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Sintering behavior of 3D printed barium titanate composite scaffolds for bone repair

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Abstract: Additive manufacturing of novel biomaterials with additional stimulating functions represents a promising strategy for bone repair. In this study, a systematic investigation of the necessary thermal post-treatment of 3D printed barium titanate composite ceramics to achieve the desired mechanical properties for bone regeneration is presented. The maximum sintering temperature was varied from 1320 °C to 1380 °C in 10 K intervals. After sintering, the samples were systematically characterized with respect to their porosity and mechanical properties. Specimens sintered at 1380 °C exhibit a considerably densified microstructure and improved mechanical integrity compared to specimens sintered at lower temperatures.

I. Introduction

Piezoelectric bone replacement materials represent a novel and innovative therapeutic option for the treatment of bone defects. The stimulation of bone by a piezoactive material is intended to induce the ingrowth of natural bone to the implant. It has been shown that piezoelectric materials have a positive influence on bone regeneration, even though the therapeutic effect is not yet fully understood [1]. The combination of piezoelectric materials with additive manufacturing (AM) processes can unite essential advantages. By this approach, it should be possible to manufacture an autonomous, electrically stimulating implant with adapted defect geometry and designed osteoconductive and osteoinductive properties. However, intensive research is necessary to achieve this goal, as there are great challenges in this field such as the AM of scaffolds with mechanical properties meeting the requirements of bone-engineering applications. To improve the mechanical properties of 3D printed barium titanate ($BaTiO_3$) composites, we applied different sintering temperatures and studied the effects in terms on scaffold mechanics, porosity, and microstructure.

II. Material and methods

For the binder jetting process, a powder blend mixture was used as described in a previous publication [2]. This mixture was subsequently processed with a VX500 3D printer (Voxeljet AG, Friedberg, Germany). Cylindrical test specimens were produced and subjected to different temperature treatments to remove the polymeric phase and subsequently densify the 3D printed specimens. The polymeric phase was removed from the specimens (debinding) in a debinding furnace (L9R, Nabertherm GmbH, Lilienthal, Germany) at 300 °C for 1 hour and at 500 °C for 2 hours. Subsequently, the specimens were subjected to a sintering treatment at 600 °C (3 hours), 1000 °C (2 hours), and a varied maximal sintering temperature ranging from 1320 °C to 1380 °C in 10 K steps. The specimens were examined for porosity using a microCT scanner (Skyscan 1076, Bruker, Kontich, Belgium) with a subsequent 3D analysis, as described previously [2]. The microstructure was assessed using a scanning electron microscope (SEM) Merlin VP compact (Carl Zeiss AG, Jena, Germany) coupled with an electron dispersive X-ray spectroscopy (EDX) detector XFlash 6/30 Co. (Bruker, Berlin, Germany). The compressive strength was investigated using a Zwick Z050 universal testing machine with a crosshead speed of 0.5 mm/s.

III. Results and discussion

All samples were successfully treated with the corresponding sintering parameters and have largely retained their shape (Fig. 1).

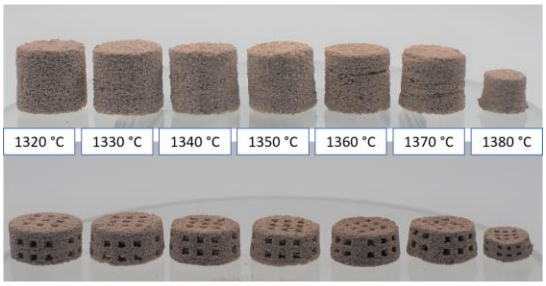

Figure 1: Macroscopic images of 3D printed BaTiO3 composite specimens according to the respective sintering temperature, showing a strongly increased shrinkage at 1380 °C.

A slight increase in the shrinkage of the specimens is observed, which shows a jump between 1370°C (~40 % vol. shrinkage) and 1380°C (~80% vol. shrinkage). The shrinkage is accompanied by a strong densification of the structure. This is particularly evident in the 3D analysis

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based on the microCT data. The increase of the sintering temperature in 10 K intervals up to 1370°C shows a minor influence on the porosity and compressive strength (Fig. 2). The porosity is around 50-60%, with a slight tendency to decrease as the temperature increases. This high porosity is caused by the powder mixture which is not compacted by the 3D printing process. Moreover, the burn-out of the polymer matrix further increases porosity. The high porosity has a significant influence on the resulting compressive strength of the scaffolds, which is less than 5 MPa at sintering temperatures of up to 1370 °C. Although this is sufficient for handling, the specimens cannot be used as a bone replacement scaffold, especially in load-bearing areas. However, a further rise of the maximum sintering temperature by 10 K to 1380 °C lead to a significant reduction of the porosity below 10 % and a simultaneous increase of mechanical strength (Fig. 2). The compressive strength raised up to 30 MPa, which is comparable to the mechanical strength of bioceramics produced in binder jetting [3], [4]. Consequently, the scaffolds might conceivably be used in less load-bearing bone areas.

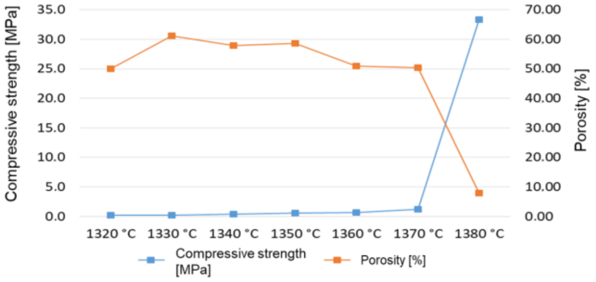

Figure 2: Changes in porosity versus compressive strength as a function of the applied sintering temperature. A significant transition between 1370°C and 1380°C is observed, which is characterized by a strong reduction in porosity and a simultaneous increase in compressive strength.

The densification and simultaneous change of the microstructure were confirmed by SEM (Fig. 3). A change in microstructure from a particulate structure with numerous pores and sintered necks at 1320 °C to a much more dense, lamellar microstructure at 1380 °C was observed (Fig. 3A, 3C). EDX analysis indicated a chemical change of the microstructure. The signals of the individual elements shift strongly in the specimens sintered at 1380 °C compared to the specimens sintered at 1320 °C. Mainly Ba and P can be detected in the lamellar structures, while the Ca and Ti signals can be found in the granular microstructure (Fig. 3C, 3D). Due to the increased sintering temperature, we suggest that ion lattice exchange may have occurred, which can promote the formation of calcium titanate and barium phosphate [5]. A beginning liquid phase sintering can probably be excluded, since the melting point of both HA and BaTiO$_3$ is above 1600 °C [6], [7]. Considering a potential application as bone replacement material, sintering at higher temperatures is probably preferable, as it drastically increases the mechanical properties, even if it is accompanied by a loss of microporosity, which may promote osseointegration. The determination of the cytocompatibility and piezoelectric properties will be the subject of further investigations.

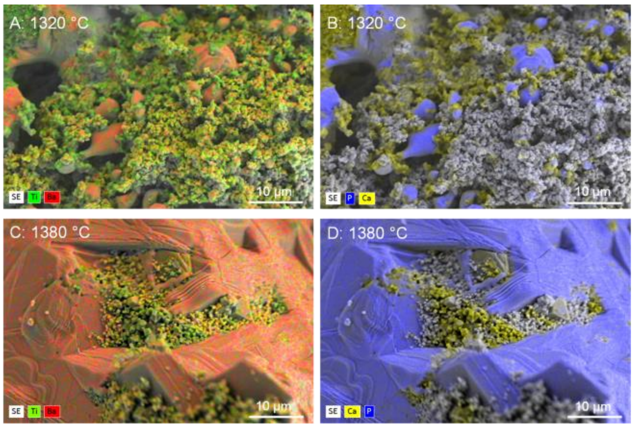

Figure 3: EDX maps of differently sintered BaTiO3 composite specimens showing the change in microstructure and elementary composition induced by elevated temperature.

We hypothesize that the densified microstructure will also promote elevated piezoelectric properties compared to the high porous specimens, allowing to create piezoelectric functional bone engineering scaffolds.

IV. Conclusions

By increasing the sintering temperature to 1380 °C, strong densification of the microstructure of 3D printed BaTiO3 composite specimens could be achieved. The densification significantly improves the mechanical strength (> 30 MPa) and provides important implications for the development of piezoelectric bone replacement materials.

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AUTHOR'S STATEMENT

Conflict of interest: Authors state no conflict of interest.

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