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Generation of bio-compatible titanium alloy surfaces by laser-induced wet treatment

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ABSTRACT

A laser-induced surface treatment in wet conditions was developed for improving the biocompatibility of titanium alloys. Disk-shaped titanium samples were soaked in a calcium nitrate solution and subsequently irradiated by a Yb fiber pulse laser beam, creating a modified surface layer containing calcium and oxygen elements. The modified layer exhibited optimal properties for treatment at a defocus distance of −1 mm and for a calcium nitrate concentration of 10%. The apatite-forming ability of the modified surface was affirmed in bioactivity tests performed in the simulated body fluid. It was shown that a Ca-rich layer was stably generated by the modified treatment process. The generated Ca-rich layer demonstrated superior biocompatibility, suggesting increased hydroxyapatite content.

1. Introduction

While dental implants have been used to replace missing teeth since the mid-1960s, their use has become especially widespread in recent years. Currently, dental implants are used as support structures for single crowns and bridges that restore a larger span of missing teeth or dentures. Implants are manufactured using titanium, because this metal is compatible with body tissues and can bond to the adjacent bone during healing [1–4]. However, the long duration of several months required for titanium and its alloys to directly bond to bone is disadvantageous. To shorten the bonding time and stabilize the fixtures, special surface modification treatments of titanium alloy are required. Various surface modifications enhancing the bioactivity of titanium alloy have been reported, including sandblasting, acid etching, plasma treatment and anodic oxidations [4–9]. Among the surface properties, the roughness and chemical composition are considered to be the most important parameters for implant – tissue interaction and osseointegration. In one impressive report, the surface arrays of TiO_2 nanotubes containing calcium, generated by a hydrothermal treatment, demonstrated excellent bioactivity [4].

Recently, laser technology has been widely applied in the surface modification of advanced structural materials [10–15]. A high-quality, high-frequency pulse laser is expected to achieve a highly efficient surface treatment at localized target areas. Moreover, a laser irradiation-induced wet treatment has been previously investigated by us [15]. In this method, the surface is treated to obtain a layer containing a particular chemical component in the solution. A wide range of possible solutions can be selected, and the thermal damage to the treated surface can be avoided by minimizing the laser energy. In this study, laser-induced wet treatment was performed in a calcium nitrate solution to generate a titanium alloy surface containing the calcium element. The apatite-forming ability of the formed surface was affirmed in bioactivity tests performed in simulated body fluid (SBF).

2. Coordination of experiments

2.1. Laser-induced wet treatment

Fig. 1 shows the experimentally tested laser-induced wet treatment system together with an image of the sample surface during laser irradiation. The sample held on the upper surface of a stage is immersed in a water bath filled with the calcium nitrate solution and irradiated with a Yb fiber pulse laser placed above the bath. The liquid level, defined as the distance between the surfaces of the specimens and the liquid, was carefully adjusted to 1 mm. The laser irradiation conditions are listed in Table 1. To investigate how the energy density of the laser beam affects the generated modified layer, defocus distances of 0, −1 and −2 mm were used. The defocus distance and laser scanning method are shown in Figs. 2 and 3, respectively. The spot size and power density of the laser for different defocus distances are listed in Table 2. The power density was calculated by dividing the measured laser power by the size of the focal point at each focal length. Table 3 presents the chemical composition of the commercially pure titanium used in this study. The diameter and thickness of the specimens were 15 and 4 mm, respectively. Prior to laser irradiation, the specimen surfaces were polished with emery papers and mirror finished

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with diamond powder. The sample surfaces were analyzed by laser microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and Raman spectroscopy.

2.2. Bioactivity test

To evaluate the *in vitro* bioactivity of the treated samples, the samples were soaked in 1.5 SBF (a solution with an ion concentration 1.5 times greater than that of the simulated body fluid) and their apatite-forming ability was evaluated. The composition of 1.5 SBF was as previously reported by Kokubo et al. [16,17]. The samples were inserted in culture vials containing the SBF for 7 days at 37 °C.

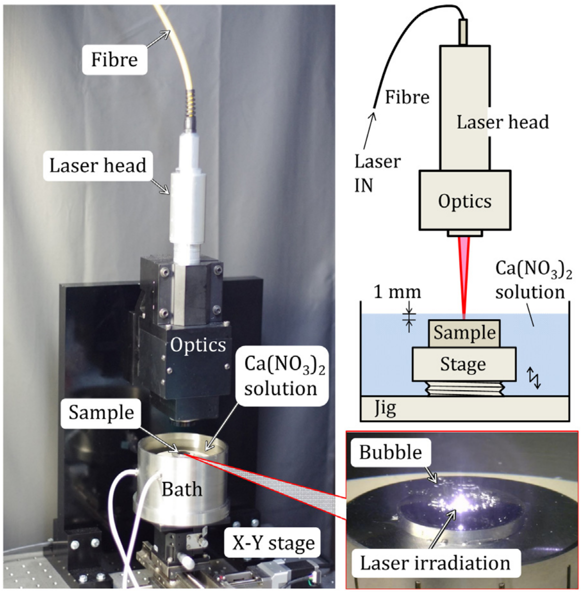

Fig. 1. Overview of the laser-induced wet treatment system.

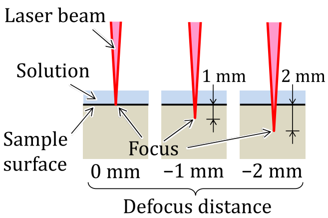

Fig. 2. Definition of defocus distance.

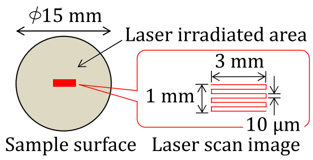

Fig. 3. Laser scanning method.

Table 1
Conditions of laser irradiation.

Wavelength	1064 nm
Pulse width	100 nm
Repetition frequency	100 Hz
Scan rate	50 mm/min
Scan pitch	10 µm
Solution	Calcium nitrate ($Ca(NO_3)_2$)
	Concentration: 2%, 5%, 10% and 15% Pure water

Table 2
Spot size and laser power density at different defocus distances.

Defocus, mm	Spot size, µm	Power density, W/mm^2
0	8	3710
−1	170	82
−2	339	21

Table 3
Chemical composition of titanium samples (mass%).

N	C	H	Fe	O	Ti
0.03	0.08	0.013	0.25	0.20	Bal.

3. Generation of surface modified layer by laser-induced wet treatment

The SEM images of the laser-irradiated surface at different defocus distances and the corresponding average surface roughness values (measured by a laser microscope) are shown in Fig. 4. The surface appearance depends on the defocus distance and is roughest under the on-focus condition. This roughness is attributed to the greater degree of melting with increasing laser power density and minimizing the spot size.

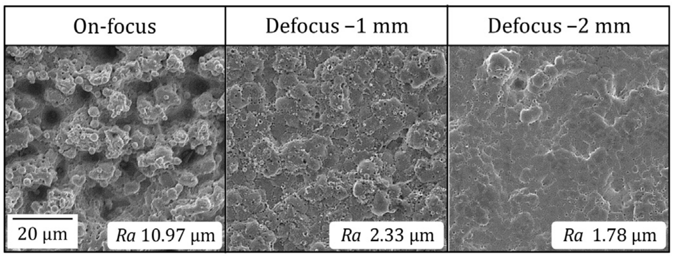

Fig. 4. SEM images of the laser-irradiated surface under different defocus conditions.

Fig. 5 shows the cross-sectional SEM images of the laser-irradiated surface and the results of EDS mapping in the same region. At a defocus distance of −1 mm, calcium and oxygen elements are clearly observed in regions (A) and (B) of Fig. 5, respectively. The thickness of the modified layer is approximately 1 µm under this defocus condition. When the defocus distance is doubled to −2 mm, the presence of both elements is attenuated. Under the on-focus condition, although both elements are clearly observed, the profile and thickness of the modified layer are unacceptably irregular.

The surface element concentrations of Ti, Ca and O in the modified layer at various defocus distances are shown in Fig. 6. The surface element concentration of Ca is maximum at a defocus distance of −1 mm (see Fig. 6(b)). Correspondingly, the peaks of the surface element concentration of Ti and O are slightly lower at a defocus distance of −1 mm (see Fig. 6(a) and (c), respectively).

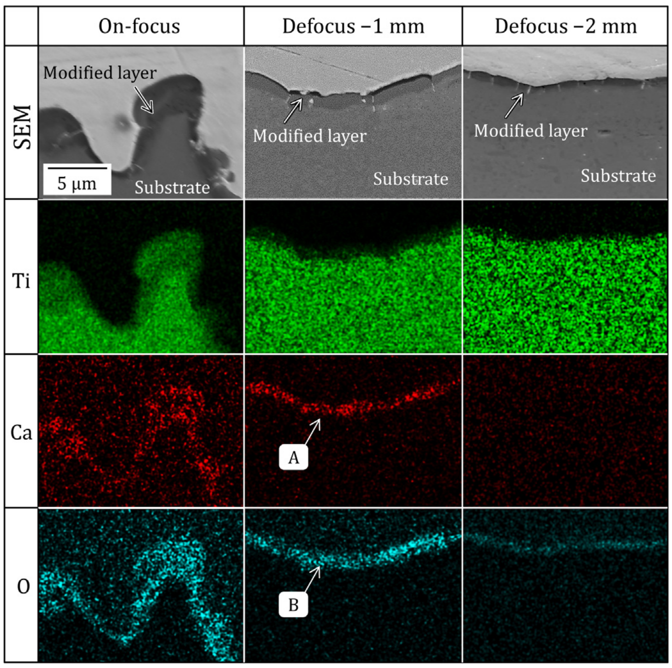

Fig. 5. Cross-sectional SEM images and EDS surface mappings.

To investigate the effect of the density of the dissolved calcium nitrate on the formation of the modified layer, the laser radiation tests were performed for $Ca(NO_3)_2$ concentrations ranging from 2% to 15%. In these tests, the defocus distance was set to −1 mm. The surface element concentrations of Ti, Ca and O in the modified layers

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