The Effect of Vacuum Leak Rate on Sintering of Porous Titanium Scaffold

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Titanium is a highly reactive metal and its high-temperature processing has to be done at a high-vacuum atmosphere. In this research, porous titanium scaffolds were fabricated using the space holder method for dental reconstruction purposes. Accordingly, the samples were sintered in two different vacuum furnaces at the vacuum level of 0.013 Pa, including high-vacuum leak rate (HLR) and low-vacuum leak rate (LLR). The microstructural study using the scanning electron microscope revealed that there was no significant difference in the microstructure of the samples. A compression test on the porous titanium scaffolds indicated that the HLR sample had less strength than the LLR sample. X-ray diffractometry also revealed that, besides the titanium peaks, the HLR sample included titanium oxide phases, unlike the LLR sample. Therefore, both vacuum chamber design and a vacuum leak rate of the furnace are parameters which are effective on the sintering of the porous titanium scaffold and should be considered.

Keywords *Sintering; Titanium scaffold; Oxidation; Vacuum furnace*

I.   INTRODUCTION

Titanium and some of its alloys have been used for load bearing implantation or bone and dental reconstruction purposes, because of their high strength, biocompatibility, and superior corrosion resistance *in vivo* [1]. However, bio-inertness and higher elastic modulus are the weaknesses of titanium, as compared with the human bone, leading to bone loosening or weak implant fixation [2]. To overcome these problems, porous titanium scaffolds have been fabricated to improve the biological fixation of titanium implants to the surrounding jaw bone [3]. Also, some surface treatment techniques have been applied on titanium by researchers to enhance the bio-functionalization of the titanium surface [4−6].

For example, Tan *et al.* reported that a coating of TiO_2 on the surface of titanium promoted better osteoblasts cell adhesion and spreading, as compared to the naked one, as well as the higher cell proliferation. Titanium oxide can improve the bioactivity and ensure the faster osseointegration of titanium implants [4].
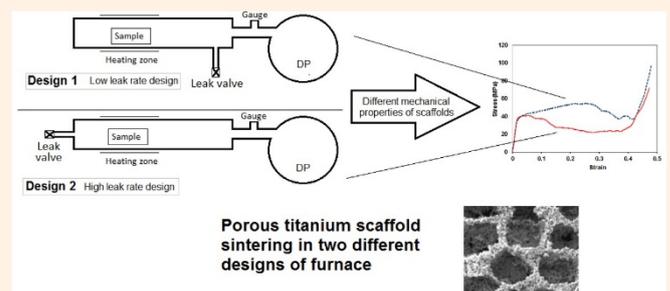
Many different methods have been used to fabricate porous titanium scaffolds; different values of mechanical properties have been reported for porous titanium scaffolds. The elastic modulus of titanium scaffolds including 80, 84, and 55 vol% porosities has been reported to be 2.87, 0.58, and 0.5 GPa by Wen *et al.* [7], Manonukul *et al.* [8], and Rubshtein *et al.* [9], respectively. Non-uniformity of the macropore size [8], the presence of micropores at the struts of the scaffold [10], and different parameters of processing [9] have been introduced as the possible reasons for these differences. However, we believe in the presence of another

parameter influential on porous titanium scaffolds fabrication, which has not yet been considered by the researchers.

Because of the high affinity of titanium and its oxidation at high temperatures, titanium processing is done in vacuum furnaces. In the vacuum furnace, beside the vacuum level, the vacuum leak rate is also an important parameter. The mismatch between the results of mechanical testing of different researchers on porous titanium scaffolds can be due to different vacuum leak rates of furnaces which will result in air diffusion to the chamber of the furnace during sintering [11]. Also, the geometry of the vacuum furnace and the position of gas inlet/outlet of the furnace can affect the flow passing inside the furnace, probably affecting the quality of the sintered products [12].

So, in this research, the vacuum leak rate and the position of the vacuum leak valve were chosen as the processing parameters whose effect on the properties of titanium scaffold sintering in a vacuum furnace had not been investigated before. Porous titanium scaffolds were fabricated using the space holder method. In this method, metal powder was mixed by a spacer agent and cold compact, then the spacer agent particles were removed from the pellet, and finally the obtained porous structure was sintered at high temperatures. Of course, spacer removal can be done during sintering or after that [13].

II.   MATERIALS AND METHOD

A.   Porous titanium scaffold fabrication

Titanium powder of grade 2 (particle size of 43 μm, OSAKA Titanium Technologies Co., Japan) as the matrix of the scaffold and NaCl particles (Wako Pure Chemical Industries, with the mesh size of 45−50, Japan) as the space holder agent were used for the fabrication of porous titanium scaffolds including 60 vol% nominal porosity. This was done using the space holder method. Accordingly, the scaffolds were sintered in vacuum furnaces with a horizontal
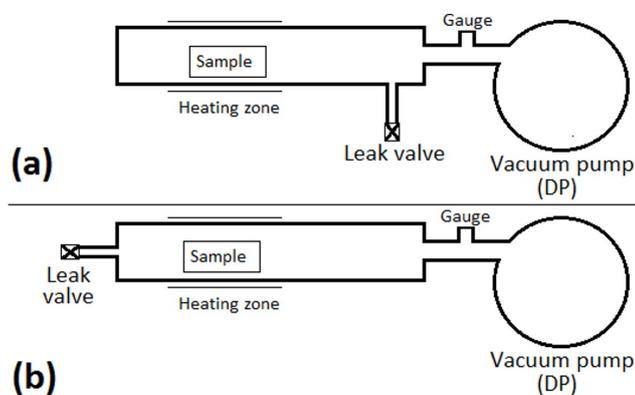
Figure 1: Vacuum furnace setup for (a) the low leak rate and (b) high leak rate conditions.

cylindrical chamber of the size of ϕ7 cm × L60 cm (the inner volume of 2310 cm^3) including the vacuum level of 0.013 Pa and different vacuum leak rates and designs (Figure 1). More details of processing have been reported previously [14]. According to Figure 1(a), the leak valve (for breaking the vacuum at the end of the process) was installed between the sample and the diffusion vacuum pump or DP (including the leak rate of 4×10^{-7} Pa m^3 s^{-1}). Figure 1(b) presents another setup whose leak valve was installed after the sample (including the leak rate of 3×10^{-3} Pa m^3 s^{-1}). The leak rate value introduces the amount of the diffused air to the vacuum furnace and so affects the partial pressure of oxygen at the furnace during sintering. Actually, in the case of the high leak rate furnace, the DP compensates more diffused air to the vacuum furnace and maintains the vacuum level at a constant value of 0.013 Pa.

B.   Scaffold characterization

1.   SEM observation

The microstructure of the porous titanium scaffolds was observed using the scanning electron microscope (SEM; Philips, XL 30) in the secondary electron mode at the accelerate voltage of 20 kV and the beam spot size of 3−5 nm.

2.   Phases identification using XRD

To identify the possible phases in the titanium scaffold after sintering, X-ray diffractometry (XRD: Philips X'Pert MPD) was used with the radiation source of Cu Kα ($\lambda = 1.5405$ Å), in the range of $2\theta = 20-80°$ at the rate of 1° min^{-1} and a step size of 0.05°.

3.   Compression test

To compare the mechanical properties of the scaffolds, a compression test was carried out using a universal testing machine (HOUNSFIELD: H30KS), according to ISO 13314 [15]. The compression test was performed on cylindrical samples with the diameter and the height of 8 mm at room temperature and the crosshead speed of 0.5 mm min^{-1}. Assessment of each sample was repeated three times and the average values were reported ($n = 3$).

4.   *In vitro* apatite formation ability assessment

The apatite formation ability of high-vacuum leak rate (HLR) and low-vacuum leak rate (LLR) samples was investigated by immersing the samples into the simulated body fluid (SBF) at 37°C without stirring for 7 days, according to the Kokubo protocol [16]. After the time point of 7 days, the samples were taken out, gently rinsed with distilled water, dried at 40°C for 24 h, and gold coated using the sputter coater. Finally, the surfaces were studied by SEM to compare the size and number of apatite particles formed on the surface of the samples and their chemical composition were investigated using energy dispersive spectroscopy analysis (EDS: EDAX element silicon drift).
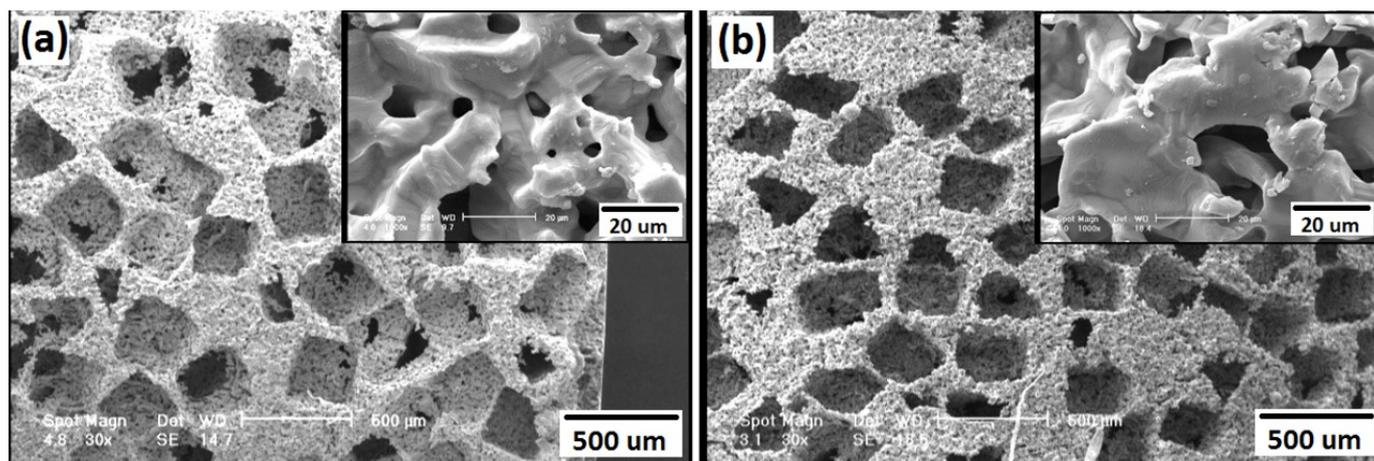
Figure 2: SEM micrograph for (a) LLR and (b) HLR samples.

III. RESULTS

A. Microstructural observation

As presented in Figure 1, the samples were sintered at two different setups, including a low leak rate (LLR sample) and high leak rate (HLR sample) conditions. The leak rate of these furnaces was mainly because of their leak valves (two different valves). In the HLR condition, the sample was exposed to the more air flow during heating and sintering. So, more air was diffused to the furnace and passed through the titanium samples at high temperatures during sintering.

The results of the microstructural study of titanium scaffolds using the SEM are presented in Figure 2. SEM micrograph of the HLR and LLR samples revealed that there was no significant difference in terms of their microstructure. Both samples included macropores replicated from spacer particles and micropores because of titanium powder shrinkage during sintering, reminding the gap between irregular titanium powders [17].

B. Phases identification

XRD patterns for the LLR and HLR samples are presented in Figure 3. According to this figure, the LLR sample only consisted of the sharp peaks of titanium (PDF No. 00-001-1198) and no contamination or oxidation was detectable. Contrastingly, the HLR sample consisted of the peaks of titanium (PDF No. 00-001-1198) and titanium oxide (rutile TiO_2: PDF No. 01-088-1175), indicating titanium oxidation during the sintering process. In this sample, not only the furnace had a leak rate higher than that of the LLR sample, but also the diffused air to the furnace passed through the surface of the heated sample. This phenomenon resulted in more titanium oxidation during the sintering process. It seems that the leak rate and the position of the vacuum pump relative to the positions of sample and leak valve (or any other leak source) are essential for sound titanium sintering. In the furnace of the LLR sample, diffused

Figure 3: XRD patterns for (a) LLR and (b) HLR samples.

air to the furnace was possibly entrapped directly by the vacuum pump without passing the sample. So, the chance of titanium oxidation during sintering was decreased.

C. Mechanical properties

The engineering stress-strain curves for the LLR and HLR samples are presented in Figure 4. Both curves consisted of the elastic region, the plateau stress, and the densified region, which were related to the compression behavior of the LLR and HLR samples [18]. Quantitative data were extracted from these diagrams according to the ISO 13314 standard. The plateau stresses of the LLR and HLR samples were 52.01 ± 0.15 MPa and 26.71 ± 0.21 MPa, respectively. Also, the densification regions for the LLR and HLR samples started at the strains of 46% and 41%, respectively, indicating fewer strains for the HLR sample in comparison to the LLR sample. It means that the LLR sample had higher mechanical properties in comparison to the HLR sample. Although there was no significant difference between their microstructures, partial oxidation of titanium (according to the results of X-ray diffraction) could adversely influence its

Figure 4: The engineering stress-strain curves for (a) LLR and (b) HLR samples.

mechanical properties in the case of the HLR sample. Partial oxidation of the titanium powders during sintering led to titanium oxide formation at the surface of the titanium powder particles and inhibited titanium powder bonding completely. This phenomenon resulted in less mechanical properties of the HLR sample as compared with the LLR sample.

D. *In vitro* apatite formation

The SEM micrographs of the LLR and HLR samples after immersion in the SBF solution are shown in Figure 5. It was evident that a few apatite particles were formed on the surface of the LLR sample. Titanium is bioinert and has no apatite-forming ability; however, even sintering in the LLR furnace affected the surface of the porous titanium sample, resulting in a few apatite formations. However, in the case
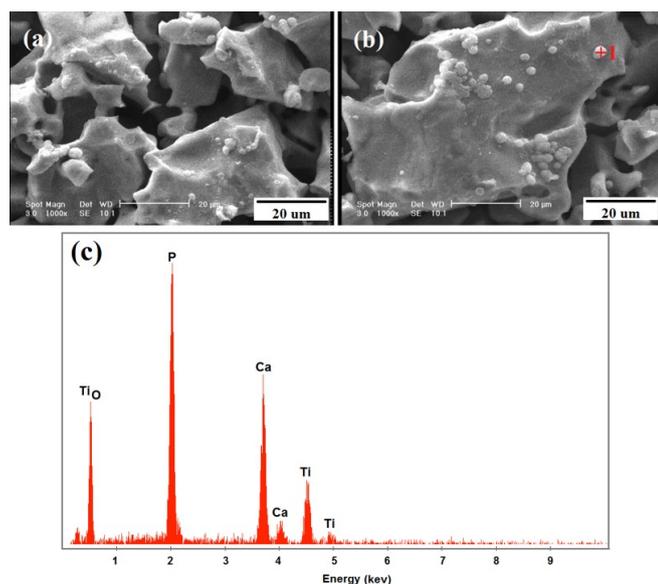
Figure 5: SEM micrographs for (a) LLR sample and (b) HLR sample after immersion in SBF. (c) EDS spot analysis of point 1 in panel (b).

of the HLR sample, more hydroxyapatite particles were formed over the surface, indicating the better apatite formation ability of the HLR sample, as compared with the LLR sample. As Figure 5(c) indicates, the chemical components of the deposited particles on the surface of the HLR sample after immersion in SBF are Ca, P, and O ions, which are the main constituent of hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$). This evidently proved more oxidation of the HLR sample during sintering.

IV. DISCUSSION

Titanium is a promising candidate for dental reconstruction purposes. However, the bio-inert behavior of titanium reduces its osseointegration ability. So, numerous surface treatment and porous titanium scaffold fabrication techniques have been developed to improve the bio-functionalization of titanium implants. Titanium direct oxidation is a simple and effective method for titanium surface treatment [19]. In this research, by using a high leak rate valve and positioning it after sampling, a partial air flow was made on the porous titanium scaffolds during sintering in a vacuum furnace, resulting in the partial oxidation of the titanium scaffold. Fabricated titanium scaffolds included both micropores (<10 μm) and macropores (almost 350 μm) at their structures, which improved the osseointegration of the scaffold [20].

In the vacuum furnaces including the high leak rate, more surrounding gases (air) penetrated into the chamber and, so, more time was required to reach a specified vacuum level during vacuum pumping [21]. More air penetration and flow into the chamber of the vacuum furnace, during the heating of high affinity metals such as titanium or magnesium, could result in more surface oxidation. So, the position of the leak valve and the sample in the furnace should be addressed carefully. For example, when the sample was placed between the leak valve and the vacuum pump [Figure 1(b)], more penetrated air passed through the heated sample, in comparison to a situation wherein the leak valve was placed between the sample and the vacuum pump [Figure 1(a)]. Thus, it seems that, for sound sintering of a high affinity metal, all parameters including the vacuum level, the vacuum leak rate, and the design of the furnace are important and influential.

Although titanium sintering at the high leak rate furnace resulted in better apatite-forming ability, more titanium oxidation during sintering reduced the mechanical properties of the titanium scaffold. This oxidation happened on the surface of all particles of titanium, which resulted in a thin layer of TiO_2 formation at the surface. The thin layer of TiO_2 reduced the sinterability of particles and their bonding to each other; therefore, mechanical properties were declined.

So, it seems that the vacuum level of the furnace and its leak rate, as well as the setup of the furnace are important parameters that should be considered for the optimum titanium scaffold sintering.

V. CONCLUSIONS

In this research, the effects of the vacuum leak rate and the design of the vacuum furnace on the properties of the sintered titanium scaffold were investigated. The results indicated that the design of the vacuum furnace and its leak rate affected the chemical and mechanical properties of the titanium scaffold. Both mechanical properties and the apatite-forming ability of the titanium scaffold were affected by increasing the leak rate of the vacuum furnace. Therefore, to ensure sound and high strength titanium porous scaffold fabrication via powder metallurgy, both the level of the vacuum of the furnace and the leak rate of the furnace should be considered as important parameters for titanium sintering.

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