FILAMENT FOR 3D PRINTING OF HIGH-STRENGTH CERAMICS: STRUCTURE AND PROPERTIES

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Abstract

The ceramic composite filament for 3D printing of high-strength ceramics by the FFF/FDM method was prepared in an extruder from feedstock in the form of granules containing micro- and nanoparticles of zirconium oxide and with a low content of plasticizer. An optical and thermal analysis of the filaments and the comparison with commercially produced filament for 3D printing of ceramics were performed. Our goal was to create a filament with the lowest possible binder content and maximize the density of the ceramic mass so that after debinding and sintering the printed products achieve mechanical properties comparable to technical ceramics produced by classical methods such as powder pressing or injection molding.

Keywords: Ceramics, 3D printing, FDM method, zirconia, zirconium oxide

1. INTRODUCTION

The rapid advancement of additive manufacturing technologies has revolutionized various industries, enabling the fabrication of complex and intricate structures with high precision and customization. Among these technologies, 3D printing has emerged as a prominent player, offering innovative solutions for diverse applications.

This approach was further bolstered by the development of the Fused Filament Fabrication (FFF) or Fused Deposition Modeling (FDM) method, a revolutionary technique enabling the conversion of digital designs into tangible objects.

One of the remarkable extensions of 3D printing is its application in the realm of ceramics. [1,2] The exact date of the first 3D printing of ceramics is difficult to establish, as it was a gradual development of various technologies and approaches to printing ceramics, however, its history stretches back over two decades. [3-5] The combination of ceramic materials and additive manufacturing techniques presents a promising way for creating functional components with tailored properties. In this context, the focus of this study lies in the preparation and analyse of structure and properties of a specialized filament tailored for 3D printing of high-strength ceramics.

1.1 Zirconia ceramics

Zirconia (ZrO_2) exists in several different crystal structures depending on temperature and the presence of certain dopants. The most common crystal structures of zirconia are monoclinic and tetragonal. The monoclinic phase is stable at temperatures below 1170 °C. This phase is known for its expansive properties due to phase transformation. At temperatures above 1170 °C, the monoclinic phase changes to a tetragonal crystal structure, which is thermodynamically stable in the temperature range of 1170 - 2370 °C. This phase has a higher density than the monoclinic phase. Zircon crystals can go from a very simple crystal to a rather complexly faceted form. The typical simple tetragonal crystal of zirconia is a tetragonal prism terminated with four sided pyramids at each end. There is also a cubic zirconia structure. This phase is stable at very high temperatures and is often present as an intermediate in the sintering of zirconia. [6]

Zirconium oxide is often used in ceramics in a stabilized form with the addition of yttrium oxide (Y_2O_3), which creates a crystal structure called tetragonally stabilized zirconium oxide. Thanks to the presence of yttrium oxide, the tetragonal phase of zirconium oxide is stabilized even at lower temperatures and the transformation into a monoclinic phase is prevented, which improves its mechanical properties and resistance to cracks. [7]

1.2 Composite ceramic filament for FDM

Filaments for 3D printing are essentially composite materials composed of ceramic particles (such as zirconia oxide, alumina oxide, hydroxyapatite, yttria oxides, various combinations of these particles, etc.) and a binder component. The binder system is a mixture of thermoplastic materials, among which a thermoplastic polymer (e.g., a polymer based on polypropylene or polyamide), as well as a wax, a tackifier (an agent to improve adhesion), a plasticizer and an elastomer predominate. Binder system provides a balanced set of properties such as strength, tackiness, flexibility, elasticity, plasticity, and viscosity to achieve optimal rheology and properties for the 3D printing process [8]. This complex combination of properties enables the correct modeling of the material during printing, which ultimately leads to the production of high-quality and precise ceramic components. The binder also presents a challenge as, to achieve the desired strength of the printed ceramic object, subsequent steps of binder removal (known as debinding) and ceramic consolidation (sintering) are necessary.

1.3 Debinding and sintering

The presence of the binder poses a potential obstacle during the post-printing stages. To achieve the final desired properties of the ceramic object, the printed filament must undergo a debinding process. During this step, the binder is removed (chemically, thermally, or both) from the ceramic structure, leaving behind a porous green body that retains the shape of the printed object. Subsequently, the sintering process takes place. Sintering involves heating the green body to high temperatures, allowing the ceramic particles to fuse together, eliminating porosity, and resulting in a dense, solid ceramic component.

The challenge lies in the careful balance between binder removal and sintering. While the binder aids in printing and handling, it must be effectively eliminated to avoid defects in the final ceramic structure. Simultaneously, the sintering process must be precisely controlled to achieve the desired densification and mechanical properties.

2. EXPERIMENTAL PART

2.1 Material

Inmaflow K2012 (**YPSZF** = yttria partially stabilized zirconia feedstock) in the form of ceramic granules from Inmatec Technologies GmbH was used for the laboratory preparation of filament. For comparison, commercial ceramic filament for 3D printing Zetamix Zirconia (**ZZF** = Zetamix Zirconia filament) from Nanoe (FR) was analyzed. Their properties are in **Table 1**. Both materials contain a binder system which can be partially removed using an organic solvent (acetone). Both products are manufactured from yttria-stabilized zirconia supplied by Tosoh Corporation (JPN) and contain approximately 14 % of binder. However, they are intended for different applications - ZZF is intended for 3D printing, while YPSZF is intended for CIM (ceramic injection molding process). In addition, ZZF has a limited period of use. The spools are delivered vacuum-packed, after opening they must be stored in a cool place. It gradually becomes fragile and unusable for printing.

Table 1 The composition and recommended processing temperatures of Inmaflow ceramic feedstock K2012 and Zetamix Zirconia ceramic filament [9,10]

Material	Chemical composition	Binder content	Printing or injection molding temperature	Thermal debinding temperature	Sintering temperature	Density of sintered ceramics
Inmaflow K2012 (YPSZF)	$ZrO_2{\cdot}Y_2O_3$	14.5 %	110 - 150 °C	< 325 °C	1400 - 1500 °C	$6.05\ g{\cdot}cm^{-3}$
Zetamix Zirconia (ZZF)	$ZrO_2{\cdot}Y_2O_3$	14 wt.%	180 °C	< 500 °C	1475 °C	$3.5\ g{\cdot}cm^{-3}$

2.2 Laboratory filament production

Composite ceramic filament was produced from feedstock using the Filafab PRO 350 Ex (GB) extruder. The material in the form of granules was transported through a hopper into the working chamber of the extruder, where it was heated (about 120 °C) and continuously extruded through a nozzle, which is calibrated to a size of 1.75 mm, using a screw device. This size is standard for all 3D printers that use the FDM method. The extruded material in the form of an endless filament was immediately wound onto a spool, whose peripheral speed on the wound diameter was synchronized with the speed at which the material was extruded from the nozzle (25 rpm).

2.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) offers insights into the thermal degradation of the polymer matrix. TGA monitors changes in sample weight depending on temperature or time. The sample is placed on a special device holder and exposed to heating in a controlled environment. During heating, thermal reactions such as evaporation, decomposition or oxidation occur. TGA monitors the mass of the sample and records its changes as a function of temperature. The resulting thermogram (graph showing mass changes of the sample as a function of temperature or time) provides information such as the temperature of the beginning and end of the thermal reactions and the weight loss of the sample. TGA was performed on the Inmaflow K2012 feedstock and Zetamix Zirconia filament using a TGA Q500 V20.13 thermogravimetric analyzer (TA Instruments, USA). The analysis was carried out in synthetic air (20 % oxygen, 80 % nitrogen) at a temperature of 25 to 650 °C, with a temperature increase of $10\ °C{\cdot}min^{-1}$.

2.4 SEM analysis

Commercial and laboratory-prepared filaments, as well as ceramic particles contained in feedstock granules and in commercial filaments, were optically analyzed using a scanning electron microscope UHR SEM Ultra Plus, Carl Zeiss (DE). The ceramic particles were obtained from YPSZF and ZZF through the chemical debinding process recommended by the manufacturers to remove the binder, in an acetone bath of several hours.

3. RESULTS AND DISCUSSION

3.1 Density of filaments

The density of both filaments was determined by simple measurement and weighing. Our laboratory-made filament from feedstock had a density of $3.4\ g{\cdot}cm^3$, the density of the commercial ZZF filament was $3.2\ g{\cdot}cm^3$. This is a promising result considering the subsequent printing and post-processes where the binder will be removed from the printed objects, if already at this stage the density of our filament is slightly higher than the density of commercial filament.

3.2 Thermogravimetric analysis (TGA)

TGA results are shown in **Figure 1** and **Figure 2**.

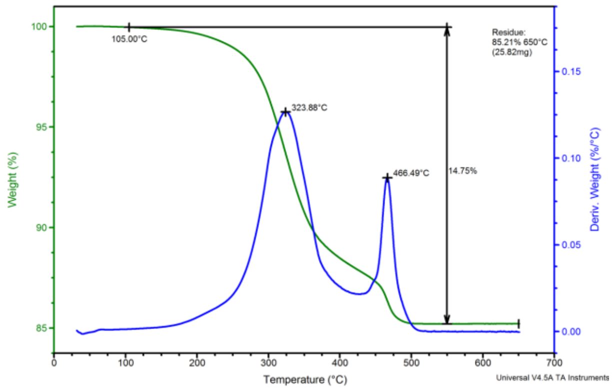

Figure 1 TGA of Inmaflow K2012 feedstock and Zetamix Zirconia filament

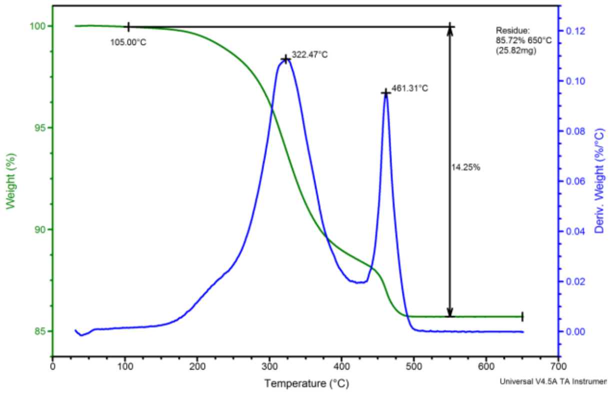

Figure 2 TGA of Zetamix Zirconia filament

TGA confirmed that both studied materials contain the similar amount of binder, which was around 14.75 % for YPSZF and 14.25 % for ZZF. The binder in the feedstock is based on polyamide, the binder in the filament is based on polyolefins. According to thermograms, their properties differ only very slightly. The two maximum peaks on the curve corresponding to the derivative of the thermogravimetric curve appear in very close temperature values for both materials, namely 324 (respectively 322.5) °C and 466.5 (respectively 461) °C. However, it can be seen that the binder in the filament is a little more volatile and its thermal degradation and combustion took place more quickly. But in the end, the total weight loss of both samples was very similar. E.g., at a temperature of 323 °C the weight loss of YPSZF was around 3.5 % and a weight loss of ZZF was around 3.8 %.

3.3 Optical analysis (SEM)

Zirconia ceramic particles were leached from YPSZF and ZZF using acetone to partially remove the binder system. These particles were analyzed by electron microscopy (**Figures 3 and 4**). Images are taken at the same magnification (25,000x). The size, shape and arrangement of zirconium ceramic particles of both materials are practically the same. The size of the particles was around 100 nm and they formed clusters of different sizes, most often with a width of 0.6 μm.

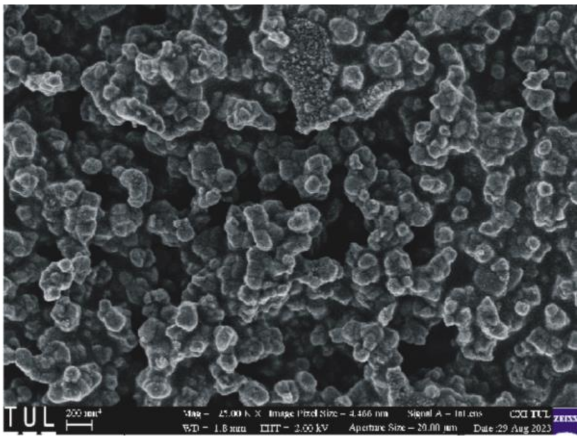

Figure 3 Zirconia ceramic particles leached with acetone from Inmafeed K2012 feedstock.

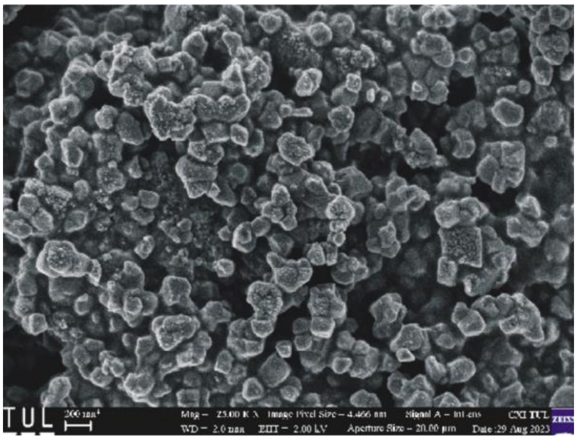

Figure 4 Zirconia ceramic particles leached with acetone from Zetamix Zirconia filament.

Other images were taken with an electron microscope from the fracture cross-section of both filaments, i.e., from the filament produced in the laboratory by extrusion of YPSZF (**Figure 5**) and from ZZF (**Figure 6**). In these images, which were taken at the same magnification (5,000x), the difference in the internal structure of the filaments is already visible. The homogeneous, compact structure of the laboratory extruded filament contrasts with the disordered structure of the commercial filament, in which there are many vacancies and inhomogeneities.

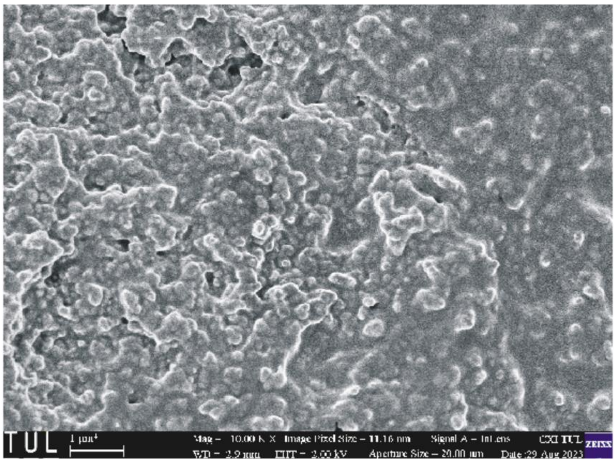

Figure 5 Cross-sectional structure of filament prepared by laboratory extrusion from Inmaflow K2012 feedstock.

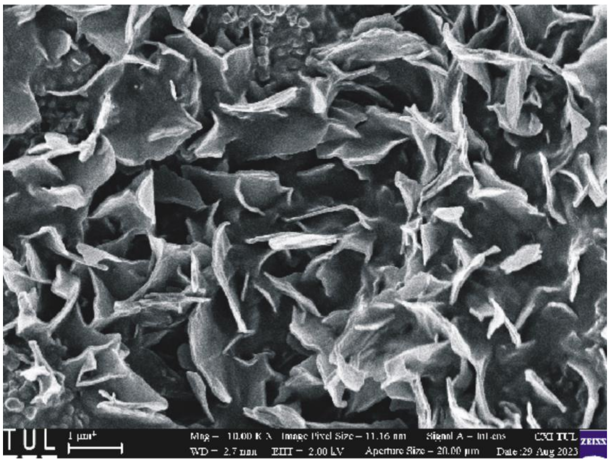

Figure 6 Cross-sectional structure of Zetamix Zirconia filament

4. CONCLUSION

Our goal is the preparation of 3D printed technical ceramics, the strength of which would be comparable to technical ceramics produced by classical methods such as powder pressing or injection molding. We believe this could be achieved with the use of filament for 3D printing with a lower proportion of binder or with the use of more compact filament. Both tested filaments contained approximately 14.5 wt. % of binder and zirconium particles of around 100 nm size forming clusters. However, they differed fundamentally in the morphology of the fracture cross section and in the value of density (before debinding and sintering). Verification of the printability and strength characteristics of both materials will be the subject of our further research.

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