Effect of sintering temperature on microstructure of TiO$_2$ scaffold

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Abstract  Due to an excellent biocompatibility of titanium dioxide (TiO$_2$), it is promising to use as scaffolds for inducing bone formation. The well-interconnected pore scaffolds were fabricated by sponge replication method in order to promote osteoblast ingrowth and vascularization. The viscosity of the slurry was adjusted by addition of calcium chloride (CaCl$_2$) which led to more uniformity and densification. The effects of sintering temperatures on microstructure were analyzed by scanning electron microscope (SEM) and microcomputed tomography (Micro-CT). Our experiments showed that the higher sintering temperature increased the grain size and more uniformity of the scaffold. Furthermore, the struts became more rounded and microcracks were not observed which probably correlated to the higher density of scaffold. Thus, it is suggested that optimization of sintering temperatures might allow better control of grain growth and result in more microstructural uniformity.

1. Introduction
Titanium dioxide (TiO$_2$) is well known as the promising material for biomedical applications due to its excellent biocompatibility and good osteoconductivity [1-2]. The most widely used technique for fabrication of well-interconnected pore TiO$_2$ scaffolds is sponge replication method. In order to promote osteoblast ingrowth and vascularization, the polymer that used as the template should have the desired pore size that must be open and large enough so that the cells can migrate into the scaffolds [3].

It is worth noting that the biocompatibility and bone cell proliferation are crucial factors for these custom-made scaffolds. Therefore, the interconnectivity of the scaffold will be more considerable than mechanical properties. However, since the scaffolds are highly porous, the mechanical properties are limited and may thus have insufficient strength to be machinable shaping for used [4].

The strength of the scaffolds is strongly dependent on the size and observation of cracks and flaws in the struts structure [4]. Nevertheless, the mechanical properties may be improved by optimizing the processing steps in the fabrication technique. The aim of this study was to investigate the effect of sintering temperatures on the microstructure of well-interconnected TiO$_2$ scaffolds.

2. Experimental
2.1. Polymer foams
The polyurethane ester foam templates with 60 pores per inch (Bulbren S, EurofoamGmbH, Germany) were used in this study. The foams were cut to cylindrical templates of 15 mm in diameter and 10 mm in length by punched them out with a metal stamp.

2.2. Scaffold fabrication
The slurry was controlled with the solid content of 65 wt% which prepared by adding 65 g of TiO$_2$ powder (Degussa, P25) into 35 ml of 0.1 M CaCl$_2$ solution. The TiO$_2$ slurry was stirred at rotation speed of 1,000 rpm for 30 minutes until the slurry mixture was homogeneous, but the higher amount of powder resulted in agglomerated slurry. The slurry viscosity was adjusted by small addition of 1 M HCl.

The polymer foams were then dipped into the TiO$_2$ slurry, excess slurry was squeezed out by a roller, make sure that only thin layer of the slurry left on the surface of polymer foams. According to the sponge replication method which is one of the template techniques, the surface charge of the replica and TiO$_2$ powder in slurry must be in opposite charge in order to promote the good attraction for both components. This is a main reason to select the polyurethane ester sponge used as the replica because the carbonyl group in sponge can act as electron donor. TiO$_2$ powder in the slurry at acidic pH displayed the positive charge. The sample were dried at room temperature for at least 12 hours. Before sintering the scaffolds, the polymer template was burned out at 450°C at a heating rate of 1°C/min. After 1 h soaking time at 450°C, the temperature was raised to between 1350°C and 1500°C at a rate of 1°C/ min and the soaking time was set to 3 h. After that the sintered scaffolds were then cooled down to room temperature.

2.3. Characterization
The crystal structure of the sintered TiO$_2$ scaffolds was studied by X-ray Diffractometer (XRD, D8-Advanced, Bruker AXS Model D8, German), using Cu Kα radiation (λ = 1.5406 Å; 40 kV and 40 mA). The microstructure was observed by scanning electron microscope (SEM, JEOL JSM-6480LV). The scaffolds were fixed on aluminium stubs and viewed with backscattered electrons at 15 kV accelerating voltage. Micro Computed Tomography (Micro-CT, Scanco Medical, Switzerland) was used to determined 3D scaffold structure. Scaffolds were placed in a plastic holder and using a voltage of 70 kV, current of 113 μA.

3. Results and discussion
The sintered TiO$_2$ scaffolds between 1350°C and 1500°C were analysed by XRD to determine their phase are presented in Figure 1. The data showed that the sintering process of the TiO$_2$ scaffolds produced TiO$_2$ with rutile crystalline structure.

After sintering of TiO$_2$ scaffolds at various temperatures between 1350°C and 1500°C with soaking time for 3 h, the microscopic appearances are shown in Figure 2. As-sintered scaffold at 1350°C showed the scaffold struts with hollow structure (indicated by an arrow) due to elimination of the polymer foam template. One side of the walls of the struts had collapsed inward resulting in folded strut appearance which had a direct effect on mechanical strength of the scaffold. Furthermore, the longitude cracks along some of the struts were observed (indicated by a rectangle). At 1400°C, the cracks along the edge of the struts still observed but decreased significantly. By the time, the grains size was increased. As the sintering temperature was increased to 1450°C, the folded struts had developed into a solid structure with rounded corners and the earlier cracks along the struts were disappeared. Moreover, the small grains were reduced and resulted in more uniform grain size. At 1500°C, the scaffold struts showed denser and among the grain boundaries became more three-dimensional. The struts showed the uniform small grain size and the grain boundaries were clearly observed. This is confirmed that the higher sintering temperature, the better strength of TiO$_2$ scaffolds.
Figure 1. XRD pattern of sintered TiO$_2$ scaffold at selected sintering temperature, 1500°C.

Figure 2. The effect of sintering temperatures on the microscopic appearance of TiO$_2$ scaffolds.

The pore structure of sintered TiO$_2$ scaffolds are showed in Figure 3. The sintered scaffolds maintained the original struts and pore shape of the template and formed highly interconnected pore structure as shown in Figure 4. For all four different scaffold sintering temperatures, the average porosity was above 92%.
Figure 3. 3D micro-CT images of the sintered TiO$_2$ scaffolds at different sintering temperatures.

Figure 4. Micro-CT cross-section images of the sintered TiO$_2$ scaffolds at different sintering temperatures.

4. Conclusions
This study showed that increasing of the sintering temperatures could improve the microstructural uniformity of TiO$_2$ scaffolds which fabricated by sponge replication method. The desired pore architecture was also controlled as shown in well-interconnectivity and high porosity as high as 92%, which is good for promoting of bone cell proliferation. The crucial point that should take into account in the next step is cytotoxicity testing of the as-prepared scaffolds to bone cell. Moreover, the strength of the scaffolds might be improved by the optimization of the sintering temperatures, soaking time, multi-step dipping in the slurry. However, improvement in other processing parameters may also allow further enhancement in mechanical strength in order to produce machinable custom-made scaffolds.

5. References
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