1. Introduction

Ceramic injection molding (CIM) is routinely used to fabricate ceramic parts of all shapes, sizes and ceramic materials [1,2]. During CIM, a ceramic powder plastified by a thermoplastic binder is injected at high pressure into a closed mold. The feedstock cools down and solidifies to give the green body, which is then debound (removal of the binder by solvent and/or thermally) and sintered. Due to its high throughput, CIM is very economical for parts fabricated in large quantities. However, mold making is time consuming and expensive and once the mold is fabricated, changes in the geometry of the molded parts can hardly be incorporated [3]. An example of a simple steel mold is shown in Fig. 1A. 3D printed molds provide a cheap and fast alternative to classical steel molds for prototyping purposes or low volume production [4-8]. The 3D printed mold is typically inserted into a steel adapter piece with cavities on both sides (Fig. 1B). The 3D printing method of choice is usually stereolithography (SLA) or direct light processing (DLP) due to their higher dimensional accuracy and smooth surface of the printed molds in comparison to fused deposition modeling (FDM). 3D printed molds are mostly limited to simple straight-pull molds with two sides as shown in Fig. 1C. Freeform injection molding (FIM) is a novel method to overcome this limitation [9-11]. In FIM, the mold is 3D printed from a soluble resin and is dissolved after injection molding. The usage of sacrificial molds opens up new possibilities for more complex geometry since design restrictions regarding undercuts do not apply. One example of a sacrificial mold is shown in Fig. 1D.

The advantages of 3D printed sacrificial molds over classical hardened steel molds are summarized in Table 1. Most importantly, fabrication of 3D printed sacrificial molds is considerably faster and less expensive. A point that should not be underestimated is that prototyping using 3D printed sacrificial molds is feasible for any small company, laboratory or start-up, since the requirements for heavy machinery and highly specialized operators are lower. It should be mentioned that a detailed cost analysis would be dependent on many factors including cost of the material, cost of the 3D printers, cost of other equipment, cost of energy, cost of labor etc. Every single one of those factors has a huge cost range depending on the geometry, size, quantity and material of the desired part. The same is true for machined molds. In summary, a detailed cost analysis is beyond the scope of this study and just a broad cost range based on our experience is given in Table 1.

In this paper, FIM and CIM are combined to produce high quality ceramic parts with complex geometries that could not be injection molded with any other method. For the first time, sacrificial molds are printed from polyvinylalcohol (PVA) in an FDM printer. FDM printed PVA molds withstand the harsh conditions during injection molding (high pressure and temperature) and yield high quality parts of even...
complex geometries. Parts were molded from commercial Al2O3 feedstock as well as from a composite feedstock developed in our lab containing MoSi2 particles [12]. MoSi2 is an electrically conductive intermetallic material with thermal stability up to 1800 °C and is therefore common in high temperature applications [13,14]. MoSi2 containing samples were tested in glowing experiments to show that they can be used as resistive heating elements.

For comparison to the FDM printed PVA molds, sacrificial molds were also printed from resin by direct light processing (DLP). A resin recipe from literature [15] was adapted to yield water soluble molds with higher resolution than PVA molds printed by FDM. Higher resolution allows the injection molding of parts with finer details, as demonstrated on a screw thread, and smoother surface.

Two component injection molding (2 C-IM) is widely known in thermoplastics industry [16–18]. The method is relatively straightforward for thermoplastics, but poses additional problems in CIM, mainly since the shrinkage behavior of the two materials during sintering has to be matched carefully. Examples of 2 C-CIM are therefore scarce [19–26]. In the last part of the present study, 2 C-CIM using sacrificial 3D printed molds is demonstrated for the first time. The two target parts were a MoSi2 heating element with zones of different electrical conductivity as well as a nonconductive crucible with integrated conductive heating coil.

### 2. Materials and methods

All CAD was done in Fusion 360 software from Autodesk. PVA molds were printed using an Ultimaker 3 FDM printer and PVA filament supplied by Ultimaker. Layer height was set to 0.1 mm and wall thickness to 6 lines. A triangular infill with 50% infill density was used. Otherwise, the standard settings for PVA as recommended by Ultimaker were used.

Sacrificial molds were also printed on an Asiga Max X DLP printer using a resin formulation reported by Liska et al. [15] N, N-Dimethylacrylamide (20 g, 99%, Aldrich), Methacrylic acid (20 g, 99%, abcr) and Methacrylic anhydride (3.5 g, 94%, Sigma-Aldrich) were added to a beaker, Polyvinylpyrrolidone (6.5 g, MW 10′000, Sigma-Aldrich) was added portionwise and the solution was stirred and ultrasonicated until a clear solution was obtained. The solution was filtered before usage in DLP. The following
For Al₂O₃ samples, thermal debinding was done stepwise with holding periods at 400, 450 and 500 °C and sintering at 1650 °C. For MoSi₂ containing parts, thermal debinding was performed in air atmosphere at 500 °C before switching to argon atmosphere while keeping the temperature for one more hour at 500 °C. For sintering, the oven was heated under argon to 1250 °C and kept at this temperature for 5 h. Some MoSi₂ parts were sintered in an Al₂O₃ powder bed to avoid structural deformations during sintering.

For the glow tests, the surface of the contact arms of the sintered samples was ground using a Dremel minidrill tool and subsequently coated with colloidal Silver paste. Current and voltage were controlled by a TDK-Lambda Gen300–11 power source.

SEM imaging was conducted on a Phenom XL Desktop SEM (Thermo Fischer Scientific).

3. Results and discussion

In the design of a sample for FIM, many of the design rules for classical injection molding parts do not apply. Most importantly, undercuts are allowed. This drastically increases design freedom and complex structures such as spirals are moldable without special consideration to avoid undercuts. The sacrificial mold is then designed by constructing a cube or cylinder, which is at least 1 mm bigger than the ceramic sample in all directions, and subtracting the ceramic part from the mold. Gates and vents are added according to the specifications of the injection molding machine used. For the example shown in Fig. 3a double helix with three turnings was designed. The wall thickness in this example is 4 mm. The part was subtracted from a rectangular block with rounded edges and the gate was placed at the top arch of the helix. This block was printed on an Ultimaker 3 from PVA filament. For most PVA molds, infill densities of 100% were used to obtain maximal strength. However, lower infill densities of 50% were also successfully tested, but the wall thickness was set to at least 1 mm. An adapter piece was designed and printed from UV-curable resin on a Prusa SL1.

The parts were injection molded on a BOY XS machine using commercial Al₂O₃ feedstock or MoSi₂/Feldspar/Al₂O₃ composite feedstock developed in our laboratory [12]. Two drawbacks of the method presented herein are the limited injection pressure and temperature. The double helix shown in Fig. 3a was successfully molded using injection pressures of 50–90 bar. With lower pressures, the PVA mold is not filled completely, while higher pressures lead to cracking of the PVA mold. It was found that the injection temperature should be below 150 °C, since
the PVA mold already softens at this temperature. This factor reduces the choice of binder systems for preparation of the feedstock. Nevertheless, all feedstocks based on LDPE, EVA, PEG, and other low melting temperature polymers are still feasible. However, the temperature limitation does not apply to sacrificial molds printed from water soluble resin. Additionally, the feedstock must not take damage in contact with water (swelling etc.), since after injection molding, PVA molds were immersed in a water bath to dissolve the PVA. This process takes from 12 h up to two days, depending on the size and geometry as well as the infill density used to print the PVA mold and on how frequently the water bath is exchanged. Ideally, the water bath also serves to pre-debind the molded parts if the feedstock contains a water-soluble auxiliary binder.

The remaining steps are identical to classical CIM: green body processing, thermal debinding, sintering, and finally testing of the finished part. The advantage of the method presented herein lies in the fact that this “designing – manufacturing – testing” cycle can be repeated very cost and time efficiently.

Fig. 4 shows a collection of green bodies injection molded in PVA molds. CAD drawings of the target parts together with the respective PVA molds (A). Green bodies after injection molding and dissolving the PVA molds (B). Sintered spiral part in glowing test at 460 W power input (C).
undercuts and complex geometries do not increase the cost and time required to fabricate the mold.

More examples of samples with complex geometries are displayed in Fig. 5 (green bodies) and Fig. 6 (sintered samples). Those parts were molded using an Al₂O₃ feedstock. The spinal disk prosthesis (Fig. 5, bottom right) features some bridges as thin as 0.8 mm as well as a pyramidal surface with pyramids of 1.5 mm side length, proving that even delicate structures can be fabricated with PVA molds.

The surface morphology of rod-shaped samples injection molded with a steel mold and a 3D printed PVA mold were compared by SEM (Fig. 7). The fine lines on the PVA mold samples are visible by eye and SEM and originate from the filament 3D printing of the PVA mold. The distance between the lines therefore corresponds to the layer height used for 3D printing which was 0.1 mm in the case of the sample in Fig. 7. If those lines are undesired, the green bodies could be sanded or polished before sintering. No differences are visible between steel mold and PVA
samples in the bulk of the material.

Sacrificial molds for injection molding can also be 3D printed by stereolithography (SLA) or direct light processing (DLP) using a water-soluble resin. For this purpose, a resin recipe reported by Liska et al. was adapted (15). Dimethylacrylamide and methacrylic acid were used as the monomers to ensure fast curing and solubility in water. Polyvinylpyrrolidone was added as a filler and together with the crosslinker methacrylic acid anhydride increased the resolution. The dye Solvent Yellow 93 was found to improve curing times and overall print quality.

The sacrificial molds shown in Fig. 8 were rinsed with acetone after printing to wash away any excess of non-cured resin inside the mold. Injection molding with resin molds is identical to the process described above with PVA molds. The sacrificial mold was then dissolved in basic aqueous solution (0.1 M NaOH) at 50 °C. This process completely dissolved the mold in less than 12 h and the green parts were immersed in a water bath for pre-debinding for a few days, according to the auxiliary
binder used in the feedstock. The Al₂O₃ dental implant prototypes shown in Fig. 8D underwent debinding and sintering at 500/1650 °C to give the final parts.

In general, SLA and DLP both have a higher resolution than FDM [27] since the size of the laser used in SLA (approx. 0.1 mm) or the pixel size in DLP (0.05–0.1 mm) is smaller than the nozzle used in FDM (typically 0.4 mm). For parts with filigree details such as a screw thread (Fig. 8, Fig. 9), printing a mold by SLA or DLP is preferential. The resolution difference is clearly visible in Fig. 9, where the CAD image is compared to sintered parts molded from DLP resin molds and FDM PVA molds. In this example, the layer height and line width used for FDM are too close to the dimensions of the screw thread, whereas DLP can provide the required high resolution. It should be noted that the printing direction plays a crucial role in FDM and to a lesser extent in DLP. Therefore, the quality of the screw thread in Fig. 9C could be improved by printing the mold horizontally instead of vertically. Nevertheless, the resolution would still be surpassed by DLP or SLA.

Two component ceramic injection molding (2 C-CIM) is also possible using FDM printed PVA molds. A U-shaped heating element was chosen as a proof of concept part. Classically, those parts consist of a thin arch and much thicker contact arms, so that only the arch glows due to the higher resistivity [28]. A different approach is the usage of two different materials with lower conductivity for the arch and higher conductivity for the contact arms [26]. For this purpose, MoSi₂/Al₂O₃/feldspar composites with MoSi₂ content of 15 vol% and 18 vol% were chosen for the arch and contacts, respectively. Firstly, PVA mold and ABS adapter pieces were designed by CAD (Fig. 10A–C). The gates for the two materials were added in such a way that the materials could be injected from two sides of the PVA mold by turning the PVA mold around after injecting the first material. After the first injection, the screws were removed, the PVA mold was turned around and the second feedstock was injected from the backside (Fig. 10D–E). PVA was then dissolved in water at 40 °C and the parts were simultaneously pre-debound. Next, the green bodies were thermally debound and sintered (Fig. 10F–G). Finally, the feasibility of the method was proven by glow tests showing that only the arch of the part glows while the more conductive contact arms remain much colder (Fig. 10H).

An additional approach to 2 C-CIM was employed to fabricate a ceramic crucible with integrated heating coil (Fig. 11). For this purpose, a non-conductive crucible was molded using a PVA mold. After dissolving the PVA mold, the green body was pressed into the PVA mold for the heating coil. Two similar feedstocks were used for the crucible and heating coil to assure compatible sintering behavior of the components.
and avoid mechanical stress and improper sintering in the final parts. For the crucible, a MoSi2/Feldspar/Al2O3 composite with a low MoSi2 content of 10 vol% yielded an insulating crucible. For the heating coil, the same composite with 18 vol% MoSi2 content gave the desired conductivity. Glow tests then showed that the sintered 2 C crucible worked as intended (Fig. 11-J).

4. Conclusion

Freeform injection molding (FIM) with sacrificial molds is a promising tool to speed up prototyping. In this study, FIM is extended to ceramic feedstocks to produce a variety of parts with demanding geometries such as spirals, cages and helices from Al2O3 feedstock as well as MoSi2 containing composite. The injection molds were FDM printed from PVA. This fast and simple method is limited when it comes to very fine structural details. Therefore, a screw thread was fabricated using FDM printed PVA molds as well as DLP printed sacrificial molds. This comparison showed that DLP printed molds are indeed preferable when compared to FDM printed PVA molds as well as DLP printed sacrificial molds. This potential of sacrificial molds for 2 C-CIM was demonstrated by fabricating a MoSi2 heating element with higher conductivity in the contacting arms as well as the ceramic crucible with integrated heating coil. Both samples were successfully operated in glowing tests.

Funding

Some of the results of this work were produced within the framework of Swiss Innovation Agency – Innosuisse funded projects 29990.1 IP-ENG and 30021.1 IP-ENG.

CRediT authorship contribution statement

Rene Wick-Joliat: Conceptualization, Investigation, Visualization, Writing – original draft. Maurice Tschamper: Investigation. Roman Kontic: Conceptualization, Investigation. Roman Kontic: Investigation, Visualization, Writing – review & editing.

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.

Acknowledgment

The authors would like to thank Leister Technologies AG and Metoxit AG for their cooperation and support as well as Sijia Liu for taking photos shown in Fig. 11.

References