Influence of tensile edge design and printing parameters on the flexural strength of ZrO2 and ATZ bars prepared by UV-LCM-DLP

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ABSTRACT

Lithography based Ceramics Manufacturing (LCM), i.e., Digital Light Processing (DLP) is one of the Additive Manufacturing (AM) techniques that is being widely used for the production of ceramic parts. Additionally, the development of photocurable slurries and the influence of the printing parameters on the fabricated parts properties are also receiving high attention. In this work, ZrO2 and ATZ materials were used as a case of study to evaluate the flexural strength of the fabricated parts, using our own developed UV-curable slurries. The influence of the tensile edges shape of the bars, tilting speeds, layer thickness and printing direction were evaluated, obtaining the highest flexural strength values for the 200 μm round shape bars, faster tilting speeds, 25 μm layer thickness and printing in the Z direction for ZrO2 and in the Y for ATZ.

1. Introduction

The research on the Lithography based Ceramics Manufacturing (LCM), i.e., Digital Light Processing (DLP), is growing exponentially in the last years. In general, it is expected that in future Additive Manufacturing (AM) technology will help to save costs and time in parts production. However, currently there are several limitations that should be solved or minimised to improve the properties of the fabricated parts [1–3]. These limitations are mainly associated with the layered structure, which influences the surface quality and mechanical properties, among others [1–3].

In this context, several works (not only using LCM) focused their objective in the influence of the printing parameters on the final features of the 3D printed pieces [4–8]. However, in the last years, the interest for the development of photosensitive ceramic slurries is growing [9–16], and the comparison between different methodologies to prepare them is receiving high attention [17]. ZrO2 [14,18,19] and Al2O3-ZrO2 [20] materials are two of the ceramics widely used to optimise the 3D printing procedure and the subsequent thermal treatment because of their high interest in the medical/prosthetic field [21]. For such applications, to know the limitations depending on the orientation of the part is mandatory due to the different movements or forces that the ceramic part should resist without neither deterioration nor breaking down.

This work is based on the combination of both objectives: the development of UV-curable slurries and the influence of the printing parameters on the fabricated parts. For this purpose, we selected ZrO2 and ATZ materials as a case of study, using the one-step methodology recently reported [17]. The shape of the tensile edges, the tilting speeds, the layer thickness and the printing direction were evaluated. 4-point bending methodology was used to study the influence of the printing parameters on the flexural strength of the fabricated bars.

2. Experimental

2.1. UV curable slurries preparation

ZrO2 and Al2O3-ZrO2 photocurable slurries were prepared in one-step according to the procedure recently published [17]. Submicrometric powders of ZrO2 (Tosoh Corporation, Japan) and Al2O3 (Taiwei Chemicals and Co. LTD., Japan) were dispersed in a liquid phase constituted by Miramer M200 (MIWON, South Korea) and Genomer 5695 (Rahn A. G., Switzerland) as reactive binders, benzyl alcohol (Meck, Germany) as diluent, Solsperse 41000 (Lubrizol Advanced Materials S. L., Spain) as dispersant and Irgacure 1173 (BASF, Germany) as photoinitiator. After mixing, a planetary ball milling treatment during 20 min at 300 rpm was applied and then, the slurry was kept on a rolling bench for 24 h.
2.2. Parts design

Three different CAD files for the 4-point bending testing bars were designed as is shown in Fig. 1. The main difference between them resides in the tensile edges, which are usually chamfered for the mechanical testing. Three different CAD models were created: (1) raw bar with sharp edges, (2) 100 μm rounded tensile edges and (3) 200 μm rounded tensile edges. Moreover, as the shrinkage during printing process occurs, the original CAD files were scaled to compensate that, using CAD models with the following dimensions: 30 × 2.9 × 2.6, 30 × 3.2 × 2.3 and 32 × 2.9 × 2.3 mm³ for the Z, Y and X printing directions, respectively (Fig. 1).

2.3. Digital Light Processing and printing parameters

The ceramic parts were printed by DLP, using the custom-made equipment Cerafab 7500 (Lithoz GmbH, Austria) with a lateral resolution of 20 μm working with an UV light source of \( \lambda = 365 \, \text{nm} \). The layer thickness was set at 12, 25 and 37 μm (total range = 10–100 μm) and the intensity of the lamp was set at 18.760 mW/cm². The influence of the tilting up and down speeds (up/down) were tested comparing samples produced at 30/15 (fast) and 15/5 (slow) steps/s. Moreover, the printing direction was also changed in order to evaluate the flexural strength. The printed parts were cleaned by using a commercial cleaning solution (LithaSol 20, Lithoz GmbH, Austria) together with compressed air. The exposure energy employed was \( \sim 100 \, \text{mJ/cm}^2 \).

2.4. Debinding and sintering processes

After cleaning, the printed parts were debinded (PY 12 H 1300 8, Pyrotec, Germany) at 800 °C following a program shown in a previous work [9]. Then, they were sintered (Carbolite HTF 1800, Carbolite Gero, United Kingdom) at 1450 °C for 2 h using a heating rate of 5 °C/min till 800 °C and 2 °C/min from 800 °C to 1450 °C, and a cooling rate of 5 °C/min. Both thermal processes were carried out under air atmosphere.

2.5. Flexural strength measurements

Uniaxial bending tests were performed using a 4-point bending setup, with load spans of 10 and 20 mm. The sintered bars size were 25 × 1 × 2.5 ± 0.1 × 2.0 ± 0.1 mm³ and the edges of the tensile side were manually chamfered (using a 22 μm mesh SiC disc) just for one set of bars with sharp edges [22]. It should be noted that the rounded bars exhibited 100 and 200 μm rounded tensile edges after sintering (measuring from the sharp corner to the rounded one, extrapolating both sides and using the bisector). For the experiments, a universal testing machine type Zwick/Roell 2005 (ZwickRoell, Germany) with a 5 kN load cell was used, with a cross beam speed of 1 mm/min and a pre-load force of 10 N. Sets of 10 bars were used for testing the influence of the printing parameters and the bars tensile edges (sharp, chamfered and 100 or 200 μm rounded edges).

3. Results and discussion

Initially, to identify the influence of the tensile edges shape and tilting speed, ZrO₂ bars were tested. When both parameters were established (the highest strength was obtained in each case), ATZ bars were also tested.

3.1. Influence of the tensile edges shape: sharp, chamfered and rounded

Table 1 shows the average flexural strength and its standard deviation of a set of 10 bars with different tensile edges shapes. The lowest value

<table>
<thead>
<tr>
<th>Edges</th>
<th>Flexural strength (MPa)</th>
<th>Chamfered</th>
<th>R-100 μm</th>
<th>R-200 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sharp</td>
<td>567</td>
<td>474</td>
<td>606</td>
<td>646</td>
</tr>
<tr>
<td>Standard deviation (MPa)</td>
<td>113</td>
<td>176</td>
<td>92</td>
<td>104</td>
</tr>
</tbody>
</table>

Fig. 1. Representation of the final bars dimensions, shapes and layered structure used for 4-point bending measurements.
and the highest standard deviation were obtained for the chamfered bars. This could be associated to the introduction of defects during chamfering, decreasing the mechanical properties of the material. The bars with the sharp edges (no modifications) exhibited a behaviour between the rounded and the chamfered bars, which delimited an interval of 200 MPa. Moreover, after rounding the edges, for each 100 μm of depth, the flexural strength increased around 40 MPa, but the standard deviations remained in the same order. Here it is important to highlight that the chamfering of the edges should be < 20 μm; however, as the layer thickness was set at 25 μm and the bar will have a layered structure, we discarded this possibility and we tried to study a kind of extrapolation of the chamfering effect printing directly a ‘rounded’ bar. It should be advised that the shrinkage of the bars during sintering is homogeneous in all directions, which allows keeping the original round edge proportions, being after sintering around 100 and 200 μm (from the sharp corner to the rounded one). Something interesting is that even exhibiting a layered structure, the round edge improves the flexural strength of the pieces. This opens a new possibility because the chamfering is removed, which is critical in pieces with layered structure, avoiding the creation of defects neither coming from the printing procedure nor from the slurry properties. Moreover, removing the sharp edges, the accumulation of the stresses on them also disappears, which helps to understand the characteristics of the parts, decreasing the effects coming from the sample preparation and measurement procedures.

Based on the results, the printed bars for testing the influence of the other parameters were the rounded ones with 200 μm of depth.

3.2. Influence of the tilting speeds

The tilting speeds are the approximation or detachment velocities between the building platform and the VAT. Together with the exposure time, this parameter will strongly influence on the time necessary to complete the job. This is the main reason to test whether the quality of the bar is affected using a faster program. Table 2 shows the results of the flexural strength and its standard deviation for the 200 μm rounded bars printed with different tilting speeds. Observing the results, the bars printed using the faster process exhibited a higher flexural strength and lower standard deviation than the ones obtained using the slower velocities. This could be related to the surface tension of the liquid phase (stronger at lower speeds), which can decrease the adhesion between the layers. Moreover, the comparison between both speeds allowed us to reduce the printing time in ~30 min, without affecting significantly the flexural strength.

Based on that, the rest of the experiments were performed using the fast process.

3.3. Influence of the layer thickness

It is well known that the layer thickness will strongly influence on the properties and surface quality of the fabricated parts [19]. In Fig. 2, the flexural strength of the ZrO2 ATZ 200 μm rounded bars printed with different layer thicknesses is shown. In both cases, a similar trend can be observed. It is quite interesting that the surface quality in the case of the bars printed with 12 μm layer thickness was quite high, being the layered structure almost impossible to detect with the naked eye. However, the mechanical properties dropped from 550 to 650 to around 100 MPa. This can be explained by the closed porosity observed in the previous studies [17], which is a defect that can influence stronger when the layer is thinner (Fig. 2). Moreover, in the case of the ATZ, this porosity was found mainly in the interphase of the layers, which confirms this assumption and the necessity of improving the slurry recipe [17].

In the case of the bars printed with 37 μm as layer thickness, the difference in the mechanical properties is around 150 and 200 MPa lower for ATZ and ZrO2 bars, respectively. In both cases, this effect can be associated to the lower curing depth/layer thickness ratio, which is 3 for bars printed with 25 μm and around 2 for the bars printed with 37 μm layer thickness. In the case of the 12 μm thickness, the ratio is around 6, which a priori should improve the adhesion between layers and reinforce the layered structure; however, as the number of layers increases, the effect of the bubbles also increases, which provokes the strong decrease in the flexural strength.

From this study, the highest mechanical properties were achieved by using a layer thickness of 25 μm, which will be the one used for the study of the influence of the printing direction.

3.4. Influence of the printing direction

Using the parameters studied before (layer thickness 25 μm, tilting speeds 30/15 and the bar shape with 200 μm rounded edges), 10 bars of each material (ZrO2 and ATZ) were printed in the three different directions (in total 60 bars) showed in Fig. 1. The printing in the X direction could not be completed because the necessary time was around 24 h and the slurry was not totally stable during this period. The viscosity increased with the time, which could be related with solvent evaporation, and more bubbles were formed, appearing defects on the bars that provoked the break down and the interruption of some of them. Because of that, it was possible to print just 1/4 of the job. From this point of view, an important limitation was found, which is translated to the conclusion that just 8 mm approximately (320 layers) can be printed in height (perpendicular to the printing platform). This limitation is because the slurry is put in the VAT since the beginning, and is not being dispersed periodically as in the case of the commercial cartridges. Maybe by using cartridges to dispense the slurry, this limitation could be removed/minimised. Comparing the other two directions, interesting differences between both materials can be observed (Fig. 3). In the case of zirconia bars, the ones printed in the Y direction exhibited a lower flexural strength (439 ± 95 MPa) in comparison to the Z direction (646 ± 104 MPa). However, in the case of ATZ bars, an opposite behaviour is observed (although the difference between both directions is smaller and the standard deviations overlap), obtaining 542 ± 135 MPa and 642 ± 81 MPa for the Z and Y directions, respectively. This smaller difference

Table 2

<table>
<thead>
<tr>
<th>Tiling up/down speeds</th>
<th>30/15 (fast)</th>
<th>15/5 (slow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural strength (MPa)</td>
<td>646</td>
<td>517</td>
</tr>
<tr>
<td>Standard deviation (MPa)</td>
<td>104</td>
<td>132</td>
</tr>
</tbody>
</table>

![Fig. 2. Flexural strength values as a function of the layer thickness. Schematic representation of a defect in bars structure with different layer thicknesses.](image-url)
can be explained by the presence of alumina agglomerates in the slurry, as it was recently published [17], due to the difficulties to break them down because of the submicrometric size of the primary particle size.

Fig. 4 shows the fractography images obtained by optical microscopy of the ZrO2 and ATZ bars printed in the Y direction. It can be clearly seen how in the case of ZrO2, perpendicular cracks to the tensile side appeared, which are oriented in the same direction than the layers of the bar. This phenomenon was also observed in other pieces (not shown); however, in the case of ATZ bars, this effect was not detected. In both cases, the fracture origin was observed on the surface of the tensile side as well as for the bars printed in Z direction [17]. Based on that, it is clear that the Al2O3 is playing a key role, maybe also its agglomerates as we suggested above. The presence of the agglomerates could redistribute the stresses created along the body of the bar, which could minimise/inhibit the delamination effect. We should remind that in our previous work [17], the layers of the ATZ bars were observed while the layers of the ZrO2 ones not. This would explain an easier delamination of the bars during the experiment; however, this was not observed and a different explanation must be found in the ATZ bars. Taking into account the similar particle size, the unique explanation would be the alumina agglomerates that, depending on the layer orientation, could affect enhancing (Y direction) or reducing (Z direction) the flexural strength. Nevertheless, if the standard deviation is also taking into account, the alumina agglomerates could be acting minimising the influence of the printing direction on the flexural strength, i. e., there is not a significant change in the value. To know if this is the reason, further studies are necessary using a different milling strategy, dispersing agent or another alumina raw material.

4. Conclusions

In this work, the influence of the printing parameters on the flexural strength of ZrO2 and ATZ parts fabricated using our developed UV-curable slurries is studied. Based on the results, the following conclusions can be drawn:

1. The edges of the tensile side influenced the flexural strength of the ZrO2 bars, obtaining 567 ± 113, 474 ± 176, 606 ± 92 and 646 ± 104 MPa for the sharp edges, chamfered, 100 μm and 200 μm rounded bars, respectively.
2. The higher tilting speeds allow us to fabricate parts faster and with higher flexural strength.
3. The layer thickness strongly influenced the flexural strength, obtaining the highest values for the samples prepared with 25 μm cast thickness and the lowest one with 12 μm. However, the surface quality (lower layered appearance) is higher when the layer thickness decreases.
4. The printing direction has a key role on the flexural strength, having a lower impact in the ATZ bars than ZrO2 ones. For ZrO2 bars, the values obtained for the Z direction is 646 ± 104 MPa and for the Y one is 439 ± 95 MPa. However, in the case of ATZ bars, an opposite trend was observed (542 ± 135 and 642 ± 81 MPa for the Z and Y directions, respectively). The current methodology did not allow us to print successfully in the X direction.

Fig. 3. Flexural strength values of the ZrO2 and ATZ materials and representation of the bars printed in Y and Z directions.

Fig. 4. Fractography images obtained by optical microscopy of the ZrO2 and ATZ bars printed in the Y direction. The fracture origin is indicated with the yellow square and other defects with red circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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