Investigation of the influence of 3D printing modes with ceramics and sintering on the shrinkage process of thin-walled models

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Abstract. The subject of this study focuses on the effect of 3D printing and heat treatment of thin-walled models made of ceramic paste. The plates with dimensions of 20*5*40 mm were used as the models. The methodology includes the creation of ceramic objects using 3D printing by the SLA method (stereolithography) and their further heat treatment. The surface quality and the shrinkage percentage of samples printed in different modes and thermally processed under different conditions are compared. It was found that with a decrease in layer thickness and particle size, as well as an increase in the duration of heat treatment, the surface quality of the samples improves and the percentage of shrinkage decreases approximately 2 times. Using new modes and improved heat treatment conditions, samples with the least number of cracks and a lower percentage of shrinkage were obtained, which allows using this process to create ceramic products of higher quality. The method of creating ceramic products used in the work in the future can be applied in such industries as aircraft manufacturing, medicine, biotechnology and other fields.

1. Introduction

3D printing of ceramics is a relatively new direction in the field of additive technologies, which is developing rapidly along with technologies for 3D printing with polymers and metals. It is believed that the technology of SLA (stereolithography) is the most famous and popular technology for 3D printing of ceramics and is widely used throughout the world [1-4].

One of the innovative and rapidly developing areas at the junction of biotechnology and materials science is the biological treatment of ceramic masses. This post-processing method improves the technological and consumer properties of ceramic products. Microorganisms in the composition of ceramic masses produce the formation of a number of metabolites and in combination have a biotechnological potential to change the properties of ceramic masses for the better. This technology can be used after 3D printing of ceramic materials [5-7].

The process of forming ceramic products using 3D printing has been widely developed and has reached high levels of accuracy and roughness of the product. However, since the 3D printing of ceramics involves the use of ceramic paste based on ceramic powder and a photosensitive polymer
(the chemical composition, percentage, and chemical reagents used may be different depending on the manufacturer), the product was manufactured by means of additive technologies. [8-11]

At the moment, there are many foreign studies on the influence of 3D printing parameters on the surface quality of the product [12,13]; however, most of them relate to printing with polymers, where the resulting product is the final product and does not require subsequent heat treatment.

2. Experimental setup
To perform the study, the Russian 3D printer “AF200” for ceramics was used (manufacturer - Additive Manufacturing LLC). Ceramic plates were used as samples (Figure 1).

![Figure 1. 3D model of ceramic plates](image)

The Triangulatica program (in the public domain) was used to develop and select the parameters of the 3D printing, such as layer thickness, beam movement strategy, beam movement step, and others. For greater purity of the experiment, 9 plate samples (3 of each type) with different characteristics were printed. The main parameters of the samples and print modes are presented in Table 1.

| Plates №1 | Plates №2 | Plates №3 |
|-----------|-----------|-----------|
| Dimensions | 20x5x40 mm | ceramic paste (porcelain in the form of a powder with a particle size of up to 5 microns in combination with a polymer binder) with a solid content of 44% | 50 μm |
| Material | solid, height - 1 mm | 25 μm |
| Raft | Scan speed | 11000 mm/s | 100 μm |
| Layer thickness | Beam movement strategy | Simple bidirectional | 150 μm |
| Beam movement strategy | Beam movement step | 100 μm |
| The distance between the wall and the internal movement of the beam | 80 μm | 54 minutes |
| Print time | 18 minutes | 110 minutes |

After separation from the substrate surface and washing with water, the obtained samples (Figure 2a) were placed in a furnace. The heat treatment in the furnace has 2 stages: the removal of the binder (debinding process) and the sintering of the samples. These processes were carried out in one furnace, but in different temperature conditions.
To study the influence of the environment in which the heat treatment is carried out, three groups of plates (3 plates in each group) were distributed in the working zone of the furnace (Figure 2b) [14, 15].

![Figure 2a. Samples obtained using 3D printing by the SLA method](image)

![Figure 2b. Location of samples in the furnace](image)

Heat treatment conditions at the stages of debinding and sintering of the products are presented in Table 2.

| Temperature conditions at the stage of debinding | 150 °C | Time to reach, min | Duration, min |
|-----------------------------------------------|--------|--------------------|---------------|
| t, °C                                          |        |                    |               |
| 150                                           | 60     | 60                 |               |
| 320                                           | 240    | 360                |               |

| Temperature conditions at the stage of sintering | 150 °C | 320 °C | 450 °C | 600 °C | 780 °C | 900 °C | 1050 °C |
|-------------------------------------------------|--------|--------|--------|--------|--------|--------|---------|
| t, °C                                            | 60     | 150    | 60     | 60     | 60     | 60     | 60      |
| Time to reach, min                               |        |        |        |        |        |        |         |
| Duration, min                                    | 0      | 0      | 60     | 0      | 0      | 60     | 0       |

As a result of heat treatment, 3 groups of plates with a large number of cracks, tears and leashes were obtained. The LEVENHUK DTX 90 training microscope was used to examine the structure of the samples. The appearance of the samples under the microscope is presented in Table 3. The samples were examined at a 60-fold increase. At this stage of the study, a larger increase is not required, since the samples have many visible cracks after sintering.

Based on the appearance of the samples under a microscope, it was concluded that the location of the samples in the additional medium (under a layer of quartz or under zirconium balls) increases the number of cracks and geometric deviations along the axes. Therefore, the location of ceramic objects at the stage of heat treatment in the free position in the furnace makes the heating more uniformed. In addition, it becomes easier to remove the polymer in the product composition.
Table 3. Appearance of samples at 60x magnification

| In the box | Under zirconium balls | On the surface of zirconium balls |
|------------|-----------------------|----------------------------------|
| 100 μm     | ![Image](100_1.jpg)   | ![Image](100_2.jpg)   | ![Image](100_3.jpg)   |
| 50 μm      | ![Image](50_1.jpg)    | ![Image](50_2.jpg)    | ![Image](50_3.jpg)    |
| 25 μm      | ![Image](25_1.jpg)    | ![Image](25_2.jpg)    | ![Image](25_3.jpg)    |

Based on the results, the following conclusions have been made:

1. The chemical composition of the polymer requires refinement for the more gradual and smooth debinding process.
2. It is essential to reduce the size of the powder fraction from 5 microns approximately to 0.01 - 1 microns.
3. It is necessary to increase the percentage of ceramic powder in the paste from 55% to 65% to reduce the percentage of shrinkage.
4. It is required to increase the duration of debinding and sintering processes to reduce the likelihood of leashes and cracks.
5. An adjustment of the beam movement strategy is required in order to increase the density of the product after printing. With the new strategy, internal shading (the filling pattern of the laser beam path along the inner area of the layer) starts at an angle of 45 ° and changes its direction with each layer by 90 °. In this connection, we receive a mesh filling structure and additional polymerization of each previous layer when the current is illuminated.

The above findings were applied to print a new plate. To prepare the ceramic paste, a smaller powder was used (particle size in the range 1-0.01 μm), the concentration of the powder in the paste was 50%, and the printing strategy was also changed. The printed plate went through a heat treatment process. To increase the speed of heat treatment, the debinding and sintering processes were performed sequentially and were not separated, the total time was 28 hours. Adjusted heat treatment conditions are presented in Table 4.
Table 4. Adjusted Heat Treatment Conditions

| t, °C | Time to reach, min | Duration, min |
|------|--------------------|---------------|
| 150  | 60                 | 0             |
| 320  | 150                | 330           |
| 450  | 60                 | 60            |
| 600  | 120                | 60            |
| 780  | 150                | 60            |
| 900  | 90                 | 60            |
| 1250 | 360                | 120           |

Thus, it was possible to obtain a sample with significantly smaller deviations in geometry, less shrinkage, and better surface quality. Figure 3a shows the appearance of the plate, and figure 3b shows the view of the plate under a training microscope.

![Figure 3a. The appearance of the plate.](image)

![Figure 3b. View of the plate under the microscope.](image)

Measurements were also made of the percentage of shrinkage of the sample along 3 axes. Thanks to the change in the composition of the paste, printing and heat treatment modes, it was possible to reduce the percentage of shrinkage almost 2 times (Figure 4).

![Figure 4. Comparison of percent shrinkage of samples](image)
3. Conclusion

Based on the results, the following conclusions have been made:

- The location of the samples in the free position in the furnace allows achieving the most uniform heating, and also makes the debinding process more stable, which in turn leads to better surface quality with fewer cracks and leashes.

- Reducing the size of the fraction of ceramic powder and increasing its concentration in the paste can reduce the percentage of shrinkage of the product and make this process more uniform. It should be noted that these parameters also affect the viscosity of the paste, which in turn can lead to the impossibility of polymerization. The search for the optimal composition of ceramic paste requires the more detailed study.

- Changing the beam movement strategy for 3D printing allows you to increase the density of the final product, and as a result, reduce the percentage of shrinkage.

The performed experiments have a positive result and require additional research. It is necessary to prepare the experimental series for 3D printing of samples based on ceramic paste with a powder percentage of 50% and higher, as well as strength testing of these samples.

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