Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 29 (2009) 403–409
www.elsevier.com/locate/jeurceramsoc

Development of high solid content aqueous 3Y-TZP suspensions for direct inkjet printing using a thermal inkjet printer

E. Özkol *, J. Ebert, K. Uibel, A.M. Wätjen, R. Telle

Department of Ceramics and Refractory Materials, RWTH Aachen University, Mauerstrasse 5, D-52064, Aachen, Germany

Received 14 May 2008; received in revised form 20 June 2008; accepted 23 June 2008
Available online 13 August 2008

Abstract

An aqueous 3Y-TZP suspension with 24.2 vol.% solid content was developed for "Direct Inkjet Printing" (DIP). The printing unit was a common HP-DeskJet printer. The suspension was adjusted in terms of particle size, viscosity, and pH-value, so that it became compatible with the printing system. Therefore, suspensions of various compositions were prepared and printed two-dimensionally to analyze the influence of several organic additives on printability. The printouts were evaluated and typical printing errors were classified. The composition of the suspension was optimized and successive and error free single layers of 3Y-TZP were printed. The suspension was examined and characterized in terms of particle size and distribution, composition, viscosity, surface tension, pH-value, vapour pressure, and the *Ohnesorge* number. A printed 3Y-TZP layer of 12 μm thickness was sintered to full density.

Keywords: Shaping; Suspensions; Direct inkjet printing; ZrO_2

1. Introduction

Generation of individually shaped ceramic components is of crucial importance for structural, functional, and biomedical ceramics. In the recent years solid free-forming of ceramics has been a subject of intensive research. Several fabrication methods were developed,[1–3] including methods using colloidal building modules, which are classified as direct ink writing (DIW) techniques.[4] Direct inkjet printing (DIP) is categorized in DIW techniques. DIP is briefly described as the generation of 3D structures by the layer-wise deposition of drops of suspension using a printing device. The advantages of this technology are the high density of green compacts and sintered components, generation of parts revealing final properties with relatively high production rates (rapid manufacturing), high planar (resolution of the printer) and lateral (solid content of each deposit) precision of components, generation of any design including cavities,[5] and a controllable composition of the component[6] (functionally graded materials).

In previous studies on DIP of ceramics, continuous[7] and drop-on-demand (DOD) printers were used. Piezoelectric and thermal (bubble-jet) printers are the two main classes of commercial DOD printers. These differ in droplet ejection mechanism, which functions either by a displacement of a piezoelectric diaphragm or by a volume expansion through thermally generated vapour bubbles. Therefore, bubble formability and the boiling temperature of the ink are main factors in thermal inkjet printing.

Ceramic structures were printed with an aqueous 10 vol.% 3Y-TZP suspension using a thermal printer.[8] A high resolution was not possible because of the low drying rate of the deposits with low solid content. In order to assist the drying a higher solid content or an external drying device would be helpful to realize a higher resolution and faster production rates.

Piezoelectric printers were also used to print aqueous and organic media-based suspensions.[9–16] The maximum solid content was reported for an alcohol based 14 vol.% ZrO_2 suspension.[10,11] Micrometer-sized ceramic pillars and thin walls were printed, which have a ceramic content of 63 vol.% after evaporation of the volatile fraction. In order to assist the drying of deposited layers a hot air blower was mounted. Neither a uniform height nor a considerably good resolution was achieved because of non-uniform drying of the printed

* Corresponding author at: Department of Ceramics and Refractory Materials, RWTH Aachen University, Mauerstrasse 5, D-52064 Aachen, Germany.
Tel.: +49 241 8094901; fax: +49 241 8092226.
E-mail address: oezkol@ghi.rwth-aachen.de (E. Özkol).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.06.020

structures and different printing behaviour in *x*- and *y*-axis. The structures were sintered to almost full density.

Alternatively, ceramic particles were dispersed in wax media and the dispersion was printed at 110–120 °C using a heated piezoelectric printhead.[12] A maximum solid content of 40 vol.% was reported for an Al_2O_3 suspension. Three-dimensional structures were printed but no information about sintering and microstructure was given. Although this technique is classified under DIP technology, a DIP-specific high resolution and high final density was not likely to be achieved.

In the previously published studies, fluid dynamics of droplet formation was investigated[4,12] and described by the *Ohnesorge* number given by

$$Z = \frac{(We)^{1/2}}{Re} = \frac{\eta}{(\gamma \rho a)^{1/2}} \tag{1}$$

where *We* is the Weber number, *Re* is the Reynolds number, η is the viscosity, γ is the surface tension, ρ is the density, and a is a characteristic length, respectively.

According to these experiences it is quite obvious that development of a perfectly printable ceramic suspension is the first step to produce components with high resolution and full density with DIP using thermal inkjet printers. The ink must be entirely compatible with the printing unit. This is in particular important when aqueous suspensions are used. Addition of organic non-polymeric molecules adjusts the vapour pressure and boiling temperature of the suspension according to *Raoult's law* (Eq. (2)), so that a continuous and defect-free printing is possible. An unsuitable vapour pressure of the ink causes a sudden and undesired bubble formation, which results in clogging in the nozzles due to particle agglomeration followed by an overheating of the printhead and an error message to the controller. The high solid content of the ink should enable a uniform drying and a high resolution of the printed structure. The volatile fraction of an aqueous suspension could be evaporated during printing, which would ensure a green body with less organic and high ceramic content.

In this study, a 3Y-TZP ink meeting all these requirements was developed and characterized, which was an inevitable step for the DIP technology as a rapid manufacturing method.

2. Experimental procedure

2.1. Printing unit

A HP DeskJet 850c® was used as the printing unit. The printhead cleaning device was replaced by a humid sponge. The print orders were sent using the driver software of HP DeskJet 930c® in form of MS Word® files.

The black ink cartridge (HP 51645a) was utilized for printing experiments of ceramic suspensions. The printhead of the cartridge possesses 300 nozzles each of ∼30 μm diameter, corresponding to a resolution of 600 dpi. Fig. 1 shows a SEM image of the printhead. The nozzle plate was partially torn away for better observation and understanding of the printing mechanism. On the right hand side, resistor elements are visible in the chambers below the nozzle plate, each being associated with an individual nozzle placed in front of the nozzle plate, which is now partially removed. Two nozzles on the nozzle plate are seen on the left. Each resistor element is supplied with ink from the feedstock through a channel. The feedstock is separated from the main ink reservoir by a metallic filter of about 20 μm mesh size. Resistor elements are controlled by a microprocessor and connected via conductive lines. In operation, signals agitate one or more elements to heat up and to create a bubble of ink-steam in the target chamber so that a droplet is expelled through the nozzle toward the print medium. Printing of any characters or shapes is explained by heating a set of resistor elements in a particular order.[17]

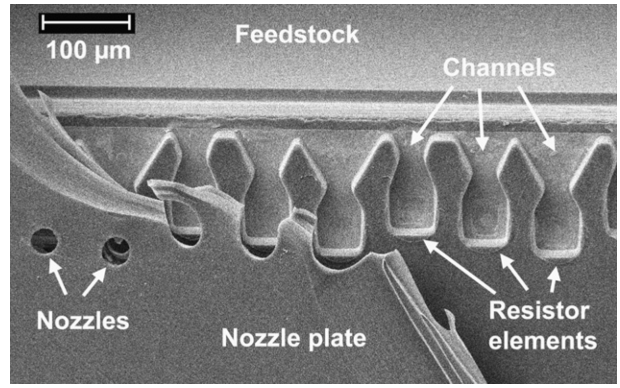

Fig. 1. SEM image of a thermal printhead (HP 51645a).

Commercially available black ink cartridges were used. Original ink was filled and printed to ensure that none of the nozzles was defective. The perfectly operating cartridges were emptied and flushed with a mixture of ethanol and water and placed in an ultrasonic cleaner until no residue of black ink was detected in the nozzle region.

2.2. Materials and preparation of suspensions

A pure ZrO_2 powder (Zirconium Oxide UPH, Framatome ANP Cezus, France) and a 3Y-TZP powder (Z-3YS-E, Tosoh Corp., Japan) were dispersed and attrition milled in aqueous media using ZrO_2 milling beads ($\phi = 1$ mm). The particle size and distribution was measured by laser-scattering (Mastersizer 2000, Malvern Instruments, UK). The pure ZrO_2 powder has an initial ultimate particle size (d_{90}) of 2.75 μm prior to attrition milling, while the primary crystallite size of the 3Y-TZP powder was in the range of 30–100 nm (Fig. 2) as proven by transmission electron microscopy (Philips CM 30, Eindhoven, The Netherlands).

Suspensions with high solid contents and viscosity levels <20 mPas were stabilized using Dispex N40 (Cievag AG, Germany) for pure ZrO_2 and Dolapix CE64 and PC75 (Z&S, Lahnstein, Germany) for 3Y-TZP. Several organic additives (Table 1), which are all miscible with water, were added to the suspensions to optimize the printability. The additives are commercial humectants to prevent drying and clogging, which were chosen according to the material safety data sheets of several commercial inks such as HP C3825A, C6656A,