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Surface modification of titanium implants using bioactive glasses with air abrasion technologies

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Abstract A growing number of surface treated titanium implants are routinely used in dental and orthopaedic surgery, with a view to enhancing integration capacity with osseous tissue. This study examines the use of bioactive glass 45S5 as an alternative abrasive and osteoproductive surface modification material. Abrasive blasting of commercially pure titanium with bioactive glass 45S5 produced an irregular finish with a surface roughness average (S_a) of 1.1 μm as determined by white light interferometry, backscattered and secondary electron microscopy. The roughness attained compares favourably with currently used implant designs. Further, Energy Dispersive X-ray Analysis (EDXA) and backscattered electron microscopy demonstrated that bioactive glass was distributed across the titanium surface and retained within fissures and roughened surface features. Being an osteoproductive material, this is advantageous as it is expected that the modified metallic surfaces will acquire osteopromotive properties, and thus be of benefit to the process of implantation in osseous tissue.

Introduction

A growing number of titanium implants are routinely used in dental and orthopaedic surgery for load bearing and passive medical applications. The excellent biological behaviour, superior corrosion resistance under physiological conditions and acceptable bone modulus matching justify the choice of commercially pure (cp) titanium and its alloys (Ti-6Al-4V) as materials for load bearing medical and dental implants [1]. However, although dental implants have a long proven clinical history as a restorative option, the acceptance is still low as a high degree of patient compliance is required and healing periods of atleast 3 to 6 months are necessary for the maxilla and the mandible, respectively. While newer early loading implant techniques that are reliant on primary mechanical fixation are becoming available, the majority of implants currently used rely mainly on osseointegration for their in-service stability.

It is widely accepted that the clinical success of such implants in dental applications is related to achievement and maintenance of a strong direct osseointegrated bond between the implant and the host osseous tissue [2], and that osseointegration is strongly affected by both physical and chemical properties of the surface. A number of authors have investigated the *in vitro* effect of differentially treated titanium and steel surfaces on the differentiation and proliferation of primary and established osteoblasts [3–9]. It was found that pure titanium gave rise to high proliferation rates and elevated levels of osteoblast-specific differentiation markers, such as alkaline phosphatase activity and osteocalcin expression. ASTM Grade 1 titanium has been shown to promote an increased collagen and calcium deposition in vitro, using a SOAS-1 cell line, when compared to grade 4 titanium [5]. Currently, most dental implant systems are made of commercially pure titanium because of its high biocompatibility *in vivo* and the very favourable osteointegrative response in the mandible and maxilla [6,10].

Pre-clinical and clinical studies have shown that the degree of implant roughness correlates strongly to the de-

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gree of osseointegration of both dental and orthopaedic implants [11–16]. A rough surface allows greater mechanical interlocking and exposes a higher surface area for integration. However, an optimum surface roughness is thought to exist, with an S_a value between 1–2 μm[15]. It is to be noted however, that the mechanisms and factors underlying the response of osteoblasts to modified surfaces remain poorly understood.

Based on these observations, a number of methods for surface roughening of titanium have been devised and implemented for use in commercial implants. Grit blasting, based on the bombardment of a surface with abrasive particles of high kinetic energy, is the most commonly used roughnening technique at present. Acid etching, (with hydrofluoric acid, for example) is also frequently employed alongside the blasting regime. On impact with a metal surface, the abrasive particles induce a localised plastic deformation and substrate removal.

The general consensus is that the particle size is influential on surface topography and roughness [17], contributing directly to energy deposition via imparted kinetic energy ($Ke = 1/2\ mv^2$) assuming the velocity of particles in the gas stream remains fairly constant. Abrasive blasting is most commonly conducted using particles of inert titanium dioxide (TiO_2) or alumina (Al_2O_3).

Aluminium oxide particulates have been shown to become embedded in titanium surfaces, remaining as surface contaminants, despite ultrasonic and other cleaning regimes [18–23]. These Al_2O_3 residues have been implicated in toxicity issues, including disrupting osteoproductive environments [22,23], potentially promoting osteolysis, fibrous encapsulation and interface failure. Thus, shortcomings of existing abrasive materials, such as damaging aluminium oxide remnants following the traditional blasting procedure have mandated the current research into alternative osseointegration friendly materials for the attainment of titanium surface roughening by abrasive blasting.

Any alternative abrasive material must achieve sufficient surface roughening without compromising the resulting material biocompatibility or osseointegrative capacity. The use of bioactive materials as abrasives may offer an alternative approach to tissue repair. Bioactive materials undergo a series of chemical changes that allow interaction with surrounding tissues and promotion of bone and interface formation, a process known as bioactive fixation [22]. In this study, the use of bioactive glass 45S5 as an abrasive osteoproductive surface-modifying material has been investigated. It is hypothesised that following the blasting procedure, remnant particles of bioactive abrasive remaining on the treated titanium surface will still produce a biologically active hydroxycarbonate apatite layer *in vitro* and *in vivo*, as observed for particulate bioactive glass [22]. This phase is chemically and structurally similar to the mineral phase of human bone, permitting direct interface bonding to host tissues. A further advantage of grit blasting modification of the titanium surface is the avoidance of in-service delamination of interposed surface coatings, a common problem in a corrosive, stressed and cyclically loaded service environment.

It is commonly acknowledged that there is an increasing clinical demand for true bioactive dental implants [15], possibly allowing wider case selection criteria and improved implant integration rates in the more challenging osteoporotic and medically challenged patients.

The objective of this study was to modify the implant surface topography in order to increase direct bone bonding area, accelerate interface strength acquisition and introduce a complex, biologically responsive interface morphology, capable of resisting motion at the bone / material interface. Residual bioactive glass is anticipated to further promote osseointegration by direct bone bonding. Osseointegration in the presence of soluble bioactive glass 45S5 particles may stimulate additional bony ingrowth and integration, thereby achieving accelerated formation of sound, stable and complex bone-titanium interfaces.

Materials and methods

Preparation of titanium discs

Thirty 14 mm diameter, 0.7 mm depth discs of commercially pure titanium (grade 1; TIMET, Birmingham, UK) were prepared by manually punching using a 3000 lb lever press and die system (RS Supplies, Corby, UK) from 1 m^2 stock sheet material. The discs were subjected to a sequential cleaning regime of acetone degreasing, rinsing in ethanol, sonication in deionised water and air-drying.

Production of particulates

Bioactive 45S5 glass was prepared by mixing 45 g SiO_2 , 41.9 g Na_2CO_3, 43.7 g $CaCO_3$ and 6 g P_2O_5 (all Sigma, Dorset, UK) by agitation and fusing in a 75 cm^3 platinum crucible in a high temperature furnace (BLF-1700 Carbolite, Hope, UK). The temperature was ramped to 1200 °C at a rate of 10 °C min^{-1}, dwelling at 1200 °C for 60 min, prior to a second rise to 1400 °C at the same rate. After 120 min, the molten bioactive glass was removed from the furnace, quenched in deionised water and dehydrated in absolute ethanol to prevent continued bioactive surface reactions. After ethanol removal by filtration and evaporation at 60 °C for 30 min, the frit was homogenised in a Pulverisatte 2 automatic grinding unit (Fritsch, Idar-Oberstein, Germany) at a constant down-force of 30 N. The powder was sieved into > 125 μm, 125–90 μm, 90–53 μm,

53–32 μm and < 32 μm fractions for 120 min using an automatic shaking unit (Endecott, London, UK) and all were then stored in a desiccator until use.

Particle size characterisation

The particle size distribution for the different production and characterisation steps for the used abrasives was carried out using a CILAS 1180 laser diffraction particle size analyser (Cilas, Orléans; France). Approximately 500 mg of each powder was introduced to the analysing unit and ultrasound was applied for 30 sec to the suspension, to disperse agglomerates prior to analysis. The results were expressed graphically and numerically for the median particle size (d_{50}), the 10th percentile particle size (d_{10}) and the 90th percentile size (d_{90}) using the Particle Size Expert Software package (Cilas, Orléans; France).

Grit blasting of titanium discs

A suitable sieve fraction was identified as allowing a consistent feed of material through the abrasion apparatus and suitable for the roughening of the titanium substrate. This was attained using the 53–90 μm sieve fraction subjected to several rounds of re-sieving, the resultant particle size range of the pooled bioactive glass as given in Table 1. Powders with 10th percentile values of particle size of less than 20 μm were shown to be detrimental to the abrasion process by forming agglomerates affecting the flow in the air abrasion instrument and therefore the homogeneity of the resultant abraded surface.

20 commercially pure titanium discs were abraded with a clinical air abrasion unit (CrystalAir, Crystalmark, Glendale Ca, USA) within an evacuated chamber in which the height and the incident angle of the abrasion nozzle to the titanium surface could be altered [24,25]. The sample table within this chamber was coupled to a PC-driven, programmable horizontal linear actuator (SMAC, Horsham, UK) that allowed the specimen feed rate to be controlled. Excess abrasive was removed by applied pressurised dry air at 5 bar for 5 sec post abrasion.

Bioactivity determination

The abrasive particle bioactivity, indicated by the *in vitro* formation of a topical hydroxycarbonate apatite phase, was confirmed using 150 mg of the post-abrasion powder residue, collected from the abrasion chamber after surface treatment. Bioactivity was confirmed by immersion in simulated body fluid [26], of an ionic concentration similar to that of human blood plasma(142.0 mM Na^+, 5.0 mM K^+, 1.5 mM Mg^{2+}, 2.5 mM Ca^{2+}, 148.8 mM Cl^-, 4.2 mM HCO_3^-, 1.0 mM PO_4^{2-}, pH 7.3). Fourier transform infra-red spectroscopy (FTIR) was employed for the bioactivity testing of surface hydroxyapatite formation [27]. Each particulate sample was suspended in 100 ml of SBF Buffer in a 250 ml conical flask and placed on an orbital incubator shaker at 175 rpm and 37 °C for 24 h, after which the glass was filtered from the SBF buffer and rinsed in acetone. The samples were then air dried and tested in a SpectrumOne Fourier Transform Infrared Spectrometer (Perkin Elmer, Beaconsfield, UK) by diffuse reflectance at a resolution of 4 nm.

Table 1 Particle size distribution of bioactive glass used for titanium abrasion expressed as percentile classes

	d10 (μm)	d50 (μm)	d90 (μm)
Particle size (μm)	41.8	74.7	110.44

Surface roughness and morphology

Prepared cpTi discs (n = 8 from each group) were analysed for average surface roughness (S_a) using a white light interferometer (Zygo, Middlefield, US) equipped with a 10 (Mirau lens to form a three dimensional representation of the surface. Surface morphology was then analysed by scanning electron microscopy imaging using Hitachi S3500 and Quanta 400 FEG (FEI, Hillsboro, US) electron microscopes. Specimen were carbon sputter coated prior to visualisation. Images were obtained at a working distance of 11 mm and a constant accelerating voltage of 15 kV.

Determination of residual abrasive

In order to estimate the area covered by bioactive glass, backscatter electron microscopic images were correlated to the energy dispersive x-ray diffraction (EDAX; Oxford Instruments, High Wycombe, UK) maps created for the K-alpha emission lines of silicon, sodium, calcium and titanium. As the detector was silicon crystal based, untreated commercially pure titanium discs were introduced as a control. The percentage coverage and average size of bioactive glass clusters was determined using ImageJ (NIH; http://rsb.info.nih.gov/ij/) for four different discs and two randomly selected fields on four different discs.

Results

A consistent particle flow through the abrasion unit was obtained by the 90–53 μm fraction of bioactive glass, of a pooled particle size distribution as given in Table 1.

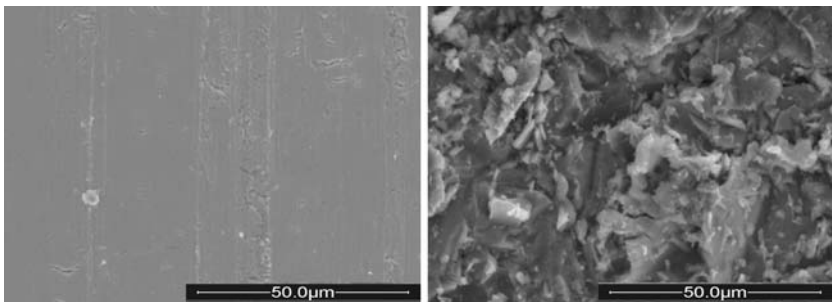

Fig. 1 Secondary electron beam scanning electron micrograph of commercially pure Ti disc (**a**) prior to abrasion, (**b**) after bioactive glass abrasion, showing an irregular rough appearance of the surface at 1200 x magnification and an accelerating voltage of 15 kV

The scanning electron micrographs obtained displayed a smooth surface finish for the untreated commercially pure titanium samples (Fig. 1a), apart from minor surface irregularities due to sample processing. Under the abrasion variables applied, the commercially pure titanium surface was roughened using bioactive glass, introducing a complex morphology to the smooth titanium substrate, comprising a range of irregular, high frequency angular topographical changes (Fig. 1b).

The roughness, as determined from white light interferometry images (Fig. 2), increased from an S_a value of 0.19 µm to a post-abrasion roughness of 1.04 µm (Table 2). This was found to be statically different by means of the student's t-test to a significance of $p < 0.001$. A similar roughness was observed within measurements of areas within one disc and between discs.

Fourier-transform infrared spectroscopy demonstrated the formation of a topical hydroxycarbonate apatite layer after 24 h incubation in simulated body fluid of the post-abrasion powder, as indicated by the appearance of characteristic HCA peaks between wavenumbers 550 and 600 cm^{-1} . This suggests bioactivity of the glass present on the titanium surface (Fig. 3).

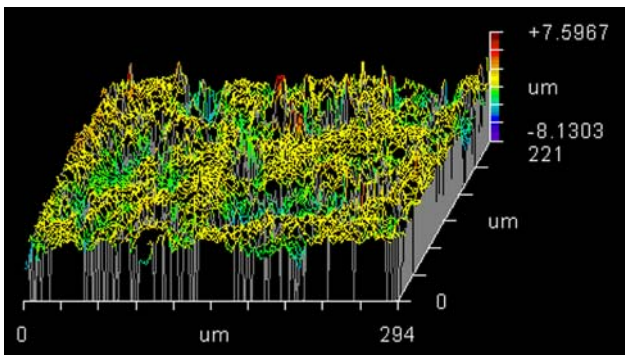

Fig. 2 White light interferometric image obtained for bioactive glass abraded commercially pure titanium

Table 2 Roughness parameters for 8 measurements (two points on four discs)

Material	Roughness Sa (SD)
Untreated Ti	0.19 µm (0.09)
Bioactive glass abraded Ti	1.04 µm (0.13)

Secondary electron microscopy did not conclusively visualise bioactive glass present in the rough surface obtained. Therefore backscatter electron microscopy and EDX mapping were attempted to visualise the surface area coverage by bioactive glass. Figure 4 contrasts the same visual field in backscatter mode and correlates this to the elemental map obtained. The bioactive glass constituent elements of sodium (Fig. 4b top left panel), silicon (Fig. 4b top right panel) and calcium (Fig. 4b bottom left panel) co-localise within the group as well as the lower mass density areas shown as darker deposits on the surface (Fig. 4a) obtained by backscatter imaging, allowing the typical presence and area of coverage of bioactive glass in the surface of titanium can be estimated by area mapping. The absence of a signal on the control discs as well as the positive co-localisation of all component elements indicated that the silicon-crystal based detector did not adversely affect the elemental maps generated, in particular the silicon trace. This indicates that bioactive glass is retained on the surface in spite of the post-preparation cleaning regimen.

The percentage area coverage of the titanium disc with bioactive glass was estimated using image analysis of the backscattered images (Fig. 5).

The percentage area coverage, as determined by ImageJ area analysis of thresholded images was 43.5 % (SD 11.2). The percentage coverage of backscattered images agrees with the value obtained for EDXA maps for Si, Ca and Na.

Discussion

We have demonstrated that 45S5 bioactive glass can be utilised to roughen commercially pure titanium surfaces to an adequate degree for modulating a favourable osteoblast response. A suitable abrasive particle size range of 90–53 µm was determined to obtain a consistent feed rate to maintain uniform abrasion of the target substrate. It was

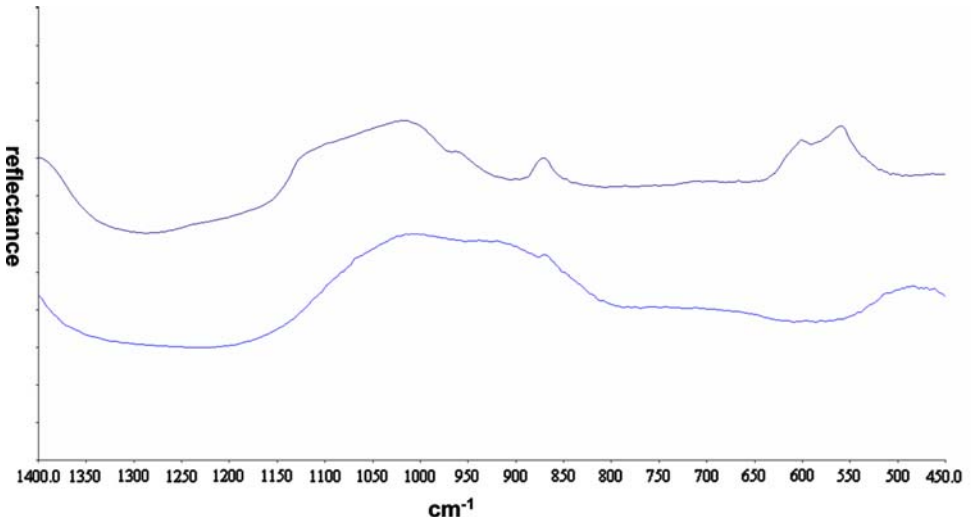

Fig. 3 Fourier-transform spectrum of unreacted (lower) and 24 h SBF immersion post-abrasion powder (upper line)

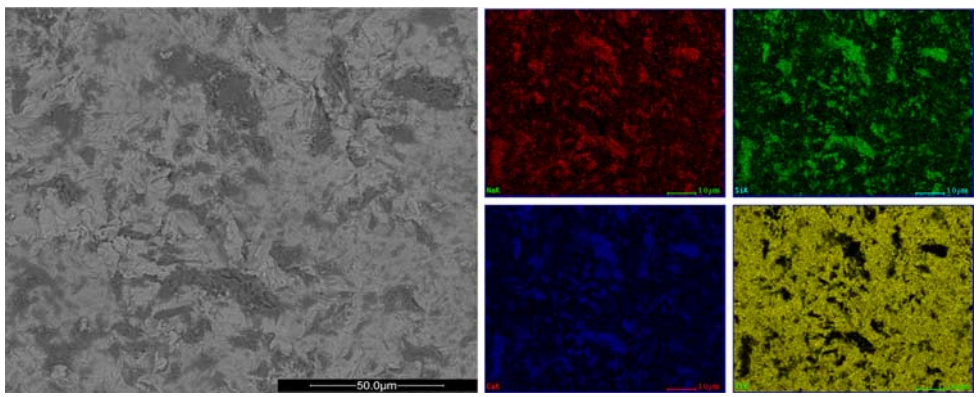

Fig. 4 (**a**) Backscatter electron micrograph of bioactive glass abraded surface at an accelerating voltage of 15 kV and a magnification of x1500 (**b**) elemental map, derived from the same field of view to (**a**), of K-alpha line peaks of sodium (red), silicon (green), calcium (blue) and titanium (yellow)

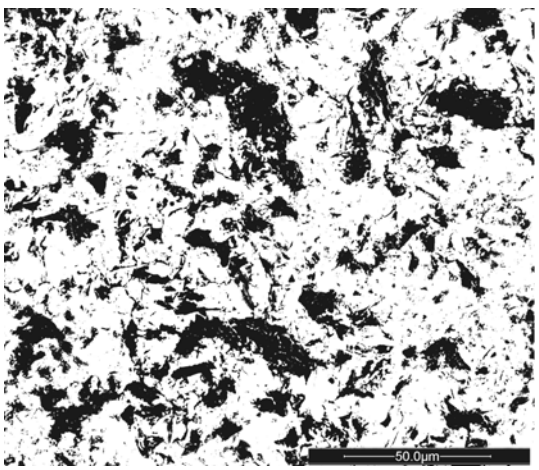

Fig. 5 Thresholded image of Fig. 4a, displaying a black/white image, showing, the dark patches selected for analysis. Percentage coverage 34%

found that particles of less than 20 µm within the abrasion blend lead to the formation of agglomerates, adversely affecting the powder flow and hence the resultant surface consistency.

EDXA mapping and backscattered electron microscopy demonstrated the retention of bioactive glass within surface features, implying that there is a mechanism for surface modification and positive benefits from surface debris. This contrasts with alumina where residual particles are stipulated to be deleterious [18,21,23]. The presence of residual bioactive glass particles in spite of the cleaning regimen suggests that a fraction of the airbrasive is retained on the surface after impingement.

Under the SEM imaging conditions applied, namely an accelerating voltage of 15 kV with respect to the bioactive glass and a conservative approach to the generation of the thresholded maps, we would expect an under-representation of the quantity of bioactive glass deposited on the surface to be obtained.

Bioactive glass abrasion can function to roughen commercial titanium implants allowing post modification of a smooth machined implant can be performed

The advantages to replacing currently used abrasives include improved control of roughening with TiO_2, and elimination of potentially toxic residual surface alumina residues by developing bioactive, osteoproductive abrasive

materials which are well known to accelerate bony healing and dissolve over time.

Both the formation of the HCA surface phase, as well as the osteopromotive properties of bioactive glass [28–32] indicate the potential of bioactive glass abrasion to lead to a bioactive, osteopromotive implant material, potentially offering improved bony integration to osteoconductive abrasives used for the abrasion of titanium substrates [4].

Due to the *in vivo* solubility of bioactive glass 45S5 it is anticipated that no wear particle effect as well as delaminating effect, as was previously observed on HA coatings [33,34] will be exerted by particles becoming detached from the titanium surface.

By means of the implant's topography and embedded 45S5 Bioglass particles, it is expected that there will be an improved rate of commitment of bone precursor cells (human mesenchymal stem cells) to osteoblastic lineage differentiation early after adhesion to the titanium surface leading to better osseointegration following implantation. Furthermore, bioactive glass has shown to be active against supra- and sub-gingival bacteria [36] further underlining the potential benefits of bioactive glass in contact with an implanted device by means of air abrasion.

Bioactive glass 45S5 would be an attractive candidate for surface modification of implanted devices as it is itself an approved bioactive material as well as having pre-existing long term safety data. Possible applications could entail the post-modification of pre-packaged or custom-made commercially pure titanium-based implants.

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