioactive glass. Moreover, the coating itself might serve only a supplementary role as substrate for attachment of a porous device made of bioactive glass. In this case, it would be the porous part that promoted and supported the ingrowth of new bone and provided mechanical interlocking of the implant in the bone. New types of implants could thus be developed that incorporated bioactive glass parts as functional elements of their design without compromising the strength of the implant and still taking full advantage of the bioactivity. These implants would also promote and support the growth of new bone.

In this work, we explored the possibility of applying CO_2 laser irradiation for coating of titanium medical implants with bioactive glass. Our main concerns were preservation of the bioactive properties of the glass after the processing and good attachment of the coating to the substrate. The specific goals of the study were: (1) to optimise the parameters used to create bioactive glass coatings on sandblasted titanium substrates; (2) to assess the *in vitro* bioactivity of glass coatings created with the use of a CO_2 laser at optimal processing conditions; (3) to compare the *in vitro* bioactivity of the coatings prepared from different bioactive and inert glass materials.

The *in vitro* test was performed in a simulated body fluid (SBF) prepared according to Kokubo *et al*. [15]. The concentrations of calcium, phosphorus and silicon ions in SBF were measured at regular time intervals. All samples were also studied by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM) and energy depressive X-ray analyser (EDXA).

2. Materials and methods

2.1. The coating technique

The bioactive glass coded 1-98 was manufactured at Åbo Akademi University, Turku, Finland [5]. The composition of the glass is presented in Table II. After the normal melting procedure, the glass was milled into powder ($< 45\,\mu m$) for coating and powder (45–315 μm) for grid blasting of the Ti-substrates. The control inert glass (flat glass) used for coating was a window-type glass crushed and milled into powder ($< 45\,\mu m$).

A 1 mm thick sheet of commercially pure (c.p.) titanium (grade 2) was used as the substrate material. The Ti-sheet was cut into $17 \times 20\,mm^2$ plates, and the surface was cleaned by sandblasting first with pure SiO_2 and then with bioactive glass powder (45–315 μm). The plates were coated with the bioactive or inert glass from a suspension of glass powder ($< 45\,\mu m$) in ethanol using a dip-coating technique. The weight ratio of ethanol to glass in the suspension was 0.7. Only one side of the Ti-substrate was processed with the laser; the glass powder was cleaned from the other side immediately after dip-coating. The substrate plates were dipped into the suspension, kept motionless, and then lifted up. After drying, the obtained layer of the glass powder was irradiated with the beam from a Synrad 25 W laser (Synrad Inc., 4600 Campus Place, Mukilteo, USA). The beam was focused with a 1.5 inch ZnSe lens. The process required the use of a mirror and a chamber equipped with a ZnSe window, to allow processing in controlled (here N_2) atmosphere. In all experiments, the laser position was fixed while the specimens were scanned through the focused beam using a computer-controlled stage equipped with two stepper motors that permitted motion in two directions. This allowed scanning with the laser beam at down to a distance of 100 μm between the neighbouring scan lines. The computer program was made using the LabView (National Instruments, USA) graphical programming environment. The program was used to control both the stepper motor stage (transition speed, density of the scan lines) and the power of the laser. A separate computer-controlled dip-coating device was employed for coating of the specimens.

Multi-layer coatings were obtained by repeating the cycle. Processing was performed in air or, in N_2 to reduce further oxidation of the substrate. The scanning speed of the motor stage was kept at 2.5 mm/s; only the power of the laser was altered, as these parameters are interconnected. The laser power was in the range 6–8 W. The power is given as measured at the end of the optical path (mirror, window) but without the lens, at the surface of the specimen. The reduction of the power is approximately 30% of the output of the laser. The laser power was measured using a power probe (Molectron PM5200, Molectron, Portland, USA). After processing, Ti-plates coated with a thin layer of glass were cut into $10 \times 10\,mm^2$ specimens, and washed in acetone in an

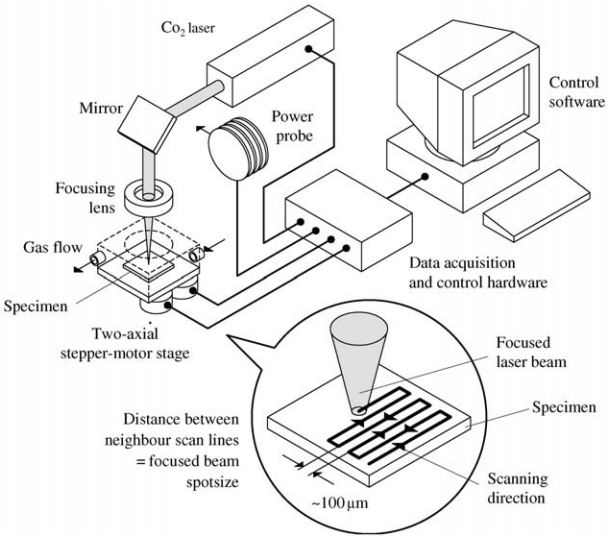

Figure 1 Equipment used for creation of glass coatings with CO_2 laser.

ultrasound bath for 5 min. The equipment is shown in Fig. 1.

2.2. Optimisation of the processing parameters

Optimisation was concentrated on the following parameters: dipping and lifting rates to obtain a powder coating suitable for laser treatment; number of coating layers required to create a coating that did not detach from the substrate; power settings for the laser and the speed of motorised stage; and processing atmosphere (air or N_2).

The quality of the coatings created with the CO_2 laser was examined by light microscopy with respect to the topography of the glass drops constituting the coating, the goal being to obtain a contact angle of $< 90^\circ$ with the lowest possible power of the laser and a reasonable number of coatings, with no signs of detachment.

Optimisation of the parameters required the following steps: creation of the glass coatings using CO_2 laser irradiation; *in vitro* bioactivity test performed in SBF (the ion concentration of phosphorus was monitored at regular time intervals); mineral analysis performed by SEM-EDX. Several studies were performed and the results of each study served as a basis for a new one, enabling us to narrow the search. Once the optimal parameters were found, a large-scale *in vitro* test was carried out.

2.3. Study of *in vitro* bioactivity of the coatings

Bioactive glass (1-98) powder (fraction $< 45\,\mu m$) was used for creation of the CO_2-laser-processed bioactive coatings on Ti-substrates. Inert controls were glass granules (fraction 315–500 μm) and CO_2 laser processed glass coatings on Ti-substrates made from inert glass powder (fraction $< 45\,\mu m$). Bioactive glass controls comprises plates ($10 \times 10 \times 0.5\,mm^3$), granules (fraction 315–500 μm), and powder (fraction $< 45\,\mu m$). Materials used in this experiment are listed in Table I. The weight of the granules was chosen according to the method described by Anderson *et al*. [16, 17], to approximate the surface area.

The specimens were immersed in SBF to study the reactivity (*in vitro* bioactivity) of the materials. The ratio of the surface area of the materials to the volume of the SBF (SA/V ratio) was 0.1 and $0.4\,cm^{-1}$. The value of $0.4\,cm^{-1}$ is common for studies on bioactive glasses and can be used to compare the results of this and other studies. In the case of our coatings, however, the surface area of the glass was small, and to ensure that the amount of SBF was sufficient to totally cover all the specimens we used the SA/V of $0.1\,cm^{-1}$ for all materials. In the case of the glass granules (fraction 315–500 μm), we also used SA/V of $0.4\,cm^{-1}$ to allow comparison with previous studies [4].

In the *in vitro* experiment, the specimens were immersed in the SBF, until removal at two, four, seven, and 14 days; at the same time the concentrations of soluble calcium (Ca), phosphorus (P), and silicon (Si) were monitored. In addition, reference samples (not immersed in SBF) of each material were studied to determine the characteristics of the materials before the *in vitro* test, to clarify the titanium/glass interface, and to reveal the possible compositional changes caused by the laser processing. Three parallel specimens of each material were withdrawn at each time point (two, four,

TABLE I Materials used in the study

Type	Substrate	Processing	Material	Codes in Figs. 5–7
Coating	c.p. Ti, $10 \times 10 \times 1\,mm^3$	CO_2-laser, 6 W, in air	Bioactive glass 1-98, powder (< 45 μm) SA/V = 0.1	bg 6WA (SAV = 0.1)
Coating	c.p. Ti, $10 \times 10 \times 1\,mm^3$	CO_2-laser, 8 W, in N_2	Bioactive glass 1-98, powder (< 45 μm) SA/V = 0.1	bg 8WN (SAV = 0.1)
Coating	c.p. Ti, $10 \times 10 \times 1\,mm^3$	CO_2-laser, 6 W, in air	Inert glass, powder (< 45 μm) SA/V = 0.1	flat 6WA (SAV = 0.1)
Coating	c.p. Ti, $10 \times 10 \times 1\,mm^3$	CO_2-laser, 8 W, in N_2	Inert glass, powder (< 45 μm) SA/V = 0.1	flat 8WN (SAV = 0.1)
Granules	—	—	Inert glass, (315–500 μm) SA/V = 0.1	gran flat (SAV = 0.1)
Granules	—	—	Bioactive glass 1-98, (315–500 μm) SA/V = 0.1	gran 1-98 (SAV = 0.1)
Granules	—	—	Bioactive glass 1-98, (315–500 μm) **SA/V = 0.4**	gran 1-98 (SAV = 0.4)
Plate, $10 \times 10 \times 1\,mm^3$	—	—	Bioactive glass 1-98 SA/V = 0.1	plate 1-98 (SAV = 0.1)

seven, and 14 days), for a total of 15 specimens per material.

The concentrations of ionic phosphorus and calcium in the SBF solution decrease when a precipitate of calcium phosphate forms on a bioactive surface. Thus, the concentrations of phosphorous, calcium, and silicon were used to evaluate the surface bioactivity. At each time point, the samples from the SBF solution (three per specimen/nine per material) were analysed by UV–Visible spectroscopy (UV-visible spectrophotometer, Shimadzu UV-1601, Shimadzu Corporation), to study P and Si concentrations. The Ca-concentration was determined by atomic absorption spectrophotometry (Perkin Elmer 460).

2.4. Characterisation of the coatings created with CO_2 laser

The composition of the glass after processing with the laser and after the *in vitro* test was examined by a SEM (LEO 1530) equipped with EDXA (Thermo NORAN Vantage). Also, a Fourier transform infrared spectroscope (FT-IR spectroscopy: Perkin Elmer Spectrum One) with the DRIFT was used to study the formation of the calcium phosphate layer on the coatings.

After the SEM–EDXA and light microscopy examination of the surface of the coatings (topography at microscale level and the formation of the calcium phosphate layer), the same specimens were embedded in PMMA and cut in cross-sections for further SEM–EDXA examination. This included the assessment of the changes and reactions in the glass caused by the processing as well as the interface between the coating and the substrate.

The coatings were examined by XRD (Philips PW-series) for the possible crystallisation of the glass due to treatment with the CO_2 laser.

3. Results and discussion

3.1. Optimisation of the processing parameters

When the focused CO_2 laser beam hits the surface of the titanium plate covered with glass powder it melts the powder locally and attaches it to the titanium substrate creating a coating that comprises numerous micro-sized ($\varnothing \sim 60\,\mu m$) glass ''drops'' (Fig. 2).

The optimisation process consisted of the following steps: creation of the glass coatings using CO_2 laser; *in vitro* bioactivity test performed in SBF, which included monitoring the content of soluble phosphorus at different time points; mineral analysis performed with SEM–EDXA. Each experiment was planned on the basis of the results obtained in the preceding experiment, thus enabling us to narrow the search. In the course of the experiments, the following processing parameters were studied in terms of obtaining the best *in vitro* bioactivity results:

- Operating speed for the dip-coating equipment to obtain a uniform powder coating suitable for further laser treatment.
- Maximum number of layers achievable by this method without detachment of the coating.
- Power settings for the laser and the speed of the motorised stage.
- Processing atmosphere (air or N_2).

Through light microscopy examination, we established that the working power range of the CO_2 laser in our experimental setup was 4–8 W. The results of the *in vitro* studies revealed that the best coatings in terms of *in vitro* bioactivity are obtained using 6 W power in air and 8 W power in N_2, and the optimal number of coating layers is three. Fig. 3 shows the concentration of soluble phosphorus in the SBF solution as a function of time, as the influence of the laser power and the number of coating layers on *in vitro* bioactivity was studied. Fig. 4 shows the concentration of soluble phosphorus in the SBF solution as a function of time, as the influence of the

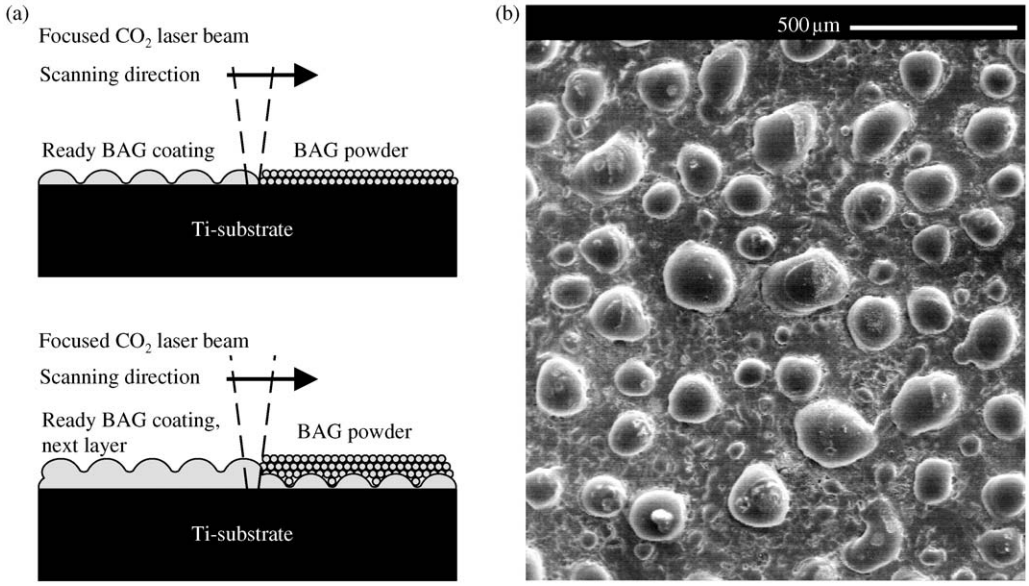

Figure 2 (a) Coating technique. (b) SEM image of the surface of a bioactive glass (BAG) coating created with CO_2 laser.

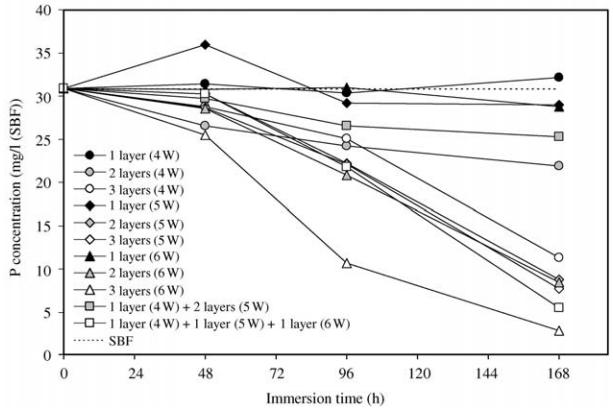

Figure 3 Effect of laser power and the number of coating layers on *in vitro* bioactivity of the coatings, evaluated as the change in P concentration in SBF with immersion time. Laser processing was carried out in air.

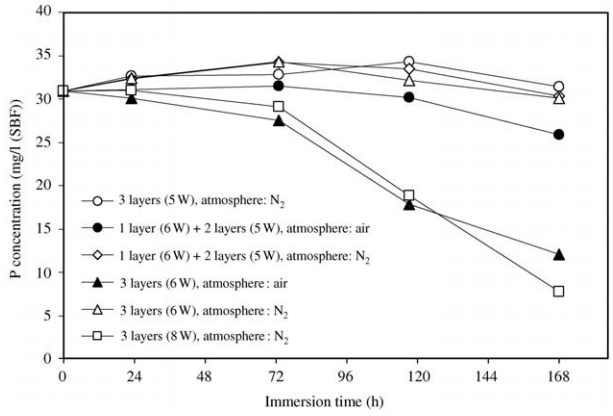

Figure 4 Effect of laser power and processing atmosphere (air, N_2) on *in vitro* bioactivity of the coatings, evaluated as the change in P concentration in SBF with immersion time.

laser power and the processing atmosphere were studied. The decrease in the P-concentration in the solution was used to evaluate the *in vitro* bioactivity.

No special mechanical tests were performed to establish the strength of the bond between the coating and the substrate. Nevertheless, the coating did withstand cutting of the 1 mm thick specimens into smaller pieces by a guillotine, without signs of detachment of the coating from the substrate.

3.2. Study of *in vitro* bioactivity of the coatings

The results of the *in vitro* test are shown in Figs. 5–7. Fig. 5 shows the changes in the concentration of Ca ions in the SBF as a function of immersion time. There are two simultaneous and competing processes here: release and precipitation of Ca ions. As far as the curves for the CO_2 laser-treated bioactive glass coatings are concerned, it seems that a larger amount of Ca is released. This might be due to a number of reasons. The glass contains larger amount of Ca than P, so that the release of P from the glass is smaller compared with precipitation of P from the SBF solution. In the case of Ca, the competitive release and precipitation processes are more distinct. Moreover, the surface area of a laser-treated glass coating may be significantly greater than the square

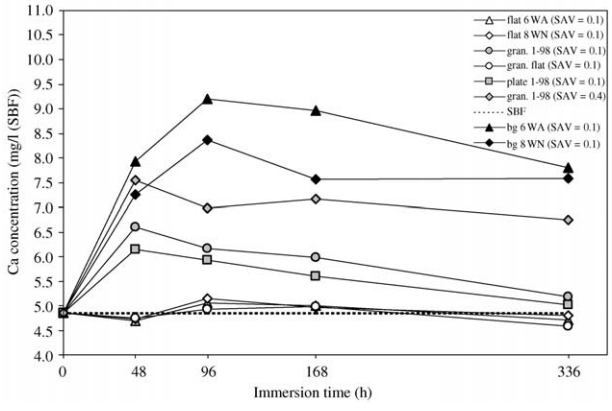

Figure 5 Change in Ca concentration with immersion time in SBF. Two types of bioactive glass coatings studied: 6 W in air and 8 W in N_2 (SA/V = 0.1). Bioactive controls: glass plate (SA/V = 0.1) and granules (SA/V = 0.1 and 0.4). Inert controls: coatings, 6 W in air and 8 W in N_2 (SA/V = 0.1) and granules (SA/V = 0.1). For codes see Table I.

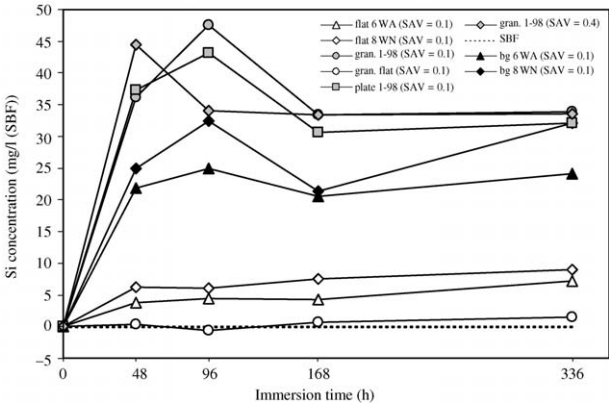

Figure 6 Change in Si concentration with immersion time in SBF. Two types of bioactive glass coatings studied: 6 W in air and 8 W in N_2 (SA/V = 0.1). Bioactive controls: glass plate (SA/V = 0.1) and granules (SA/V = 0.1 and 0.4). Inert controls: coatings, 6 W in air and 8 W in N_2 (SA/V = 0.1) and granules (SA/V = 0.1). For codes see Table I.

dimensions of a specimen. A simple mathematical approximation that takes into account the topography (glass drops) of the coating gives at least 10% increase in the surface area compared with a flat piece. If one considers the cracks and other non-uniformities (Fig. 8(a)) in the topography of the surface that are difficult to account for, the increase in the surface area will be much greater. Nevertheless, the Ca-concentration in the SBF solution clearly decreases as a function of time for the laser-treated coatings, in a similar way as for the control bioactive materials, and all the final values at 14 days are of the same order. Moreover, variation in thickness of the coating due to the topography means that the glass in the ''valleys'', where the coating is thin, will resorb earlier than the glass in the ''hills'', signifying a different *in vitro* behaviour of the laser-treated coating compared with a flat glass surface. In future *in vitro* studies, we consider taking into account the volume of the materials as well, to see if this could provide any extra information on their behaviour.

The release of Si ions from the laser-treated bioactive glass coatings is similar but slightly slower than that from the control bioactive glass (Fig. 6). A small amount of Si release can also be observed from the inert glass coatings.

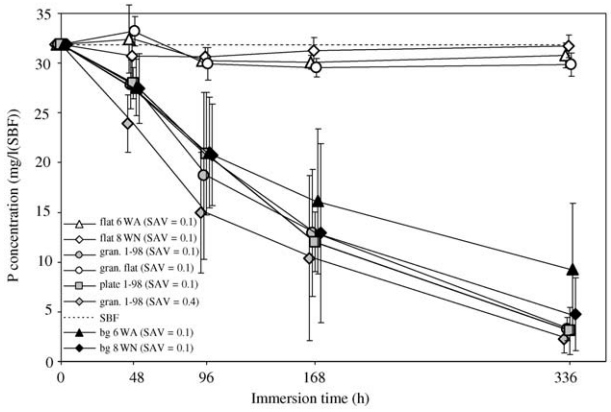

Figure 7 Change in P concentration with immersion time in SBF. Combined results of two identical series of experiments are presented. Two types of bioactive glass coatings studied: 6 W in air and 8 W in N_2 (SA/V = 0.1). Bioactive controls: glass plate (SA/V = 0.1) and granules (SA/V = 0.1 and 0.4). Inert controls: coatings, 6 W in air and 8 W in N_2 (SA/V = 0.1) and granules (SA/V = 0.1). For codes see Table I. The standard deviation vertical bars are presented as the data are the combined results of two series of experiments.

The inconsistency of the values of the Ca and Si ion concentrations at different time points is due to the combination of two factors: the design of the *in vitro* test and the dipping method used to deposit the glass powder on the substrates before the CO_2 laser processing. The difference in the thickness of the coatings resulted in deviations of the surface area of the glass coating. Moreover, with this type of *in vitro* test design, the same specimens cannot be measured at more than one time point, specimens are physically removed from the SBF for further FT-IR and SEM–EDXA analysis.

Fig. 7, showing the concentration of phosphorus, is based on the results of two experimental series and thus the amount of specimens is doubled. The P-curves for the CO_2 laser-treated bioactive glass coatings and the control bioactive glass are, therefore, smoother than the Ca- and Si-curves. The trend for the drop in P-concentration due to the formation of a calcium phosphate layer was similar in the two series.

The control inert materials were unaffected by the immersion in the SBF, and the ion concentrations remained unchanged during the test period.

3.3. Characterisation of the coatings created with CO_2 laser

Besides creating the coating by melting the glass powder, the focused laser beam also vaporises some of the glass. Although most of the vaporised glass is carried away from the substrate by the gas (air, N_2) flow in the processing chamber, some of it is deposed back on the surface. Fig. 8(b) shows that a thin layer of material has been deposited on top of the bioactive glass coating. The composition of the glass coating was studied by SEM–EDXA. The results are presented in Table II. Minor

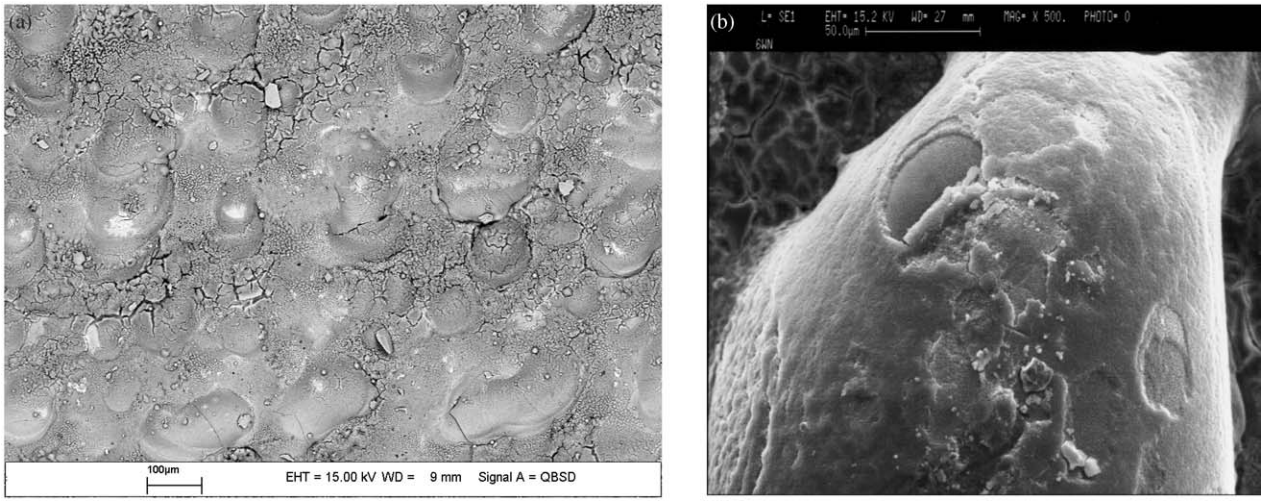

Figure 8 (a) Surface topography of a bioactive glass coating created with CO_2 laser, SEM image backscattered mode. (b) A layer of material deposited on the surface of the coating.

TABLE II Oxide compositions (expressed as wt %) of different materials obtained in the experiment

Oxides	Bioactive glass 1-98, theoretical composition	Bioactive glass 1-98, bulk, as measured by SEM–EDXA	Bioactive glass coating created by CO_2 laser, as measured by SEM–EDXA	The material deposited on top of the glass coating due to CO_2 laser processing, as measured by SEM–EDXA	Inert glass, as measured by SEM–EDXA	Inert glass coating created by CO_2 laser, as measured by SEM–EDXA
SiO_2	53.0	55.0	55.9	60.8	73.5	64.0
Na_2O	6.0	5.1	5.7	11.7	14.3	6.8
CaO	22.0	22.5	20.5	0.2	7.7	9.9
K_2O	11.0	10.1	9.4	19.9	0.0	0.2
MgO	5.0	4.6	5.5	0.8	3.5	2.9
P_2O_5	2.0	2.4	2.4	5.0	0.3	1.6
B_2O_3	1.0	Not detected	Not detected	Not detected	Not detected	Not detected
TiO_2	0.0	0.0	0.0	1.2	0.2	13.6

changes in the bioactive glass composition were observed. In a separate experiment, a thick layer of deposited material was created on a carbon tape and its composition was examined by SEM–EDXA (Table II). The deposited material was also studied in SEM at high resolutions. The composition of the vaporised and deposited material explains the changes in the composition of the bioactive glass coating. From the composition of the deposited glass material one can conclude that it is resorbable. However, the fact that this material is not completely removed by the ultrasound cleaning of the specimens might be the reason for some of the compositional changes in the glass coating, as the layers of coating are added on top of each other. Thus in future studies, we consider mechanical cleaning of the coatings in addition to applying ultrasound.

The observed changes in the bioactive glass composition due to processing with a CO_2 laser should not influence the bioactivity of the glass. Moreover, if necessary, the chemical composition of a bioactive glass intended for laser coating process could be optimised to compensate for these changes.

XRD examination of the specimens showed no signs of crystallisation of the glass to the processing with the CO_2 laser (Fig. 9). Bioactive glass powder (both amorphous and crystallised at 960 °C) and an uncoated grit blasted Ti-substrate were used as controls.

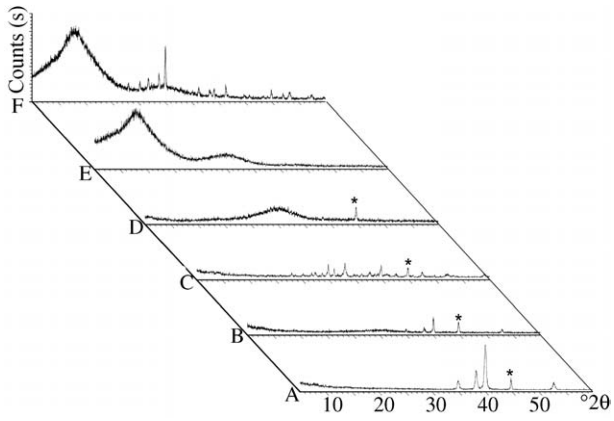

Figure 9 XRD examination of bioactive glass. No crystallization of the glass due to CO_2 laser treatment is detected in the glass. A, grit-blasted Ti-plate; B, glass-coated (1-98) Ti-plate 8 W N_2; C, glass-coated (1-98) Ti-plate 8 W N_2 heated to 960 °C; D, glass plate (1-98); E, glass powder (1-98); F, crystallised glass powder (1-98) heated to 960 °C. The asterisk indicates the peak from the aluminium specimen holder.

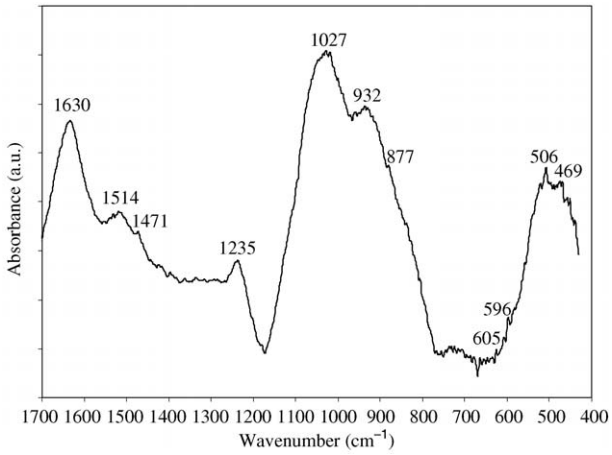

Figure 11 FT-IR spectrum of the surface of a bioactive glass coating created with CO_2 laser (8 W, N_2) after immersion in SBF for 14 days.

SEM/EDXA analysis confirmed the formation of calcium phosphate on the surface of the bioactive glass coating and the control bioactive glasses immersed in SBF solution. No reaction was observed on any of the inert glass coatings.

Fig. 10 shows cross-sections of the bioactive glass coatings removed from SBF solution at different time points. Calcium phosphate formation is seen clearly on the coatings already at four days. All the cross-sections were analysed by EDX. No reaction interface between the substrate and the bioactive glass coating was observed in any of the specimens. No cracks between coating materials and substrate or signs of detachment were observed either.

All the coated specimens and bioactive glass plates were investigated by FT-IR spectroscopy in DRIFT mode. As an example, Fig. 11 shows the spectrum of a bioactive glass coating (8 W, N_2) after immersion in SBF for 14 days. The spectra were interpreted through comparison with previously reported results [18–21]. Carbonate ν_3 vibration mode bands in the region 1650–1300 cm^{-1} are due to the surface carbonate ions. The ν_3 peak seems to be split into three peaks, at $\sim$ 1630, $\sim$ 1514, and $\sim$1417 cm^{-1}. The carbonate peak at $\sim$877 cm^{-1} corresponds to the ν_2 vibration mode, as in the hydrocarbonate apatite (HCA). The peak at $\sim$1027 cm^{-1} is the phosphate ν_3 band, which is reported to appear in the range of 1190–976 cm^{-1}. The ν_2 phosphate peak can be seen at $\sim$470 cm^{-1}. The weak ν_4

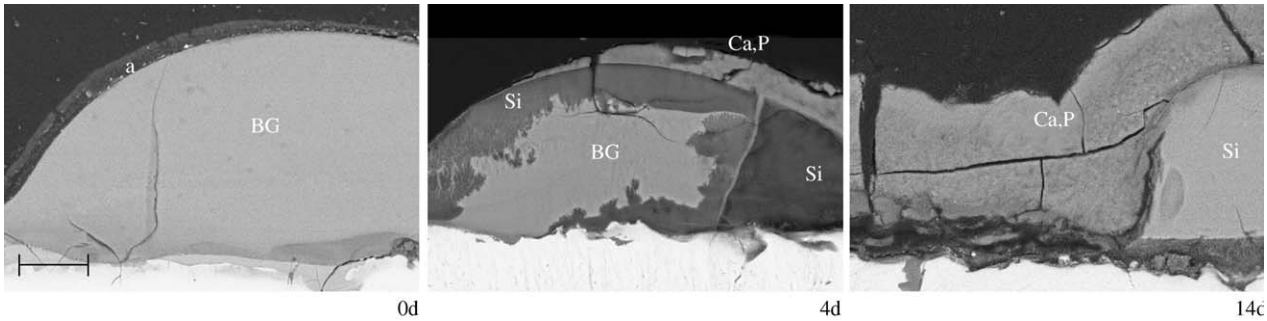

Figure 10 Cross-sections of bioactive glass coatings created with CO_2 laser removed from SBF at different time points. Formation of Si-rich layer and calcium phosphate layer is clearly visible. a = ablated glass layer.

phosphate peaks at ~ 605, ~ 596, and $\sim 506\,cm^{-1}$ are due to crystallisation of the apatite. The analysis suggests the formation of Ca, P, and HCA. However, the release of Mg ions from the glass may have slowed the formation of a calcium phosphate layer and the crystallisation of the HCA [17], and so could explain the weak P–O peaks in the $660–520\,cm^{-1}$ region. Moreover, one of the problems associated with the FT-IR method is that it does not provide analysis of the outermost layer, as the measurement is taken from a depth of 0.5–10 μm. In our study, the thickness of the glass coating varied from 5–35 μm. In the case of a thin calcium phosphate layer, the spectra obtained are probably the average spectra for the calcium phosphate layer, the silica-rich layer, and the non-reacted glass.

4. Conclusions

4.1. Optimisation of the processing parameters

The results of the present study demonstrate the possibility of creating bioactive glass coatings on titanium substrates with a focused CO_2 laser beam. Optimal parameters were found for the processing method. The system that we used for the dip-coating needs to be optimised in order to allow deposition of a more uniform layer of bioactive glass powder on the titanium substrate before the laser treatment.

4.2. Study of the *in vitro* bioactivity of the coatings

The results of the *in vitro* study indicate that the coatings created with a CO_2 laser treatment show similar *in vitro* bioactivity as the control bioactive glass, despite the changes in the composition of the glass.

4.3. Characterisation of the coatings created with CO_2 laser

The changes in chemical composition introduced by the CO_2 laser treatment of the bioactive glass were minor and had no influence on the bioactivity of the glass. No signs of crystallisation were observed. The coatings were able to precipitate calcium phosphate *in vitro*. The FT-IR data obtained from the bioactive glass coatings suggest that the calcium phosphate precipitated on the surface is a hydroxyapatite. Evidently, the processing atmosphere has an effect on the *in vitro* bioactivity, as the coatings created in N_2 were better correlated to the control bioactive glass.

The coatings appear to be firmly attached to the substrates. A separate study on the mechanical properties of bioactive glass coatings produced with a CO_2 laser needs to be carried out.

One of the advantages of using a laser beam for creating the coatings is the possibility to do this locally, on an implant surface exactly, where the implant design benefits most from the introduction of bioactive glass. New types of implants can be developed that incorporate bioactive glass parts such as coatings and porous devices as functional elements of their design.

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References

1. L. L. HENCH, R. J. SPLINTER, W. C. ALLEN and T. K. GREENLEE, *J. Biomed. Mater. Res.* **5** (1971) 117.
2. D. F. WILLIAMS, in ''Definitions in Biomaterials'', Proceedings of a Consensus Conference of the European Society for Biomaterials Chester, England, UK, 1986, vol. 4 (Elsevier, Amsterdam, 1987) pp. 24, 28 and 64.
3. L. L. HENCH and Ö. H. ANDERSSON, in ''An Introduction to BIOCERAMICS. Advanced Series in Ceramics'', vol. 1 (World Scientific, Singapore, 1993) pp. 41–62.
4. Ö. H. ANDERSSON, in ''The Bioactivity of Silicate Glass. Academic Dissertation'' (Åbo Akademi University, Turku, 1990).
5. A. ITÄLÄ, E. G. NORDSTRÖM, H. O. YLÄNEN, H. T. ARO and M. HUPA, *J. Biomed. Mater. Res.* **56**(2) (2001) 282.
6. M. JOKINEN, T. PELTOLA, J. SIMOLA, J. KORVENTAUSTA and A. YLI-URPO, in ''Proceedings of the 13th International Symposium On Ceramics in Medicine, Key Engineering Materials'', Bologna, 2000, p. 601.
7. M. PEREIRA and L. L. HENCH, *J. Sol–Gel Sci. Tech.* **7** (1996) 59.
8. D. F. WILLIAMS, in ''Definitions in Biomaterials'', Proceedings of a consensus conference of the European Society for Biomaterials Chester, England, UK, 1986, vol. 4 (Elsevier, Amsterdam, 1987) p. 38.
9. L. L. HENCH and Ö. H. ANDERSSON, in ''An Introduction to BIOCERAMICS. Advanced Series in Ceramics'', vol. 1 (World Scientific, Singapore, 1993) pp. 239–260.
10. Ö. H. ANDERSSON, K. H. KARLSSON, H. HERO, E. VEDEL, A. YLI-URPO, K. J. J. PAJAMÄKI and T. S. LINDHOLM, *J. Mater. Sci.: Mater. Med.* **6** (1995) 242.
11. J. HAUTANIEMI, in ''Oxidation and Porcelain Veneering of Ti and Pd Alloys. Academic Dissertation'' (University of Turku, Turku, 1993).
12. M. BRINK, in ''Bioactive Glasses with a Large Working Range. Academic Dissertation'' (Åbo Akademi University, Turku, 1997).
13. W. M. STEEN, in ''Laser Materials Processing'' (Springer-Verlag, London, 1991).
14. T. CHIA, L. L. HENCH, C. QIN and C. K. HSIEH, *Mat. Res. Soc. Symp. Proc.* **190** (1990) 819.
15. T. KOKUBO, H. KUSHITANI, S. SAKKA, T. KITSUGI and T. YAMAMURO, *J. Biomed. Mater. Res.* **24** (1990) 721.
16. Ö. H. ANDERSSON and K. H. KARLSSON, in ''Proceedings of the 8th European Conference on Biomaterials'', vol. 8 (Elsevier, Amsterdam, 1990).
17. Ö. H. ANDERSSON and I. KANGASNIEMI, *J. Biomed. Mater. Res.* **25**(8) (1991) 1019.
18. I. REHMAN and W. BONFIELD, *J. Mater. Sci. Mater. Med.* **8** (1997) 1.
19. M. REGINA, T. FILGUEIRAS, G. LATORRE and L. L. HENCH, *J. Biomed. Mater. Res.* **27** (1993) 1485.
20. L. L. HENCH, *J. Am. Ceram. Soc.* **74**(7) (1991) 1487.
21. J. SERRA, P. GONZÁLEZ, S. LISTE, S. CHIUSSI, B. LEÓN, M. PÉREZ-AMOR, H. O. YLÄNEN and M. HUPA, *J. Mater. Sci.: Mater. Med.* **13** (2002) 1221.

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