Fabrication of dense zirconia-toughened alumina ceramics through a stereolithography-based additive manufacturing

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\textbf{A R T I C L E   I N F O}

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B. Microstructure
B. Mechanical properties
B. Toughness and toughening

\textbf{A B S T R A C T}

We report a novel approach to fabricate dense zirconia-toughened alumina (ZTA) ceramics with excellent properties via an additive manufacturing process based on stereolithography. The XRD patterns show the ZTA sample consists of α-Al\textsubscript{2}O\textsubscript{3} and t-ZrO\textsubscript{2} with the dominance of α-Al\textsubscript{2}O\textsubscript{3}. The zirconia grain with the average size of 0.35 µm is small enough to trigger the toughening behavior of zirconia in the ZTA. The prepared ceramics showed a density, Vickers hardness, bending strength, and fracture toughness of 4.26 g/cm\textsuperscript{3}, 17.76 GPa, 530.25 MPa, and 5.72 MPa m\textsuperscript{1/2}, respectively. These properties are comparable to those for ceramics obtained through conventional ceramic processing.

1. Introduction

Due to their excellent properties, e.g., their high hardness, high strength, high fracture toughness, good mechanical strength at high temperatures and good thermal shock resistance, zirconia-toughened alumina (ZTA) ceramics have been widely used for various applications such as cutting tools, biomedical implants and structural parts [1–3]. Conventional ceramic-shaping methods, such as dry pressing, isostatic pressing, slip-casting, tape-casting [4–7] and injection molding [8], have been used to fabricate ZTA ceramics for decades. However, these conventional manufacturing techniques have limitations, and usually cannot be used for the fabrication of parts with complex shapes (internal holes, sharp corners, etc.) and parts requiring a high accuracy. These processes are also rather time-consuming and of high cost because they require the fabrication of a mold and a pots-machining processing (cutting, grinding, etc.) after sintering. Therefore, it is necessary to develop a more effective and economical approach to fabricate complex ceramic parts.

Additive manufacturing (also referred to as 3D printing) is a rapid prototyping technology and can be used to fabricate three-dimensional (3D) parts very quickly, without molds, and offers a good alternative. This new approach allows fabrication of ceramic parts with complex geometries and is more efficient than conventional shaping methods. In this approach, a ceramic part is directly produced from a virtual model by gradually adding material to eventually form the final part. This method not only saves time but also allows fabrication of parts with arbitrary geometries [9].

Preparation methods of ceramics via 3D printing could be divided into direct processing and indirect processing. For direct processing, Selective Laser Melting (SLM) offers the opportunity to fabricate complex shaped bulk ceramics directly from loose powder. For instance, Hagedorn et al. [10,11] adopted the selective laser melting technique to fabricate Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} eutectic parts and were able to achieve a density of almost 100%. Niu et al. [12] adopted a laser-based net shaping method to fabricate Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} eutectic ceramic structures and reported that the fabricated ceramics showed mechanical properties similar to ceramics obtained through conventional methods. However, Direct techniques immediately yield the sintered ceramic part but may produce a large number of defects due to internal stresses induced by temperature gradients or the very rough surfaces. Therefore, micro-cracks would occur easily in the samples due to the high local stresses [13–15].

On the other hand, stereolithography (SLA), an indirect 3D printing method which does not need a high energy laser beam, is based on the photopolymerization of a liquid resin filled with ceramic particles which could avoid the defects coming from the internal stresses and offers several advantages such as a high accuracy and a good surface finish of the product. However, most previous studies on SLA focused on improving the rheological properties and the curing behaviors of the suspension [16–22]. For instance, Griffith and Halloran discussed the...
flow behavior of ceramic suspensions and raised the cure depth model by employing a modified Beer-law [16]. Zhou et al. studied the influence of the dispersant, the volume fraction of powder and particle diameter in a new aqueous ceramic suspension [17]. Tomeckova et al. investigated the critical energy for photopolymerization of silica and alumina suspensions and spotted the relationship between critical energy dose and inhibitors, photoinitiator concentration, inert dye concentration, respectively [18]. To the best of our knowledge, the production of ZTA ceramic parts by SLA with excellent mechanical properties has not been achieved so far.

In this work, dense and crack-free ZTA ceramic was fabricated through SLA and pressureless sintering. The XRD analysis was conducted to identify the phase composition of the SLA-processed ZTA. The microstructure of the ZTA sintered body and the grain size of zirconia and alumina grains in ZTA body are characterized. Mechanical properties such as the Vickers hardness, bending strength, and fracture toughness were tested and compared with those obtained through conventional shaping methods. In addition, dentoid ceramic parts were produced as well to demonstrate the feasibility of the SLA approach to fabricate complex parts and to underline the broad application potential of this fabrication technique.

2. Experimental procedure

2.1. Powder mixture preparation

First, the as-received alumina powder (TM-DAR, d50=200 nm, BET=13.5 m2/g, TAIMEI CHEMICALS, Japan) and zirconia powder (HWYA-N-1S, d50=200 nm, BET=12 m2/g, Guangdong Orient Zirconic Ind. Sci. Tech. Co., China) were mixed together, with the weight ratio of alumina/zirconia=4:1. The mixture was then diluted in ethanol with ultrasound. After that, the mixture was ball-milled in a planetary ball mill for 6 h using zirconia balls. The suspension was then dried in an oven at 60 °C for 12 h. Finally, the dried powder was sieved through a 100 mesh screen.

2.2. Preparation of the ceramic suspension

The premixed solution used to prepare the ceramic suspension consisted of four components: acrylamide (23.75 wt%), N, N’-methylenbisacrylamide (1.25 wt%), glycerine (10 wt%), and deionized water (65 wt%). Then, the as-prepared powder was added to the premixed solution with the volume fraction of 30 vol%, and polyvinyl pyrrolidone (PVP) K-15 was selected as 1.2 wt% of the powder, which was used as the dispersant to form the ceramic suspension. The ceramic suspension was then ball-milled for 12 h using zirconia balls. The suspension was then dried in an oven at 60 °C for 12 h. Finally, the dried powder was sieved through a 100 mesh screen.

2.3. Fabrication of the ceramic parts through stereolithography

The 3D model was created using the UG software, and then the Magics software was employed to generate the supporting structure and to slice the parts. The final data was then imported into the stereolithography machine with its x-y resolution, laser beam diameter, and layer thickness of 0.1 mm, 0.06 mm, and 0.07 mm, respectively. The ZTA green body was obtained by stereolithography using the ceramic suspension mentioned above. A schematic illustration of the stereolithography process is shown in Fig. 1.

Each individual pattern layer was cured by the ultraviolet laser selective scanning on the ceramic suspension. After the first layer was cured, the supporting platform was moved down, and the ceramic suspension was recoated on the cured surface with a blade. Then, the second layer was cured analogously. These steps were repeated until the whole green body of the ZTA part was eventually obtained.

2.4. Post processing of the ZTA green body

1) Drying

After the green body was obtained, the residual water in the sample had to be removed by drying. A novel drying approach based on using PEG 400 as the liquid desiccant was adopted in this study [23]. For the PEG-based extraction process, the sample was immersed in PEG 400, which was expected to result in a uniform extraction rate in all directions.

2) Debinding

A two-step debinding profile consisting of a vacuum debinding step followed by an air pyrolysis debinding step was adopted to remove the binders in the compact, which is shown as follows: Firstly, the samples were heated at 600 °C for 3 h in vacuum with the heating rate of 1 °C/min. Secondly, the samples after vacuum debinding were heated at 1000 °C for 30 min in air with the heating rate of 5 °C/min.

3) Sintering

The samples were finally sintered at 1600 °C for 4 h in a furnace (Thermconcept, HTK 16/18, Germany).

2.5. Characterization

The density of the prepared ZTA bodies was determined employing the Archimedes’ principle using a balance with an accuracy of 0.0001 g. The theoretical density of the ZTA part used in this study was 4.28 g/cm3. The Vickers hardness was tested using a Vickers hardness testing machine (HVS-30Z, Shanghai Precision Instrument Co., Ltd., China) by applying a load of 98 N. The fracture toughness was assessed by measuring the crack lengths produced by the Vickers indentation tests under a load of 98 N after 10 s. The fracture toughness was then calculated using the following equation proposed by Niihara I [24]:

\[
K_{IC} = \frac{0.129}{3}\left(\frac{c}{a}\right)^{\frac{3}{2}} E^{\frac{1}{4}} N^{\frac{1}{4}} H^{\frac{1}{4}} \left(\frac{c}{a}\right)^{\frac{3}{2}} E^{\frac{1}{4}} (c/a > 2.5)
\]

where \(E\) is the material’s Young’s modulus, \(H\) is the hardness, \(P\) is the indentation load and \(c\) is the length of the indentation cracks. At least 10 indentation tests were performed for each sample at randomly chosen spots. The radial crack lengths were measured using an optical microscope. Ten specimens with dimensions of 25 mm (L)×2 mm (W)×1.5 mm (H) were fabricated for the flexural strength test. The
3. Results and discussion

3.1. Analysis of the phase composition and microstructure

Fig. 2 shows the XRD patterns obtained for the sintered ZTA sample. The pattern indicates that the ZTA sample consists of two phases – α-Al₂O₃ and t-ZrO₂. The α-Al₂O₃ phase appears to be predominant whereas the amount of t-ZrO₂ in the sample seems to be considerably smaller, which reflects the composition of the mixed powder.

The microstructure of the polished surface of the sintered ZTA body is revealed in Fig. 3(a). The zirconia particles were found to be well-dispersed along the grain boundaries of the alumina grains, and some of them were located at the triple junctions. In addition, the microstructure of the ZTA sample is very dense, with only a small number of pores located at the grain boundaries. The grain size distributions for the alumina and zirconia grains are shown in Fig. 3(b, c), respectively. According to Fig. 3(b, c), the mean grain size of the alumina and the zirconia grains is 1.08 and 0.35 µm, respectively. The zirconia grain size is small enough to trigger the toughening behavior of zirconia in the ZTA body [25]. Regarding the toughening mechanism, the fine ZrO₂ particles located at the grain boundaries of the Al₂O₃ inhibit the movement of the Al₂O₃ grain boundaries and suppress the grain growth of Al₂O₃. Therefore, the improvement of the grain boundary structure results in an enhancement of the mechanical properties [26].

3.2. Mechanical properties

The density of the sintered ZTA sample was measured to be 4.26 g/cm³, which corresponds to 99.5% of the theoretical density (T.D.%).
the sintered ZTA body. The mechanical properties of the sintered ZTA body are illustrated in Table 1. The average Vickers hardness, the bending strength and the fracture toughness of the ZTA ceramic were determined to be 17.76 GPa, 530.25 MPa and 5.72 MPa m$^{1/2}$, respectively.

The mechanical properties of the ZTA ceramics fabricated in this study are essentially identical to those of ZTA ceramics produced via the conventional fabrication routes mentioned above, and a systematic comparison of the mechanical properties measured in the present study with the corresponding properties of ZTA ceramics prepared through other forming techniques is shown in Table 1 [5,10,12,27,28]. In addition, a complex shape could be easily prepared using the presented SLA technique. As shown in Fig. 4, a net-shape dentoid part can be obtained through SLA without any post-processing. Therefore, the fundamental study of this paper offers an alternative approach with complex shape and flexibility for fabricating structural ceramic parts.

4. Conclusions

In summary, we reported a new way to fabricate complex ZTA ceramic parts with excellent properties via a 3D printing process based on stereolithography. ZTA ceramic is composed of the majority of α-Al$_2$O$_3$ and the minority of tetragonal YSZ according to the XRD patterns. The zirconia particles were found to be well-dispersed along the grain boundaries of the alumina grains, and the microstructure of the ZTA sample is very dense, with only a small number of pores located at the grain boundaries. The zirconia grain with the mean size of 0.35 µm is small enough to trigger the toughening behavior of zirconia in the ZTA body. The Vickers hardness, bending strength, and fracture toughness of the sintered body were 17.76 GPa, 530.25 MPa, and 5.72 MPa m$^{1/2}$, respectively. These values are comparable to those reported for ZTA ceramics prepared via conventional ceramic shaping methods.

Acknowledgements

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Table 1

<table>
<thead>
<tr>
<th>Fabrication method</th>
<th>Mass Ratio (Al$_2$O$_3$ /ZrO$_2$)</th>
<th>Relative density</th>
<th>Hardness (GPa)</th>
<th>Bending strength (MPa)</th>
<th>Fracture toughness (MPa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLA (this work)</td>
<td>4:1</td>
<td>99.5%</td>
<td>17.76 ± 0.21</td>
<td>530.25 ± 29.57</td>
<td>5.72 ± 0.50</td>
</tr>
<tr>
<td>Dry-pressing pressureless sintering</td>
<td>–</td>
<td>98%</td>
<td>18.2(GPa)</td>
<td>–</td>
<td>4.2</td>
</tr>
<tr>
<td>HIP[5]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SLM[16]</td>
<td>1:4:1</td>
<td>Nearly 100%</td>
<td>–</td>
<td>500</td>
<td>–</td>
</tr>
<tr>
<td>LENS[12]</td>
<td>1:4:1</td>
<td>Nearly 100%</td>
<td>17.15(GPa)</td>
<td>–</td>
<td>4.79</td>
</tr>
<tr>
<td>CIM[27]</td>
<td>4:1</td>
<td>98%</td>
<td>1582.4HV</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Dry-pressing Pressureless sintering[28]</td>
<td>4:1</td>
<td>–</td>
<td>1516HV</td>
<td>–</td>
<td>5.93</td>
</tr>
</tbody>
</table>

References

[20] S.F. Gentry, J.W. Halloran, Depth and width of cured lines in photopolymerizable...


