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

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## 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.

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# 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,<sup>1-3</sup> including methods using colloidal building modules, which are classified as direct ink writing (DIW) techniques.<sup>4</sup> 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,<sup>5</sup> and a controllable composition of the component<sup>6</sup> (functionally graded materials).

In previous studies on DIP of ceramics, continuous<sup>7</sup> and dropon-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.<sup>8</sup> 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.<sup>9–16</sup> The maximum solid content was reported for an alcohol based  $14 \text{ vol.\% ZrO}_2$  suspension.<sup>10,11</sup> 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

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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  $^{\circ}$ C using a heated piezoelectric printhead.<sup>12</sup> A maximum solid content of 40 vol.% was reported for an Al<sub>2</sub>O<sub>3</sub> 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<sup>4,12</sup> and described by the *Ohnesorge* number given by

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

where *We* is the Weber number, *Re* is the Reynolds number,  $\eta$  is the viscosity,  $\gamma$  is the surface tension,  $\rho$  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  $850c^{\text{(B)}}$  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  $930c^{\text{(B)}}$  in form of MS Word<sup>(B)</sup> 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  $\sim$ 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



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

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  $\mu$ m 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.<sup>17</sup>

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<sub>2</sub> 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,

 Table 1

 List of materials, materials' properties, and suppliers

| @ 20 °C                          | g/cm <sup>3</sup> | g/mole | kPa     |                            |
|----------------------------------|-------------------|--------|---------|----------------------------|
| 1,1,1-Tris(hydroxymethyl)propane | _                 | 134.17 | <0.13   | Fluka Chemie GmbH, Germany |
| 1,6-Hexanediol                   | 1.12              | 118.18 | 0.001   | Merck KgaA, Germany        |
| 2-Pyrrolidone                    | 1.11              | 85.11  | 0.004   | Merck KgaA, Germany        |
| C-Caprolactam                    | 1.01              | 113.16 | 0.00014 | Merck KgaA, Germany        |
| Ethanol                          | 0.79              | 46.07  | 5.9     | Merck KgaA, Germany        |
| Ethylene glycol                  | 1.11              | 62.07  | 0.0053  | Merck KgaA, Germany        |
| Urea                             | 1.34              | 60.06  | <0.01   | Merck KgaA, Germany        |

51645A, 51645G, and C6119A. Solid additives were dissolved in water prior to mixing with the suspensions. Liquid additives were added directly. The mixtures were homogenized using a dispersing tool (S25N-25F, IKA-Werke, Staufen, Germany). Addition of additives affects the vapour pressure of the suspension. Polymeric additives act according to *Flory–Huggins model*<sup>18</sup> depending on the concentration in the solution and non-polymeric additives obey *Raoult's law* (Eq. (2)). Only the dispersants were polymeric additives and these were added in low concentration levels (<30 wt.%) so that *Raoult's law* was valid.<sup>19</sup> Thus, the total vapour pressure values of the liquid phase of the suspensions were calculated according to *Raoult's law*, which is given by

$$P_{\text{solution}} = (P_1)_{\text{pure}} x_1 + (P_2)_{\text{pure}} x_2 + \cdots$$
(2)

 $P_{\text{solution}}$  is the total vapour pressure of the solution,  $(P_i)_{\text{pure}}$  is the vapour pressure of the pure component, and  $x_i$  is the mole fraction of the component, respectively. The total vapour pressure of the liquid phase of each prepared suspension was calculated (Tables 2 and 3). The total vapour pressure of the HP 51645A ink was also calculated to set a target value. The vapour pressure of used dispersants and "trade secret organic materials" in the ink were approximated.

A set of suspensions of pure  $ZrO_2$  with 45 wt.% (12.3 vol.%) solid content, 2 wt.% (related to solids) Dispex N40 content, and varying ethylene glycol content (up to 15 wt.%) were prepared. Ethylene glycol was chosen randomly to be tested



Fig. 2. TEM image of 3Y-TZP powder (as received).

| 1 | a | bl | e | 2 |  |
|---|---|----|---|---|--|
|   |   |    |   |   |  |

| apour pressure values (Kr a) of the +5 wt. 70 pure $2102$ suspensite | Sour pressure values (kPa) of the 45 wt.% pure $ZrO_2$ su | spensio |
|--|---|---------|
|--|---|---------|

| Sample    | Additive I (wt.%)    | Additive II (wt.%) | kPa                  |
|-----------|----------------------|--------------------|----------------------|
| PZAI-1    | -                    | -                  | 2.4                  |
| PZAI-2    | 5 Ethylene glycol    | -                  | 2.2                  |
| PZAI-3    | 7.5 Ethylene glycol  | -                  | 2.1                  |
| PZAI-4    | 10 Ethylene glycol   | -                  | 2                    |
| PZAI-5    | 12.5 Ethylene glycol | -                  | 1.9                  |
| PZAI-6    | 15 Ethylene glycol   | -                  | 1.8                  |
| PZAIAII-1 | 10 Ethylene glycol   | -                  | 2                    |
| PZAIAII-2 | 10 Ethylene glycol   | 2.5 Ethanol        | 2.2                  |
| PZAIAII-3 | 10 Ethylene glycol   | 5 Ethanol          | 2.4                  |
| PZAIAII-4 | 10 Ethylene glycol   | 7.5 Ethanol        | 2.6                  |
| PZAIAII-5 | 10 Ethylene glycol   | 10 Ethanol         | 2.8                  |
| PZAIAII-6 | 10 Ethylene glycol   | 15 Ethanol         | 3.1                  |
| PZAIAII-7 | 10 Ethylene glycol   | 20 Ethanol         | 3.5                  |
| PZAIAII-8 | 10 Ethylene glycol   | 25 Ethanol         | 3.9                  |
| HP51645A  | -                    | -                  | 2.3–2.4 <sup>a</sup> |

<sup>a</sup> For ethylene glycol and Dolapix CE64 as "trade secret organic materials" of the ink.

first. These suspensions were printed two-dimensionally and the printouts were evaluated digitally to determine the optimum amount of jetting additive. After decision of an optimum amount of jetting additive the effects of ethanol on printing were analyzed. Therefore a further set of suspensions with the same solid and dispersant content, 10 wt.% ethylene glycol,

Table 3

| /apour pressu | re values | (kPa) | of 65 wt.6 | % 3Y-TZP | suspensions |
|---------------|-----------|-------|------------|----------|-------------|
|---------------|-----------|-------|------------|----------|-------------|

| Sample   | 10 wt.% Additive I               | 1 wt.%       | kPa                  |
|----------|----------------------------------|--------------|----------------------|
| TZPAIC-1 | 1,1,1-Tris(hydroxymethyl)propane | Dolapix CE64 | 2.3                  |
| TZPAIC-2 | Ethylene glycol                  | Dolapix CE64 | 2.2                  |
| TZPAIC-3 | Urea                             | Dolapix CE64 | 2.1                  |
| TZPAIC-4 | 2-Pyrrolidone                    | Dolapix CE64 | 2.2                  |
| TZPAIC-5 | E-Caprolactam                    | Dolapix CE64 | 2.3                  |
| TZPAIC-6 | 1,6-Hexanediol                   | Dolapix CE64 | 2.3                  |
| TZPAIP-1 | 1,1,1-Tris(hydroxymethyl)propane | Dolapix PC75 | 2.3                  |
| TZPAIP-2 | Ethylene glycol                  | Dolapix PC75 | 2.2                  |
| TZPAIP-3 | Urea                             | Dolapix PC75 | 2.1                  |
| TZPAIP-4 | 2-Pyrrolidone                    | Dolapix PC75 | 2.2                  |
| TZPAIP-5 | E-Caprolactam                    | Dolapix PC75 | 2.3                  |
| TZPAIP-6 | 1,6-Hexanediol                   | Dolapix PC75 | 2.3                  |
| HP51645A | _                                | -            | 2.3–2.4 <sup>a</sup> |

<sup>a</sup> For ethylene glycol and Dolapix CE64 as "trade secret organic materials" of the ink.



Fig. 3. Printing errors: (a) Malfunctioning nozzles due to clogging, (b) inhomogeneous printing of groups of nozzles, (c) unclear printing, (d) improper printing at the beginning of the printing process and (e) unprinted regions due suspension dewetting of the nozzles.

and varying ethanol content (up to 25 wt.%) were prepared and tested two-dimensionally.

Two sets of suspensions of 3Y-TZP with 65 wt.% (24.2 vol.%) solid content, 10 wt.% of various jetting-additives (Table 1), and 1 wt.% (related to solids) of two dispersants were prepared, first set with Dolapix CE64 and second with Dolapix PC75, respectively. The suspensions were printed two-dimensionally as well and the printouts were evaluated optically and digitally.

#### 2.3. Two-dimensional printing experiments

The suspensions were filled into monochrome cartridges and were printed on black-coloured paper. The printed area appeared white since the unprinted area was left black and consequently the clogged or malfunctioning nozzles were detected. Nine of such printed white squares on black paper are shown in Fig. 3.

The course of a two-dimensional printing experiment is as follows. An MS Word<sup>®</sup> file consisting of 10 black squares each of 12.4 mm  $\times$  12.4 mm, which are placed in a single row, was printed successively 30 times. An edge length of 12.4 mm was chosen on purpose, because this length covers all nozzles on the printhead. Moreover, this is the largest value, which can be printed in a single pass of the cartridge. One experiment for a single suspension took 30 min. Though a single row of squares was printed in a few seconds the cartridge waited in idle state for almost 1 min until the next row on the next page was printed. This was a realistic test to ensure a continuous and stable printing of the tested suspension over 30 min.

The black pages with printed white squares were scanned and saved as greyscale images. Each printed block on each page was analyzed separately using a graphics editor (Adobe<sup>®</sup> Photoshop<sup>®</sup> 6.0). The "mosaic" tool of the software was used to



Fig. 4. Influence of additives on the viscosity of suspensions with Dolapix CE64.

transform the white square with black lines into a square with one colour representing the whole. Using the "pixalate" option of the software the representing greyscale level, the so-called *K*value, was measured, which is the percentage of the colour black in the printed square. The *K*-value is 0 for pure white and 100 for pure black. The colour black indicates the unprinted fraction of the square, which is representing the number of not printing nozzles.

The goal was to print perfectly and homogeneously filled white squares with high resolution on all 30 pages, which means a *K*-value of 0 on all 30 pages. Only in case of printing without any malfunctioning nozzles, it would be possible to produce ceramic parts of high resolution by printing perfect layers on top of each other.

### 2.4. Characterization of printable suspensions

All the suspensions prepared were printed two-dimensionally and printability of each suspension was evaluated individually as explained above. Additionally, particle size and distribution, viscosity, pH-value, and total vapour pressure were determined for all suspensions, in order to compare them with each other and to investigate the effects of these parameters on printing using a thermal printer.

The viscosity measurements (Figs. 4–7) were conducted using a rotational rheometer (Viscolab LC 10, Physica, Stuttgart,



Fig. 5. Influence of additives on the viscosity of suspensions with Dolapix PC75.



Fig. 6. Temperature influence on the viscosity of suspensions with Dolapix CE64.

Germany) with a double gap concentric measuring system in order to determine the viscosity at higher shear rates. Also a circulating water bath (Julabo F25, Seelbach, Germany) was used to measure the viscosity in a temperature interval of 20-65 °C. In this manner, the printing conditions in the nozzle were simulated. The viscosity of the original HP 51645A ink was measured as well. The pH-values of the suspensions were determined using a pH-electrode (InLab 417, Mettler Toledo, Gießen, Germany). The total vapour pressure of each prepared suspension was calculated using Raoult's law (Eq. (2)) and the values are listed in Tables 2 and 3.

Moreover, the finally optimised 3Y-TZP suspension was characterized in terms of surface tension and the *Ohnesorge* number (*Z*). The surface tension was determined according to the drop shape method using a video contact-angle measurement device (DAS 10, Krüss GmbH, Hamburg, Germany).

#### 2.5. Production of a thin 3Y-TZP layer

Using the finally optimised suspension, which was perfectly printable over 30 pages, a thin layer of 3Y-TZP was printed. A graphite substrate was placed on the printing path and three squares were printed on top of each other. The resulting layer was dried at room temperature and placed in a drying chamber



Fig. 7. Temperature influence on the viscosity of suspensions with Dolapix PC75.

at 100 °C for 6 h. The substrate was separated from the layer at 850 °C and the 3Y-TZP layer was subsequently sintered 2.5 h at 1450 °C.

## 3. Results and discussion

Attrition milling resulted in a  $d_{90}$  value of 0.574 µm for the pure ZrO<sub>2</sub> suspension and a  $d_{90}$  value of 0.683 µm for the 3Y-TZP suspension. The large particle size of 3Y-TZP shows that the particles exist in form of agglomerates rather than individual crystallites (Fig. 2) in the suspension.

A solid content of 70 wt.% (28 vol.%) pure ZrO2 was achieved using 2 wt.% (related to solid content) of Dispex N40 for low viscosity suspensions. The use of 1 wt.% of either Dolapix CE64 or Dolapix PC75 provided a solid content of 75 wt.% (33 vol.%) 3Y-TZP for low viscosity suspensions. The influences of various additives to the viscosity of the 3Y-TZP suspensions (Table 2) with Dolapix CE64 and Dolapix PC75 are shown in Figs. 4 and 5, respectively. The measurements were conducted at a constant shear rate of  $1000 \,\mathrm{s}^{-1}$ . The viscosities of suspensions with various additives vary from 6 to 10 mPas but are constant for long time. The viscosity of the original HP 51645A ink was measured as 5 mPas. A slightly lower viscosity level was achieved either by using Dolapix PC75 or solid additives. The viscosity behaviour for both suspensions at increasing temperatures containing Dolapix CE64 and PC75 are shown in Figs. 6 and 7, respectively. The shear rate was  $1000 \,\mathrm{s}^{-1}$  during the measurements. The viscosity values of all suspensions decrease with increasing temperature. At 65 °C the viscosity margins of suspensions gets narrower and the values range between 3 and 5 mPas. The viscosity of the original HP 51645A ink is with 2 mPas at 65 °C and is lower than all ceramic-based suspensions.

The pH-values of all suspensions (Tables 2 and 3) were in the region of 9.5–10. Addition of the organic molecules shifted the pH-values to 8–8.5, which is similar to the pH-value of 7.8–8.4 of the HP 51645A ink. The suspensions including additives were all stable in this pH-range and no deviation from the viscosity level was detected.

The two-dimensional printing experiment was the main tool to analyze and evaluate the printability of suspensions of various compositions. Five major types of printing-errors (Fig. 3) were observed during the evaluation of the printouts. The most common problem was unprinted lines (Fig. 3a), which were caused by malfunctioning nozzles. The nozzles were clogged, when the suspension was dried in the nozzles and blocked the orifices. This error was always observed in case of printing suspensions containing either an additive content <10 wt.% or an ethanol content >7.5 wt.%. The next error was an irregular printing behaviour of a certain group of nozzles (Fig. 3b). This was detected to be a printhead dependent problem, which only occurred in case of a few printheads. An unclear printing behaviour (Fig. 3c) was observed when the suspension was totally incompatible with the printing unit. This was observed only in case of printing the suspensions TZPAIP-3 and TZPAIP-5 (Table 3), which shows that this problem was definitely suspension dependent. When these two additives were added to a suspension including Dolapix CE64 instead of PC75 such an error was not observed. The first square in each line was printed improperly independent of suspension or printhead (Fig. 3d). Three printed squares are shown in Fig. 3d. The improper printed one on left was printed at the beginning of the line. This kind of a printing delay existed at the start of each printing-cycle, which disappeared at the second square of each line completely. Another printing error was exactly the opposite of improper printing of the first square. In this case there was not enough suspension left in the printhead to print full squares. The last squares in the line were not printed completely (Fig. 3e). The unprinted area always started from the middle of the square and increased in size in the following squares of the line. This occurred in case of printing suspensions containing 2-pyrrolidone (TZPAIC-4 and TZPAIP-4) or an ethanol content <7.5 wt.% (PZAIAII-2, 3, and 4), only when the pressure difference between the printhead and the surrounding was too high. This problem was solved by decreasing the pressure difference of the cartridge.

Two-dimensional printing experiments of the pure  $ZrO_2$  suspensions (Table 2) with varying additive content showed that the optimum content is 10–12.5 wt.%. This additive content prevents drying and clogging of nozzles and favours the printability. The *K*-value was below 10 in this range of additive content on all 30 pages. In the next step the effect of ethanol (as a surface tension decreasing agent) on the printability was investigated. Suspensions with constant additive and solid contents and varying ethanol content (Table 2) were printed two-dimensionally. An extreme clogging of the nozzles was observed when suspensions with ethanol content >7.5 wt.% were printed. Ethanol content <7.5 wt.% also did not favour the printing behaviour at all.

The result of two-dimensional printing experiments of 3Y-TZP suspensions showed that the printouts of the suspensions TZPAIC-1, 3, and 6 and TZPAIP-2 and 4 had a *K*-value below 10 for all 30 pages. The suspension TZPAIC-2 containing 65 wt.% (24 vol.%) 3Y-TZP, 1 wt.% Dolapix CE64, and 10 wt.% ethylene glycol had a *K*-value of 0 for all 30 pages, meaning that a stable and perfect printing of this suspension was possible.

The surface tension of the final suspension was 42 mN/m, which is close to the surface tension of the HP 51645A ink. The *Ohnesorge* number of the final suspension was calculated as 0.19, for a viscosity of 10 mPas, a surface tension of 42 mN/m, a density of  $2.15 \text{ g/cm}^3$ , and a characteristic length of 30  $\mu$ m (diameter of a nozzle orifice). This value is in the range of 0.1–1, which is needed for a successful droplet formation.<sup>4</sup>

The calculated total vapour pressure values for all suspensions are given in Tables 2 and 3. The total vapour pressure of the HP 51645A ink was calculated to be in the range of 2.3–2.4 kPa. This calculation assumes that the secret 10 wt.% additive of HP 51645A ink has a vapour pressure value between that of ethylene glycol and Dolapix CE64. An additional approximation error of 10% would set this range to 2.1–2.6 kPa. According to this calculation no drying and clogging in the nozzles could be observed in case of printing any suspension having a total vapour pressure <2.6 kPa. The results of the 2d-printing experiments for pure ZrO<sub>2</sub> suspensions (Table 2) show that the suspensions with optimum additive amount have a total vapour pressure <2.6 kPa.



Fig. 8. SEM image of a fracture surface of the sintered 3Y-TZP part.



Fig. 9. SEM image of the surface of the sintered 3Y-TZP part.

The suspensions containing ethanol, which caused an extreme clogging in the nozzles, had a total vapour pressure >2.6 kPa. According to these results, there exists a relation between the printability and the total vapour pressure of the suspensions. On the other hand, all 3Y-TZP suspensions had vapour pressure values <2.6 kPa but different levels of printability. Although there is an obvious relation between printability and the vapour pressure of the ink, this information is not enough to distinguish the fine differences in the printability.

To ensure a transition from two-dimensional experiments to DIP with the developed suspension, a simple ceramic 3Dstructure was printed. This structure was built by printing three layers on top of each other. A SEM-image of the fracture surface of the sintered part is shown in Fig. 8. The thickness of the part is uniform and about 12  $\mu$ m. There are no process related defects in the microstructure and the part reveals an almost full density. The surface of the sintered part is shown in Fig. 9. The average grain size is well below 1  $\mu$ m and the surface is also free of defects.

## 4. Conclusions

Aqueous pure ZrO<sub>2</sub> and 3Y-TZP suspensions satisfying all physical requirements and printability constraints for DIP were

prepared. The ultimate particle size of the suspension was below 1 µm and the viscosity, pH-value, as well as surface tension of the suspensions were compatible with the printing unit, which was verified by the Ohnesorge number fitting well into the range required. Two-dimensional printing experiments were conducted to analyze the effects of various organic molecules on printability. The total vapour pressure values for the liquid phase of the suspensions were calculated according to Raoult's law. It was shown that suspensions having total vapour pressure values lower than 2.6 kPa were basically printable. Finally an aqueous 3Y-TZP suspension of 24.2 vol.% solid content was developed, which was printed two-dimensionally on 30 successive pages without any disturbances. A 3Y-TZP layer was printed three-dimensionally and sintered to full density, which proved that it was possible to produce ceramic parts using the experimental setup and the developed final suspension with the DIP manufacturing technique.

#### References

- Chartier, T., Chaput, C., Doreau, F. and Luiseau, M., Stereolithography of structural complex ceramic parts. *J. Mater. Sci.*, 2002, 37, 3141–3147.
- Günster, J., Gahler, A. and Heinrich, J. G., Rapid prototyping of ceramic components. *CFI Ceram. Forum Int.*, 2006, 13, 53–56.
- Schindler, K. and Roosen, A., Cold low pressure lamination of ceramic green tapes for the manufacture of 3D structures. *CFI Ceram. Forum Int.*, 2006, 13, 27–30.
- Lewis, J. A., Smay, J. E., Stuecker, J. and Cesarano III, J., Direct ink writing of three-dimensional ceramic structures. J. Am. Ceram. Soc., 2006, 89(12), 3599–3609.
- Mott, M., Song, J. H. and Evans, J. R. G., Microengineering of ceramics by direct ink-jet printing. J. Am. Ceram. Soc., 1999, 82(7), 1653–1658.

- Calvert, P. and Crockett, R., Chemical solid free-form fabrication: making shapes without molds. *Chem. Mater.*, 1997, 9, 650–663.
- 7. Blazdell, P., Solid free-forming of ceramics using a continuous jet printer. *J. Mater. Process Technol.*, 2003, **137**, 49–54.
- Slade, C. E. and Evans, J. R. G., Freeforming ceramics using a thermal jet printer. J. Mater. Sci. Lett., 1998, 17, 1669–1671.
- Windle, J. and Derby, B., Ink jet printing of PZT aqueous ceramic suspensions. J. Mater. Sci. Lett., 1999, 18, 87–90.
- Zhao, X., Evans, J. R. G., Edirisinghe, M. J. and Song, J. H., Direct ink-jet printing of vertical walls. J. Am. Ceram. Soc., 2002, 85, 2113–2115.
- Zhao, X., Evans, J. R. G., Edirisinghe, M. J. and Song, J. H., Ink-jet printing of ceramic pillar arrays. J. Mater. Sci., 2002, 37, 1987–1992.
- Seerden, K. A. M., Reis, N., Evans, J. R. G., Grant, P. S., Halloran, J. W. and Derby, B., Ink-jet printing of wax-based alumina suspensions. *J. Am. Ceram. Soc.*, 2001, 84, 2514–2520.
- Mott, M. and Evans, J. R. G., Solid freeforming of SiC by inkjet printing using a polymeric precursor. J. Am. Ceram. Soc., 2001, 84(2), 307– 313.
- Bhatti, A. R., Mott, M., Evans, J. R. G. and Edirisinghe, M. J., PZT pillars for 1–3 composites prepared by ink-jet printing. *J. Mater. Sci. Lett.*, 2001, 20, 1245–1248.
- Zhao, X., Evans, J. R. G., Edirisinghe, M. J. and Song, J. H., Formulation of a ceramic ink for a wide-array drop-on-demand ink-jet printer. *Ceram. Int.*, 2003, 29, 887–892.
- Xiang, Q. F., Evans, J. R. G., Edirisinghe, M. J. and Blazdell, P. F., Solid freeforming of ceramics using a drop-on-demand printer. In *B00896 IMechE 1997 in Proceedings Institution of Mechanical Engineers*, 211, 1997, pp. 211–214 [part B].
- Davis, D. R., Klein, M., De Larra, C. C. M., Mueller, B., Martinez, R. P., Raychoudhury, R., et al., Method for alleviating marangoni flow-induced print defects in ink-jet printing. US Patent 5,695,820, September 12, 1997.
- Fried, J. R., *Polymer Science and Technology*. Prentice Hall, Upper Saddle River, NJ, 2003, pp. 96–102.
- Park, Y. M., Kang, J. O., Yoo, J. and Lee, J. W., Vapor pressure of the 1,1,1,2-tetrafluoroethane (R-134a)+polyalkylene glycol system. *Int. J. Thermophys.*, 2004, 25(6), 1849–1861.