Material Science and Applied Chemistry

doi: 10.7250/msac.2015.001

2015/31

Preparation and Characterization of Porous Titania Ceramic Scaffolds

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Abstract **− Biocompatible ceramics have recently attracted increasing attention as porous scaffolds that stimulate and guide natural bone regeneration. Due to excellent biocompatibility of titania (titanium dioxide or TiO_2) porous three-dimensional (3D) TiO_2 structures have been proposed as promising scaffolding materials for inducing bone formation from the surrounding environment and for enhancement of vascularisation after implantation. In this paper, 3D porous TiO_2 ceramic scaffolds were produced via polymer foam replica method. This work deals with several important issues that are considered to be important for 3D scaffolds applied to regenerate bone tissue: pore size, porosity and mechanical strength. TiO_2 ceramic scaffolds with pore size 300 µm − 700 µm and porosity > 90 % were obtained. Scaffolds showed fully open and interconnected pore structure that remained after recoating them with low viscosity TiO_2 slurry. By optimising thermal treatment conditions grain growth and collapse of struts could be controlled in a way that resulted in higher compressive strength. Recoating greatly improved compressive strength and it reached 0.74±0.08 MPa after two coatings without causing changes in the open pore structure.**

Keywords **− Titanium dioxide, scaffold, microstructure, porosity, strength.**

I. Introduction

The use of scaffolds as sacrificial templates for bone ingrowth is the basis of bone tissue regeneration. The main reasons for using bone scaffolds are: to provide an environment for bone formation, to maintain the space and at the same time to supply mechanical support to the skeleton during the healing process [1]. Thus an ideal scaffold should be three-dimensional and highly porous with an interconnected pore network for cell growth and for flow transport of nutrients and metabolic waste. The mechanical properties of the scaffold should match those of tissue at the site of the implantation [2], [3].

One of the materials that can be used to produce 3D scaffolds is titania (TiO_2) ceramics. TiO_2 have attracted particular attention for the use as a bone tissue regeneration material due to its excellent mechanical properties compared to other ceramic materials, biocompatibility and good osteoconductivity [2]−[6]. Fabrication of highly porous TiO_2 ceramic scaffolds with interconnected pore structure has been previously reported [7]−[10]. The most widely used technique for fabrication of such structures is polymer foam replica method [8]−[13]. It was invented by Schwartzwalder and Somers in 1963 [14]. The polymer that has the desired macrostructure simply serves as a sacrificial template for the ceramic coating [10]−[14]. Using polymer foam replica method a porous ceramic with porosity from 40 % to 95 % and with pore sizes between 200 µm and 2 mm can be obtained. Thus this technique is the most popular method to produce macroporous ceramics. It is also simply adjustable, flexible and relatively inexpensive [13].

The aim of the presented research was to adjust this technique to produce porous 3D TiO_2 ceramic scaffolds with interconnected pore structure. This work deals with several important issues that are considered to be important for 3D scaffolds applied to regenerate bone tissue, including pore size, porosity and mechanical strength.

II. Materials and Methods

A. Sample Preparation

TiO_2 ceramic scaffolds were prepared using polymer foam replica method. Commercially available titanium dioxide with average particle size 180 nm (Sachtleben Chemie GmbH, HOMBITAN LW – S), 5 % polyvinyl alcohol solution (Polysciences, Inc.) and deionised water were used as raw materials to prepare ceramic slurry (Table I). The slurry was homogenised by ball milling for 1 h at 300 rpm.

TABLE I

Slurry Composition

Raw material	Mass fraction, %
Titania	70
Water	21
5 % polyvinyl alcohol solution	9

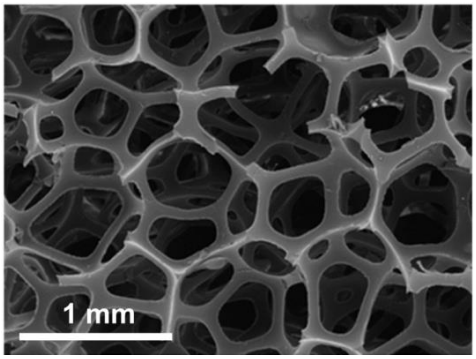

Fig. 1. SEM micrograph of PU foam template.

The polyurethane (PU) foam templates (Vitabaltic International) with fully interconnected pore structure (Fig. 1) were cut to size by punching with a metal stamp. Obtained

cylinders with 10 mm diameter were washed in ethanol using a Soxhlet extractor and dried in air. Cylindrical PU foam templates then were dipped into the ceramic slurry. Excess slurry was squeezed out of the templates to ensure that only a thin layer of slurry uniformly covered PU foam surface without blocking the pores. After drying for 24 h, the polymer was slowly burned out by heating to 450 ºC at a heating rate of 0.5 ºC/min. After 1 h holding time at 450 ºC, the temperature was raised to 1100 ºC at a rate of 3 ºC/min and held at 1100 ºC for 10 h.

The scaffolds were sintered at different temperatures (1300 °C – 1500 °C) with different holding times (10 h – 30 h). Some of the scaffolds that were sintered at 1400 ºC temperature for 20 h were additionally coated with low viscosity slurry (TiO_2 mass fraction 20 %) using a vacuum infiltration method. After slurry infiltration scaffolds were centrifuged at 1000 rmp for 1 min to remove excess slurry that could have blocked the pores, dried in air and sintered at the same conditions as previously − 1400 °C for 20 h.

B. Characterization of Materials

Identification of crystalline phases of sintered ceramics was carried out using X-ray diffraction (XRD). X-ray diffraction patterns were obtained using an X-ray diffractometer PANalytical X`Pert PRO. Cu Kα filtered radiation in 2θ range from 20° to 65° was used.

The microstructure of scaffolds was investigated using scanning electron microscope (SEM) Tescan Mira/LMU and digital microscope KEYENCE VHX 2000. Before SEM investigations samples were sputter coated with a gold layer. The samples were observed at 15 kV accelerating voltage.

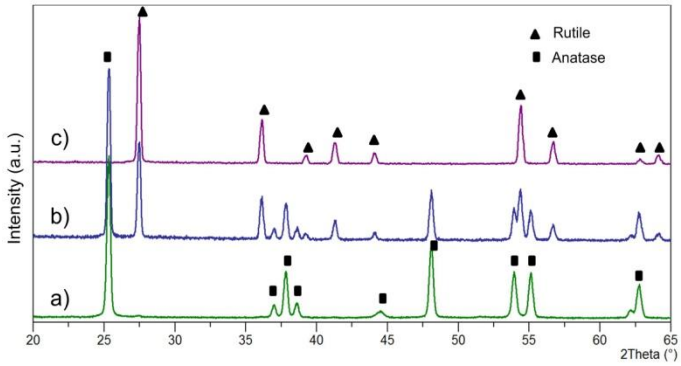

Fig. 2. XRD patterns of anatase powder (a) and of the obtained scaffolds after sintering at 1000 °C (b) or 1300 °C (c).

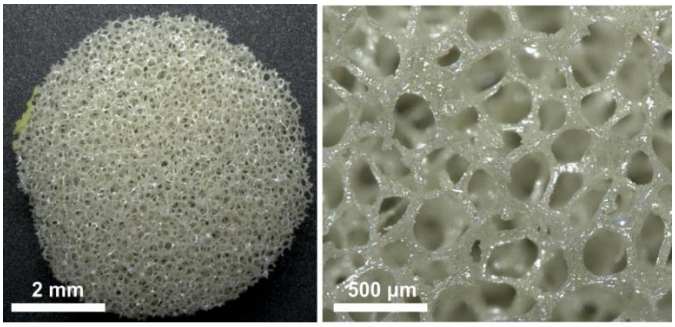

Fig. 3. Digital microscopy images of the obtained scaffolds.

Total porosity (*П*) of the scaffolds was measured using gravimetry, according to the equation:

$$П = 1 - \rho_{scaffold}/\rho_{titania}$$

Here $\rho_{titania}$ is the density of TiO_2 (rutile) and $\rho_{scaffold}$ is the apparent density of the scaffold measured by dividing the weight of the scaffold by the volume of the scaffold. Sample shrinkage after sintering was calculated by geometric method, taking into account the changes of scaffold dimensions.

The mechanical strength of scaffolds was determined using a compression test (A Static Materials Testing Machine Z010 TN (Zwick GmbH & Co. KG). Scaffolds were preloaded with 0.1 N. The speed of compression tests was 10 % per 1 min.

III. Results and Discussion

A. Effect of Heat Treatment on the Composition of Scaffolds

In order to examine the phase composition of TiO_2 scaffolds XRD was performed on TiO_2 (anatase) powder and on scaffolds after sintering at 1000 °C or 1300 °C temperature (Fig. 2). XRD pattern of samples sintered at 1000 °C showed the characteristic peaks of both TiO_2 crystalline modifications (anatase and rutile). Thus this confirmed phase transformation during scaffold sintering. In the transformation process bonds break in the anatase structure. This allows the rearrangement of the Ti-O_6 octahedra and leads to a more compact structure formation and formation of rutile phase [15]. Increasing sintering temperature up to 1300 °C a complete phase transition from anatase to rutile crystalline modification took place and stable rutile modification was obtained.

B. Porosity and Mechanical Properties

Porous TiO_2 ceramic scaffolds with fully open and interconnected pore structure have been obtained (Fig. 3 and Fig. 4). The porosity of the scaffolds was in the range from 92 % to 94 % and pore size was from 300 µm to 700 µm, independently of the sintering temperature (from 1300 °C to 1500 °C) and independently of the holding time at the evaluated temperatures (10 h to 30 h). Obtained pore size and porosity is appropriate to ensure cell migration throughout the scaffold structure and ensure vascularisation, if scaffolds are used for bone tissue regeneration.

If the temperature of thermal treatment is increased from 1100 °C to 1500 °C, grain growth occured. At 1100 °C fine-grained ceramics can be obtained, but at higher temperatures inhomogeneous grains with grain size up to 50 µm were observed (Fig. 4). As can be seen in Fig. 4, during PU foam pyrolysis process hollow struts (shown using a rectangle) and voids (shown using an arrow) in the ceramic wall structure were produced; these had a direct effect on mechanical strength of the ceramic material.

By optimising thermal treatment conditions grain growth and collapse of struts could be controlled in a way that resulted in higher compressive strength. Increasing the heat treatment temperature of the ceramic scaffolds from 1100 °C to 1500 °C resulted in grains compacting and the disappearance of microcracks was promoted, thus slightly

decreasing the defect quantity in the ceramic wall structure (Fig. 4).

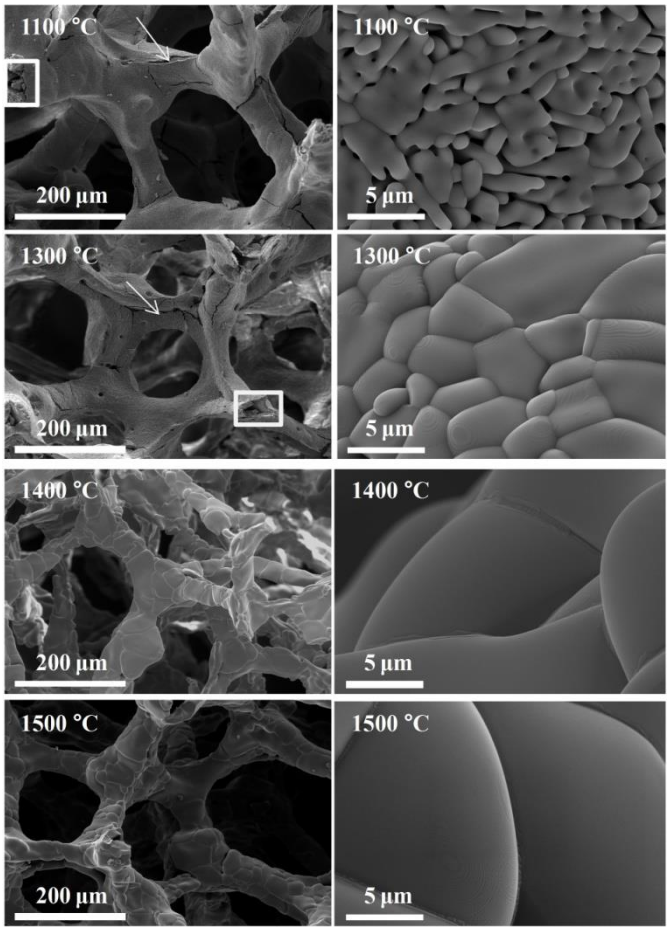

Fig. 4. The effect of thermal treatment temperature on the microstructure of the sintered scaffolds.

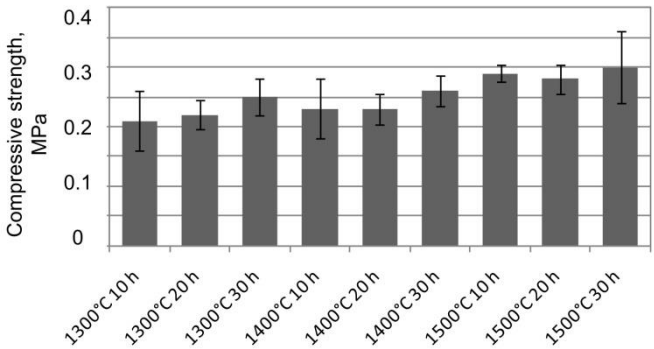

Fig. 5. Compressive strength of the sintered scaffolds.

During the heat treatment reduction of scaffold dimensions also was observed and the thermal shrinkage of the scaffold volume reached 35 % at 1100 °C and up to 60 % at the temperature range 1300 °C − 1500 °C.

The effect of sintering temperature and holding time at evaluated temperatures on mechanical strength of scaffolds is shown in Fig. 5. It was experimentally determined that increasing heat treatment temperature and holding time at evaluated temperature slightly increased mechanical strength of the sintered ceramic scaffolds and the highest mechanical strength (0.3±0.06 MPa) was obtained for scaffolds after heat treatment at 1500 °C for 30 h.

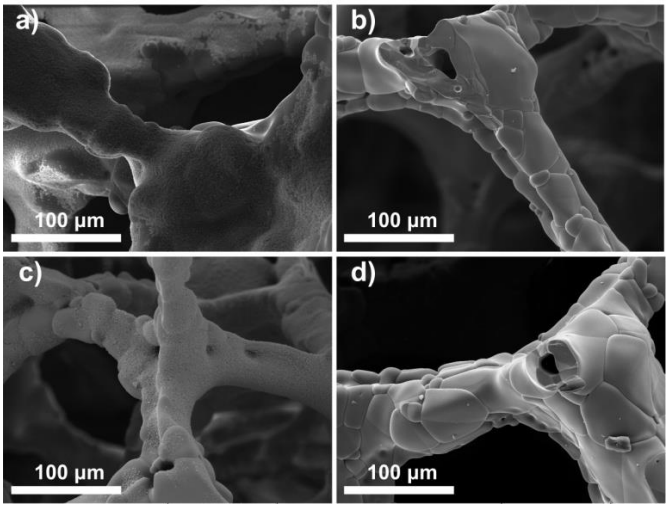

Fig. 6. SEM micrographs of TiO_2 scaffolds before (a) and after 1st coating and sintering (b); before (c) and after 2nd coating and sintering (d) .

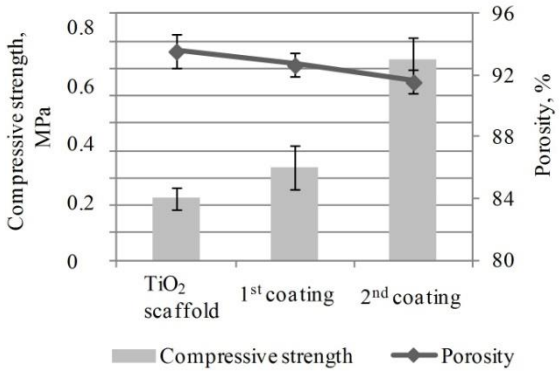

Fig. 7. Compressive strength and porosity of the recoated scaffolds.

C. Effect of Recoating Process on Scaffold Properties

Scaffolds sintered at 1400 °C temperature for 20 h were recoated with low viscosity TiO_2 slurry by vacuum infiltration method and were further sintered at the same thermal treatment conditions as before. Results showed that recoating procedure slightly decreased porosity by partially filling the micropores. Voids and folds remained in the scaffold wall structure and wall surface as illustrated in Fig. 6. As shown in Fig. 7, recoating scaffolds with low viscosity slurries improved the compressive strength and it reached 0.74±0.08 MPa after three coatings without causing significant changes in porosity and open pore structure.

IV. Conclusion

TiO_2 ceramic scaffolds with pore size 300 µm − 700 µm and >90 % porosity were produced via polymer foam replica method. Scaffolds showed fully open and interconnected pore structure that remained after recoating them with low viscosity TiO_2 slurry. By optimising thermal treatment conditions, the grain growth and collapse of struts could be controlled in a

way that resulted in higher compressive strength. Optimal sintering temperature were 1500 °C and optimal holding time was 30 h. Recoating greatly improved compressive strength and it reached 0.74±0.08 MPa after 2 coatings without causing changes in the open pore structure.

ACKNOWLEDGEMENT

This work was supported by the Latvian State Research Program "Development of innovative multifunctional materials, signal processing and information technology for competitive science intensive products" project No. 4 "New materials and technologies for evaluating biological tissue, and replace".

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Inga Narkevica, Laura Stradiņa, Vladimirs Jakušins, Jurijs Ozoliņš. Porainu titāna dioksīda keramikas pamatņu ieguve un raksturojums.

Pasaulē arvien vairāk pētījumu tiek veltīti jaunu, sintētisku biomateriālu izstrādei, kas paredzēti bojātu cieto audu aizvietošanai. Liela interese kaulaudu inženierijas pētījumos ir veltīta trīsdimennsionālām audu pamatnēm ar pilnībā caurejošu poru struktūru, jo tā var veicināt vaskularizāciju, dzīvo šūnu piesaisti un proliferāciju. Viens no biosaderīgiem materiāliem, kuru var izmantot bojātu kaulaudu aizvietošanai, ir poraina TiO_2 keramika. TiO_2 keramikai ir labākas mehāniskās īpašības nekā citiem porainiem keramiskiem materiāliem, un tai piemīt osteokonduktīvas īpašības. Salīdzinoši vienkārša metode porainu struktūru iegūšanai ir sintētiska prekursora piesūcināšana. Darbā kā prekursors poraino pamatņu iegūšanai izmantotas elastīgas poliuretāna putas. Tās tika piesūcinātas ar TiO_2 šlikeri, kas sastāv no TiO_2 (anatāza) pulvera, polivinilspirta šķīduma un H_2O. Šlikera homogenizāciju veica planetārajās bumbu dzirnavās. Paraugu termisko apstrādi veica divās stadijās: organisko savienojumu izdedzināšana (1) un porainas keramikas saķepināšana 1300 °C − 1500 °C, 10 h – 30 h (2). Daļu paraugu atkārtoti pārklāja ar zemas viskozitātes TiO_2 šlikeri un termiski apstrādāja gaisā 1400 °C temperatūrā 20 h. Parādīts, ka, izmantojot prekursora piesūcināšanas metodi, iespējams iegūt porainas pamatnes ar pilnībā atvērtu, caurejošu poru struktūru, ar poru izmēriem 300 µm − 700 µm un

porainību virs 90 %. Palielinot poraino pamatņu termiskās apstrādes temperatūru no 1300 °C līdz 1500 °C, TiO_2 keramikas graudi labāk sablīvējas, kas veicina mikroplaisu samazināšanos. Eksperimentāli noteikts, ka, palielinot termiskās apstrādes temperatūru un izturēšanas laiku, uzlabojas poraino pamatņu mehāniskā izturība. Pamatnēm, kas apdedzinātas 1500 °C temperatūrā 30 h, izturība spiedē sasniedz 0,3±0,06 MPa. Atkārtoti pārklājot porainās pamatnes ar zemas viskozitātes TiO_2 šlikeri, pēc termiskās apstrādes saglabājas atvērto poru struktūra un būtiski uzlabojas mehāniskās īpašības, sasniedzot mehānisko izturību spiedē 0,74±0,08 MPa.

Инга Наркевица, Лаура Страдиня, Владимир Якушин, Юрий Озолиньш. Получение и характеристика пористых керамических подложек на основе диоксида титана.

Во многих странах всё больше проводимых исследований связано с разработкой и созданием новых синтетических биоматериалов для замещения твердых поврежденных тканей. В инженерных разработках костной ткани особый интерес уделяется тканевым подложкам 3D со сквозной пористой структурой, способствующей васкуляризацию ткани, присоединению живых клеток и их пролиферации. Одним из биосовмещенных материалов, применяемых для замещения поврежденных костных тканей, является пористая керамика на основе диоксида титана, обладающая лучшими механическими свойствами и остеокондуктивностью. Относительно простым методом получения таких материалов является пропитка синтетических прекурсоров. В работе в качестве прекурсора для получения пористой подложки использовали эластичную полиуретанную пену, пропитанную шликером TiO_2, состоящим и порошка TiO_2 в форме анатаза, – раствора поливинилового спирта и воды. Гомогенизация шликера проводилась в планетарной шаровой мельнице, термическую обработку осуществляли в двух стадиях: выжигание органических соединений и спекание пористой керамики при высоких температурах (1300–1500 °C) с разным временем выдержки (10–30 h). Часть образцов покрывались шликером TiO_2 низкой вязкости, используя метод вакуумной инфильтрации с последующей термической обработкой в воздухе в течение 20 h. Полученные результаты свидетельствуют о том, что пористые подложки с полностью открытой проходящей структурой пор размером от 300 мкм до 700 мкм и пористостью выше 90 % получают при использовании метода пропитки прекурсора. С увеличением температуры термической обработки пористых подложек от 1300 °C до 1500 °C зерна TiO_2 керамики уплотняются более эффективно. Это способствует значительному уменьшению количества микротрещин. Экспериментально установлено, что повышение температуры и время термической обработки улучшает механическаю прочность пористых керамических подложек. При температуре обжига пористых подложек 1500 °C в течение 30 h механическая прочность образцов достигает 0,3±0,06 MPa. При повторном покрытии образцов пористых подложек шликером TiO_2 низкой вязкости после термической обработки сохраняется открытая структура пор и существенно улучшаются механические свойства подложек, значения механической прочности при сжатии достигают 0,74±0,08 MPa.