Acta Biomaterialia 6 (2010) 3318–3324

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Femtosecond laser induced fixation of calcium alkali phosphate ceramics on titanium alloy bone implant material

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ARTICLE INFO

Article history:
Received 27 November 2009
Received in revised form 2 February 2010
Accepted 10 February 2010
Available online 16 February 2010

Keywords:
Bone implant
Bioceramic coating
Titanium
Calcium phosphate
Femtosecond laser

ABSTRACT

Femtosecond lasers provide a novel method of attaching bioceramic material to a titanium alloy, thereby improving the quality of bone implants. The ultrashort 30 fs laser pulses (790 nm wavelength) penetrate a thin dip-coated layer of fine ceramic powder, while simultaneously melting a surface layer of the underlying metal. The specific adjustment of the laser parameters (pulse energy and number of pulses per spot) avoids unnecessary melting of the bioactive calcium phosphate, and permits a defined thin surface melting of the metal, which in turn is not heated throughout, and therefore maintains its mechanical stability. It is essential to choose laser energy densities that correspond to the interval between the ablation fluences of both materials involved: about 0.1–0.4 $J\ cm^{-2}$. In this work, we present the first results of this unusual technique, including laser ablation studies, scanning electron microscopy and optical microscope images, combined with EDX data.

1. Introduction

Implant material inside the human organism usually faces a number of demands. Besides being tolerated by the body for some applications, biomaterials sometimes have to be actively involved in their integration into a living process. Artificial bone implants, for example, play a bioactive role when they grow together and merge with living bone tissue. The mechanical stability of titanium and some titanium alloys is widely appreciated already in dentistry and orthopaedics. Uncoated titanium is integrated only slowly into the surrounding bone tissue and long-term stability cannot always be achieved. The properties of such an implant are considerably improved by a suitable coating of the metal. It can be accepted as a bone-like substitute by the living cells. It can be rapidly integrated and may fulfil its purpose for a long time without a mechanical loosening.

Due to the difference of the materials involved, the coating is a challenging process. Metal has to be connected to a bone-like ceramic substance [1–4]. Synthetic hydroxyapatite is used in a coating process called plasma spraying, but there the apatite layers are sometimes fissured and brittle [5]. So the deposited layer may come off when a hip prosthesis is hammered in place. The surface structure of the metal plays a vital role for a successfully fixed layer [6]. A rough metal binds the coating much better. There have been attempts to sinter the ceramic material, but the necessary high oven temperature irreversibly lowers the mechanical stability of the titanium. In the last few years there were reports about calcium phosphate coatings on Ti6Al4V that were fabricated with high power CO_2, continuous-wave, and pulsed lasers that all result in a complete melting of the ceramic material during irradiation [7–10].

Femtosecond lasers are able to ablate material in thin layers off a surface without changing the properties of the underlying bulk material. The ultrafast pulses have only very little thermal impact on the bulk material around irradiated volumes [11]. For each wavelength there are different material characteristic ablation threshold energies. With a suitable combination of two materials we expected an individually adjusted melting associated with the fusion of the two components. This aim was achieved with the titanium alloy Ti6Al4V and the calcium alkali phosphate GB14. We report on initially loosely bound GB14 powder that can be fused onto the metal surface with femtosecond laser pulses. The laser radiation penetrates the GB14 top layer and melts a thin surface film of the titanium alloy, binding the ceramic particles that are already in contact with or near the metal surface.

2. Materials and methods

2.1. Preparation of ceramic coated titanium alloy plates prior to the laser treatment

The 2 mm thick plates of the titanium alloy Ti6Al4V of medical grade have either been polished, grinded or lapped on one side. Some were round with a diameter of 16 mm, others rectangular in the size of 20 mm × 30 mm. The polished plates were only used

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doi:10.1016/j.actbio.2010.02.016

for laser sensitivity tests in order to determine the ablation threshold fluence F_{th}. A slightly rougher, unpolished metal surface was used for the dip-coating transfer of the ceramic powder. This layer consists of a calcium alkali phosphate called GB14 [12]. Its main crystalline phase is $Ca_2KNa(PO_4)_2$ [13]. With a ball mill the crystalline material was ground down to a particle size of D_{50} = 1.8 μm. For the dip-coating the powder was added to water (20–40% GB14) containing between 0% and 5% polyvinyl alcohol (PVA, Merck), the latter serving as a binder for the GB14 grains after the water has evaporated. The viscosity of the slurry was within the interval of 30–80 mPas, the dip-coating velocity between 20 and 100 mm min^{-1}. The resting duration in the slurry was 10 s. Heating of the samples to 100 °C improved the drying process. The reduction of the water content lowered the probability of damage due to water vapour pressure inside the GB14 layer during the following laser irradiation. The GB14 layer density was 1.68 g cm^{-3}. The layer thickness of about 30 μm was measured with the calibrated focus wheel on the optical microscope.

2.2. Laser treatment

Before the ceramic covered metal plates were exposed to the laser beam, the two constituents had to be investigated separately. Pure Ti6Al4V plates were used to find the ablation threshold fluence F_{th} of the metal, and GB14 covered plates were suitable for the F_{th} determination of GB14. For this investigation we used a femtosecond laser (Femtolasers, Vienna) with a centre wavelength of 790 nm. The laser emitted pulses of 30 fs duration at a pulse frequency of 1000 Hz. The number of pulses per spot could be chosen freely, and the necessary energy of the beam, for our experiments up to about 400 μJ, lay below the possible maximum energy of 800 μJ. The pulse duration could be measured with an autocorrelation device. The laser beam was focussed with a spherical mirror of a focal length of 500 mm. The beam diameter ($1/e^2$) in the focus was about 200 μm. The samples were irradiated in the focus with a series of different energies, above and below the threshold energy for ablation. The size of the laser damage was measured under a microscope. The squared diameter of the ablated area in combination with the corresponding energy yields the Gaussian beam radius, and thereupon one can calculate the fluence values [14,15], including the fluence threshold F_{th} for ablation. This procedure was carried out for different laser pulse numbers *N*, because the F_{th} values differ with changing *N*.

The ablation diameter and depth increase with rising laser energy. The damage was investigated under an optical microscope (Nikon, Eclipse L200) and with a scanning electron microscope (SEM) (Hitachi S-4100). After the illumination with the laser, the GB14 covered metal plates were rinsed with water and treated in an ultrasonic bath to remove the loose excess ceramic layer fraction. The thin layer of GB14 that remained fixed to the Ti6Al4V surface was analyzed with the SEM, and the chemical composition was measured with energy dispersive X-ray spectroscopy EDX (part of the SEM device).

3. Results and discussion

3.1. The individual properties of GB14 and Ti6Al4V

The fine crystalline GB14 powder is well recognizable in Fig. 1. Here, the average size of the particles lays around 1.8 μm. The binder as a component between the grains is not visible in the SEM image. The slurry prepared from the ceramic powder is able to form on the Ti6Al4V plate layers of thicknesses between the grain size (only 1 or 2 μm) and up to hundreds of micrometers. The thickness can be adjusted to a desired value because it is proportional to the viscosity, which in turn is proportional to the mass content of the ceramic powder. The layers investigated here have a thickness of about 30 μm. The unpolished metal plates could be covered with a smooth GB14 layer with insignificant thickness alterations towards the edges of the plates. Still after drying the layer can easily be scratched off the surface. Heating of the sample in an oven to 300 °C for 1 h does not improve the stability but simply evaporates a part of the binder, and the GB14 surface appears slightly brownish. The binder was only necessary to stabilize the GB14 particles on the metal plate to keep it in position for the laser treatment. Afterwards the fixed GB14 was bound significantly stronger to the metal, and any potentially remaining binder would not increase this adhesion.

Therefore, in the experiments the fs laser was applied only to unheated samples, since heating seemed to offer no advantage, like for example a desired closer contact of the GB14 to the metal surface. All procedures were done in air at room temperature. We shot the following series of laser pulses: single, 10, 100 and 1000 pulses per spot on the samples in rows of varying energies. The damage surface area allowed the calculation of the ablation threshold fluence F_{th}. In the Ti6Al4V surface the laser pulses produced well-defined, sharp-edged ablation craters. The sensitivity test for the GB14 layer is equally well-defined, because the laser generates distinct ablation grooves. The example in Fig. 2 shows the effect of a

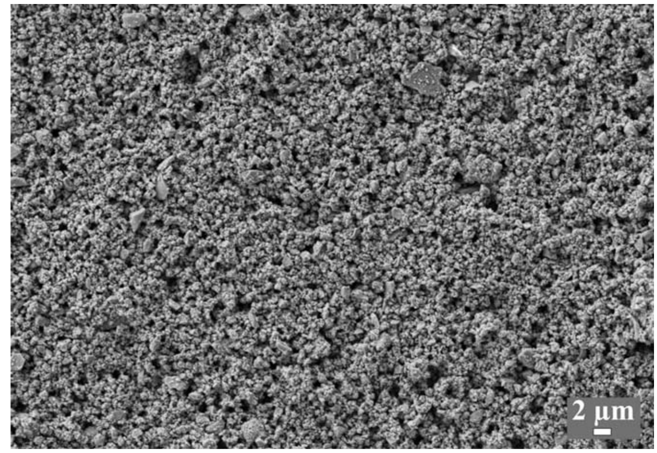

Fig. 1. SEM image of GB14 powder after dip-coating onto a Ti6Al4V plate. The suspension in water and PVA contained 23 wt.% of GB14.

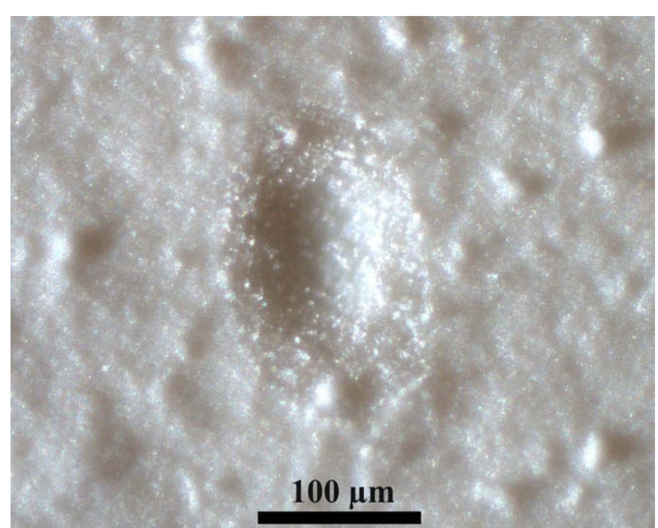

Fig. 2. Optical microscope image of the GB14 surface with an ablation crater caused by a single laser pulse of the energy density F = 2.85 J cm^{-2}.