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Experimental studies on 3D printing of barium titanate ceramics for medical applications

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Abstract: The present work deals with the 3D printing of porous barium titanate ceramics. Barium titanate is a biocompatible material with piezoelectric properties. Due to insufficient flowability of the starting material for 3D printing, the barium titanate raw material has been modified in three different ways. Firstly, barium titanate powder has been calcined. Secondly, flow additives have been added to the powder. And thirdly, flow additives have been added to the calcined powder. Finally, a polymer has been added to the three materials and specimens have been printed from these three material mixtures. The 3D printed parts were then sintered at 1320°C. The sintering leads to shrinkage which differs between 29.51–71.53% for the tested material mixtures. The porosity of the parts is beneficial for cell growth which is relevant for future medical applications. The results reported in this study demonstrate the possibility to fabricate porous piezoelectric barium titanate parts with a 3D printer that can be used for medical applications. 3D printed porous barium titanate ceramics can especially be used as scaffold for bone tissue engineering, where the bone formation can be promoted by electrical stimulation.

Keywords: additive manufacturing; barium titanate; 3D printing; piezoelectric; porous ceramic.

1 Introduction

Materials with piezoelectric properties are advantageous for various applications. They can be used in medical technology, for example in the implant technology. Through selective electrical stimulation of piezoelectrically active implants, the bone growth can be increased, the bone resorption can be reduced and the osseointegration of the implant can be improved [1–3].

Barium titanate has excellent piezoelectric properties [4]. Furthermore, studies [2, 3, 5] have shown that this ceramic is biocompatible and can therefore be used for medical applications such as implants.

There is a great desire for individualized implants, especially in the medical technology. This is where additive manufacturing comes into play. There have already been investigations regarding the fabrication of $BaTiO_3$ (BTO) via additive manufacturing [6–8], which are addressed in these studies. Besides the production via stereolithography processes, the direct fabrication via 3D printing (3DP) is described. Especially for 3DP a flowable powder is needed (mean grain size of about 50 µm). Here, the particle size and shape play an important role [9, 10]. Untreated BTO powder is mostly a non-flowable material with a mean grain size of a few microns, so that a preparation of the material (in the form of heat treatment) or an addition of flow additives is necessary [6, 11]. Therefore, this study uses a calcined BTO on the one hand and on the other hand an untreated BTO is used to which flow additives are added in order to remove powder agglomerations and increase the flowability. In the third approach flow additives are added to calcined BTO.

The resulting 3D printed components are porous, which is good for tissue engineering. Especially for implants, this porous structure is advantageous because the cells can then grow better [12, 13]. The 3D printed BTO ceramics can especially be used as scaffold for bone tissue engineering. The piezoelectric properties can be used to stimulate bone formation by applying an electrical filed during tissue engineering and *in vivo*.

2 Material and methods

2.1 Materials and material processing

For this investigation, a barium titanate (IV) – powder, <3 µm, 99% (Sigma-Aldrich, USA) is used. To bond the

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Table 1: Composition of material mixtures M1–M3.

Mixture	BTO [vol%]	Polymer [vol%]	Flow additive [vol%]
M1	70 (untreated)	20	10
D50	<3 µm		
M2	70 (calcined)	20	10
D50	63–80 µm		
M3	80 (calcined)	20	0
D50	<125 µm + 125–250 µm		

material, a soluble polymer granulate with a mean grain size of 50 µm is used. Solupor-Binder (Voxeljet AG, Germany) is used as a binder fluid. The binder partially dissolves the polymer granulate so that the ceramic particles glue together. In order to increase the flowability, the flow additive AEROSIL® R 8200 (Evonik, Germany) is used. Three mixtures of these materials were produced, as shown in Table 1.

The first mixture (M1) consists of untreated BTO, the soluble polymer and the flow additive. R 8200 makes up 10 vol%, equivalent to 1.47 wt%.

M2 contains the same ingredients as M1, but the BTO is heat-treated before. This is done by calcinating the BTO-powder at 1300°C. The heating rate is 10 K/min and the temperature is held for 4 h. Then the material is crushed with a roller as well as a mortar and pestle. Subsequently, the powder is sieved and divided into different fractions. For this mixture, a fraction of 63–80 µm is used. Again, flow additives are added due to insufficient flowability (1 wt%).

The third mixture also contains calcined BTO. Here, the fractions <125 µm and 125–250 µm are used in a ratio of 1:2. No flow additives were used, because of the good flowability of the material mixture.

2.2 3D printing

The green parts were manufactured using a 3D printer VX500 (Voxeljet AG, Germany). The parts were printed with the binder layer by layer. For this, the entry of the binder is adapted accordingly. The volume fraction of the solvent after printing is 20.87% for M1, 14.52% for M2 and 8.3% for M3.

Simple cylindrical parts (diameter 11.7 mm, height 3.51 mm) were prepared. After the 3D printing was complete, the parts were left in the powder bed for 24 h. They were then removed from the job box, cleaned with an air blower and dried for 24 h in an oven at 40°C until the binder had completely been removed.

2.3 Sintering

First, the organic components are removed. For this purpose, the 3D printed green parts are placed in an oven (L9/R, Nabertherm, Germany) at 1000 °C for 2 h under atmospheric pressure. The heating rate is 10 K/min. Thereafter, the solid state sintering is applied to sinter the parts at 1320°C for 4 h under atmospheric pressure. For this, a tubular furnace (RHTH 120–600/18, Nabertherm, Germany) is used. In order to investigate the sintered parts, SEM analyses are made.

3 Results and discussion

3.1 Increase of the flowability

As mentioned before, the flow additive R 8200 was added to the mixtures M1 and M2. The effect of the R 8200 is shown in Figure 1, based on M2.

With the increasing volume percentage of R 8200, the powder becomes more and more free-flowing. When 10 vol% is made up by R 8200, no more agglomerates can be seen, so that the material can be considered flowable. Thus, it is possible to produce a defect-free, uniform powder bed during the subsequent 3DP. The R 8200 is burned out later during the pyrolysis, which leads to a relatively high porosity.

3.2 3D printing

The 3D printed green parts are relatively unstable, but exhibit sufficient mechanical strength to allow for safe handling. The difference between loose powder and component was partly difficult to see, so that a complete exposure of the samples was often not possible (Figure 2). Nevertheless, the geometry corresponded to the CAD data with only minimal deviations (Figure 4). The amount of binder had to be increased significantly due to the addition of R 8200, because the flow additive also encases the polymer granules, so that the binder had more difficulties reaching the polymer. However, all material systems could be processed using 3DP.

3.3 Sintering and shrinkage

The sintering was successful for all parts. Figure 2 shows the green part and the sintered part for the example of M1.

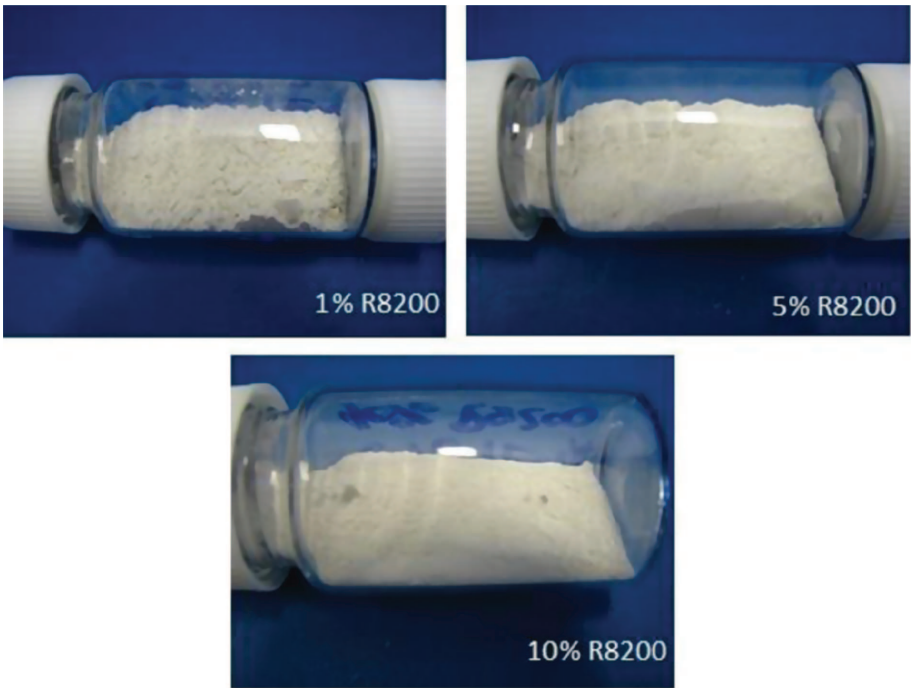

Figure 1: Increasing volume percentage of R 8200 in mixture M2.

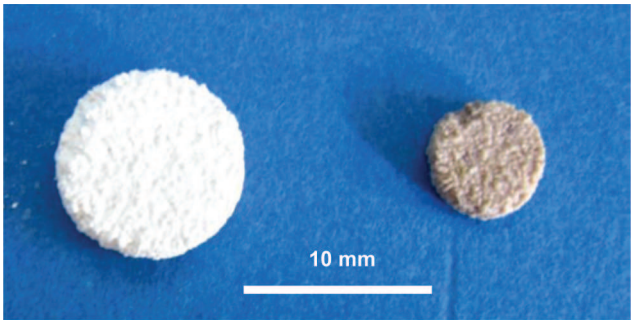

Figure 2: Green part and sintered part of M1.

The sintered parts show a brownish discoloration and a large shrinkage.

The conducted SEM images confirm successful sintering. Figure 3 shows low (500 ×) and high (2000 ×) magnification SEM images of the parts after sintering. On the images, the sintering necks are clearly visible. Grain growth is also visible, so that a sintering temperature of 1320°C appears to be sufficient. The grains are still clearly visible in the sintered parts of mixture M1. For M2 and M3, the individual grains seem to be fused together more. This is due the much larger grain size of M2 and M3 before sintering. Porosity is visible in all samples.

The shrinkage was calculated based on the volume of the samples. Due to the porous structure of the green parts, the shrinkage is very high (see Figure 4).

The shrinkage during the process chain is given in percent of the volume. The 3D printed parts only show very low variations. This is due to the already described difficult separation between loose powder and sample.

During the pyrolysis there were no changes in the geometry of the samples, so that they could be placed in the sintering furnace without breakage.

After sintering, a strong shrinkage was recorded for all parts (M1–M3), whereas the largest shrinkage was found in the components which were produced with the mixture M1. Here, the parts shrank by 71.53%. This is due to the very fine starting powder (<3 µm), whereas the polymer granules have a mean particle size of about 50 µm. This results in a high porosity and thus a strong shrinkage during sintering. The parts fabricated with M2 (40.55%) and M3 (29.51%) show a significant lower shrinkage, though it is still relatively high. It is important to determine whether the absolute shrinkage is constant. If so, the components could be scaled up before the 3DP, resulting in a lower relative shrinkage.

3.4 Medical applications

The 3D printed parts are suitable for medical applications, such as scaffolds. The sharpness of the green parts

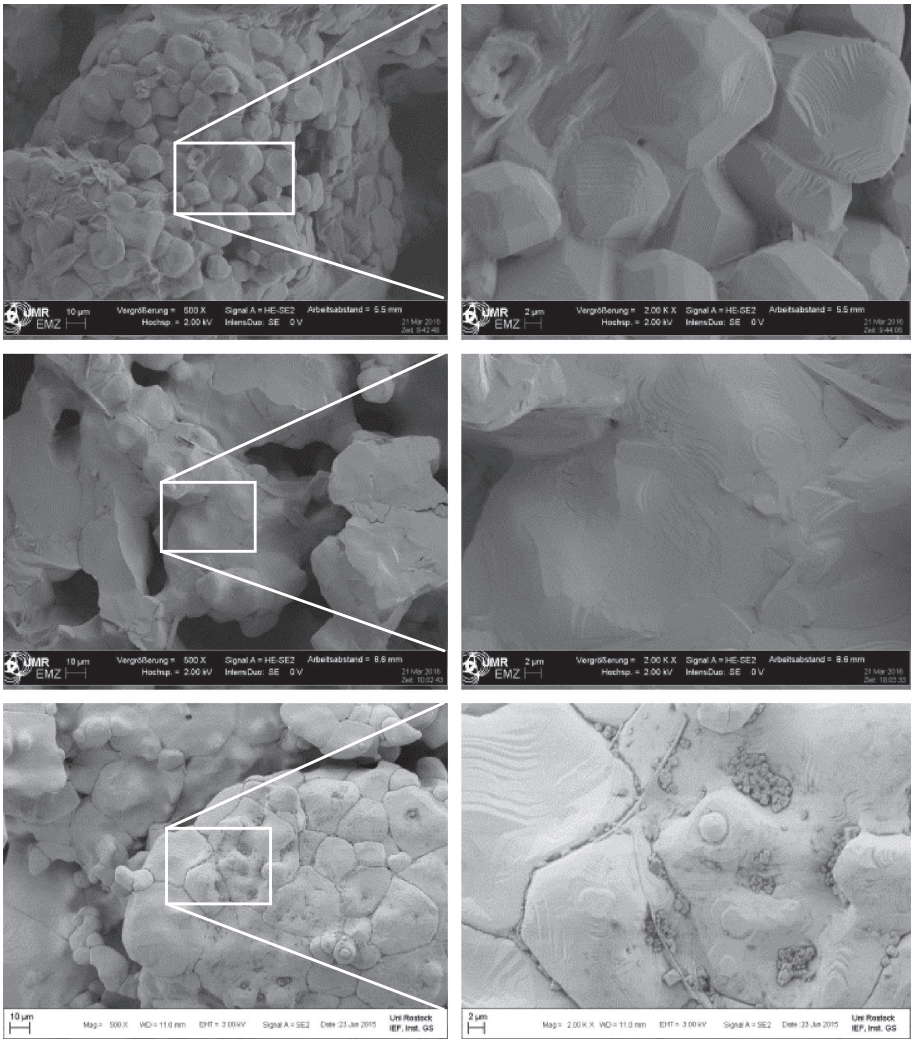

Figure 3: Low (500 ×) and high (2000 ×) magnification of the sintered parts of M1 (top); M2 (middle); M3 (bottom).

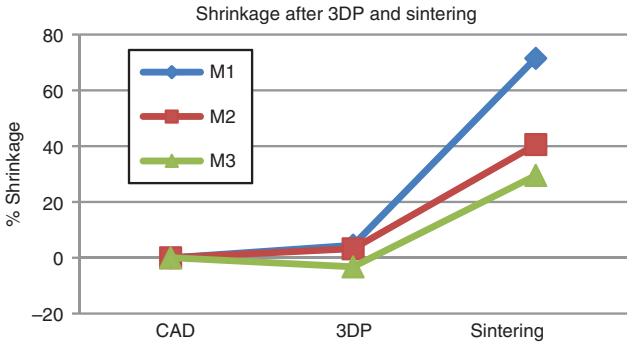

Figure 4: Percentage of shrinkage after 3DP and sintering.

should be improved, but the strength is sufficient to extract the components. The shrinkage must possibly be reduced, though a larger porosity is important for a good cell growth. Thus, each patient-specific geometry can be fabricated after controlling the process parameters.

The 3D printed piezoceramics must still be activated, but this could be done following the principle outlined in [6]. Moreover, BTO is biocompatible [2, 3, 5], and can serve as a scaffold material that can be activated by electrical fields in order to stimulate osteoblasts proliferation and differentiation of osteoclasts.

4 Conclusion

This investigation demonstrated the possibility to fabricate porous piezoelectric barium titanate parts with a 3D printer. Although the shrinkage after sintering is still high, the process can be done with thermally treated as well as untreated, non-flowable powder. The shrinkage in the parts which were produced with the heat-treated BTO is lowest. However, the expenditure for the material

preparation is very high. Particularly the resulting porosity may be advantageous for cell growth relating to electrical stimulation.

Further studies will focus on the polarisation of the 3D printed parts. This is necessary in order to use the piezoelectric effect, for example for implants.

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Author's Statement

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