Manufacturing of Ceramic Microcomponents by a Rapid Prototyping Process Chain**

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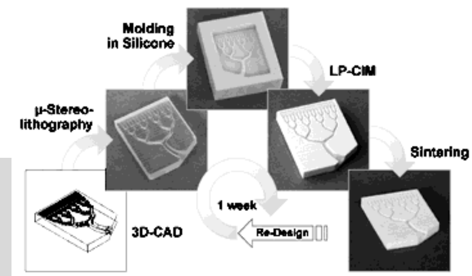

Time-intensive and cost-consuming manufacturing of new ceramic components may be improved significantly by the use of rapid prototyping processes especially in the development of miniaturized or micropatterned components. Their molding is generally very expensive and finishing is difficult to the point of impossibility. Most known generative ceramic molding processes do not provide a sufficient resolution for the fabrication of microstructured components. In contrast to this, a rapid prototyping process chain that combines micro-stereolithography and low-pressure injection molding, for example, allows the rapid manufacturing of ceramic microcomponents from functional models to preliminary or small-lot series.

1. Introduction

The materials mainly used in microengineering are silicon, plastics, and selected metals. These are materials for which a comprehensive know-how with regard to structuring techniques is available or micromolding techniques, which may be derived from macroscopic molding processes, exist. Examples are the injection molding of plastics or electroplating of metals. Use of ceramic materials in microsystems technology is of interest if their good mechanical and tribological properties, their thermal and chemical resistance, or their special physical (i.e., dielectric or piezoelectric) properties satisfy requirements that cannot be met by polymers or metals. Often, however, ceramic microcomponents are not employed because of the costs associated with their production, design, and development and because methods for the production of larger series have not yet been fully established. Moreover, design guidelines that might support the development process are still lacking in microsystems technology. A design tailored to the manufacturing process and the loads arising is exclusively based on experience gained in the macro range. This experience may not be transferred directly to the micro range, as material anisotropy and the increasing influence of effects negligible in macroscopic parts require an adequate dimensioning concept. Until appropriate construction guidelines are available, functional models and prototypes play a crucial role, as they allow an early assessment of the product and, hence, a detection of faults and verification of the concept in due time.

An accelerated supply of models and prototypes is also required for macroscopic components. In this field, this need led to the development of a number of rapid prototyping processes, i.e., processes for the generative and rapid production of three-dimensional models. However, these processes are not suited for the production of ceramic microcomponents, as they either exhibit deficits in molding accuracy or are restricted to polymer materials. This problem can be avoided and bypassed by establishing a rapid prototyping process chain including low-pressure injection molding.

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1.1. Manufacture of Ceramic Microcomponents

Ceramics have a number of material-specific advantages, but considerable difficulties are still encountered in molding and particularly in micropatterning. Machining of sintered ceramics by cutting tools, especially in microdimensions, is too difficult and expensive due to the high hardness and high melting point of ceramics. The processes developed in the past for molding in the millimeter and micrometer ranges differ in terms of manufacturing expenditure, design freedom, and achievable aspect ratio. But they all have in common that production is based on a powder-technological molding process using a negative mold and subsequent thermal compaction.[1] This results in two major boundary conditions. First, replication always requires an original mold, the dimensions of which have to take into account component shrinkage during sintering. Second, molding has to be a net-shape forming, as subsequent finishing of the structural details is impossible. (Due to their limited transferability to larger series production and the limited number of suited materials, direct molding methods of sintered ceramics, such as micromechanical processes, laser processing, and erosion techniques are not considered here.)

In slip pressing,[2,3] centrifugal casting,[4] and sol-gel casting[5] a ceramic slip is molded into a negative mold of plastic or wax. This mold is then removed chemically or pyrolytically as a "lost mold". Processes with an increased mechanical load of the molding tool, e.g., high-pressure injection molding, ceramic injection molding, CIM[6] or tape casting and stamping,[7] require metal molding tools, from which the ceramic green compact has to be demolded prior to thermal treatment. Even if the ceramic parts are not molded directly with metal tools, a metal mold is used in most cases for one of the replication steps or as an original mold (e.g., for the injection molding of plastic molds that will be used as lost molds). Depending on the required geometry and aspect ratios and the internal structural details and smoothness needed, these metal molds are produced by erosion methods, mechanical micromachining, silicon technologies, or the LIGA technique (German acronym for X-ray deep lithography, electrodeposition, and polymer molding).

In contrast to high-pressure injection molding, where the feedstock is plastified by thermoplastics of high viscosity, hot molding and low-pressure injection molding of ceramics[8,9] are based on the use of low-melting paraffins, which allow molding at significantly reduced temperature and pressure loads. So far, mainly metal molds have been employed for micromolding. They were supplied directly or indirectly by means of the LIGA technique or mechanical micromachining at high costs. Any change of design, which is frequently needed during product development, causes the development costs to rise significantly. The small mold loads in low-pressure injection molding, however, make molding possible without metal molding tools. Plastic molds may be used as well as molds cast from silicone rubber. It has already been demonstrated that the process of low-pressure injection molding is suited to mold finest details and structures with high aspect ratios.[10] Reproducibility of molding and in particular surface roughness are limited by the grain size of the ceramic powder used rather than by the molding process.

1.2. Generative Processes

In recent years, a number of processes have been developed with the objective of reducing the time needed for the development of new products by rapid model manufacturing. The first process of this type, which was patented by C. W. Hull in 1986, was stereolithography for the production of three-dimensional models from plastics.[11] However, it has become increasingly desireable to use these objects not only for design studies, but also for direct testing of the function and properties of the components. This has resulted in the development of tool-free processes, which not only allow the generative design of plastics, waxes, or paper, but also enable direct fabrication of functional models from metals or ceramics. Examples of such processes are extrusion techniques, such as multiphase jet solidification (MJS) and fused deposition modeling (FDM), 3D printing (3DP), laser-supported sintering (SLS), or laminating techniques (LOM).[12–17] In particular, recent developments in the production of ceramic green compacts by stereolithography appear to be rather promising.[18,19] However, most processes for the direct production of ceramic models still exhibit a limited resolution, a restricted level of detailing, and a rather high roughness. The dimensional accuracies, which are of the order of 0.1 mm and above[17] do not allow the production of fine, micropatterned components. Consequently, only a replication of original molds is suited for this purpose at the moment.

Stereolithography is the prototyping method that was commercialized first[20] and it still possesses the highest precision and resolution. The objective of using rapid prototyping methods in microsystems technology and, thus, avoiding cost-intensive molding of the original mold by the LIGA technique led to further developments in the generative production of polymer microcomponents.[21,22] Microstructures obtained by rapid micro product development (RMPD) are already available. RMPD is a type of microstereolithography, which reaches a resolution in the range of a few micrometers and enables parallel fabrication of a number of components.[23]

2. Rapid Prototyping Process Chain

The availability of microdimensioned original molds is the prerequisite for a rapid prototyping process chain for the production of ceramic prototypes that are dimensioned accordingly. Starting from a CAD model, rapid tooling methods and a subsequent replication step allow molds to be generated for use in low-pressure injection molding and ceramic components to be produced with structural dimensions of a few micrometers (see lead picture). The entire process takes a few days only.

2.1. Fabrication of Molds

Fabrication of the original molds by stereolithography starts with the generation of three-dimensional CAD models of the ceramic components to be produced. The data are then converted into the standard stereolithography file format "STL" and the 3D model is subjected to triangulation (i.e., it is approximated by a structure consisting of triangles).[22] By varying the number of these triangles, the amount of data and the resolution of the stereolithographic component are influenced. To take into account shrinkage during molding and sintering, the drawing may be made in green dimensions or a model having the final dimensions desired is adapted by (possibly anisotropic) scaling. These data are then used, e.g., in stereolithography to control a laser that exposes a liquid monomer on a construction platform layer by layer. The exposed spots are subject to polymerization. Prior to the curing of the next layer, the platform is lowered further into the liquid monomer. In a first approximation, the achievable geometric resolution results from the layer thickness, the beam diameter, and via beam intensity from the interaction volume of the monomer.

The original polymer molds used in this case were produced in a commercial stereolithography facility (FS-REALIZER, Fockele & Schwarze company) and by the microTEC company, Duisburg, using the RMPD technique. The stereolithography facility has a positioning accuracy of 10 μm. A solid-state laser with a spot diameter of 200 μm is used. For epoxide exposure, the construction platform was lowered in steps of 50 or 100 μm. At the microTEC company, the original molds were made of acrylates using the RMPD technique. This modification of stereolithography, which is suited for microdimensioning, allows a precision of about 5 μm. Objects with a layer thickness of only about 1 μm may be generated. For the given mold geometries, however, a layer thickness of 25 or 50 μm was sufficient. Besides selective irradiation, parts may also be produced by the RMPD mask technique.[24] This is a combination of mask technology used in photolithography and RMPD, which allows large-area exposure of the monomer layer and a considerable reduction of exposure times of 2.5-dimensional geometries.

In the next step the polymer parts are molded with liquid silicone rubber that can be demolded easily after curing. These silicone castings are the negative molds that are used directly for low-pressure injection molding. Contrary to original molds made of wax, whose structural details are often destroyed when molded by silicone, original duroplastic molds are suited to the production of a large number of silicone castings. According to the experience gained so far, each silicone mold usually allows more than 100 ceramic models to be produced. Hence, the original molds may be used for the production of larger series.

As far as macroscopic parts are concerned, molding of the ceramics has already been demonstrated using original polymer molds produced by stereolithography directly without a replication step with silicone. A mold release agent has to be used before each injection.[25] Conventional mold release agents are unsuitable for microcomponents due to their film thickness, which leads to inaccurate reproduction of edges. As a result of the negligible affinity of silicone rubber for paraffin and of the elasticity of the molds, demolding of fragile structural details of ceramic green compacts is simplified considerably. It even becomes possible to demold slight undercuts without a sophisticated tool design.

2.2. Low-pressure Injection Molding

Preparation of the feedstock, which is simple compared with those required for high-pressure injection molding, takes place in a blade kneader (double-Z kneader) that can be evacuated. First paraffin and a dispersant are melted at about 80 °C and then mixed with the ceramic powder. Afterwards, the hot molding slip is kneaded for a period of about 3–4 h. An aluminum oxide feedstock with powder of a mean particle size of 1.2 μm (MR 52, Martinswerk company), for instance, consists of about 11 wt.-% paraffin, about 1 wt.-% dispersant, and about 88 wt.-% ceramic powder. The molded green bodies possess a solid content of 62 vol.-%.[26]

The silicone molds are filled, e.g., in a commercial hot molding facility of the Peltsman company, Minneapolis, USA. For complete filling of the mold, the tool has to be evacuated before injection and the mold has to be heated to a temperature that exceeds the melting point of the paraffin. Due to the elasticity of the silicone mold, it is also necessary to adjust the machine parameters to ensure dimensional accuracy.[10] In case of the fabrication of only a few samples, manual filling of the mold may be reasonable. For this purpose, the pasty feedstock is scraped into the mold at a temperature of about 100 °C. Air inclusions are eliminated by repeated evacuation. Due to the relatively simple feedstock preparation, the low-pressure injection molding process may be easily and rapidly used for other ceramic materials. Components have been produced from Al_2O_3 and other materials (e.g., ZrO_2, $BaTiO_3$, PZT, hydroxyapatite, and an electrically conductive Al_2O_3/TiN ceramic) by this process.[26]

2.3. Thermal Treatment

Thermoanalytical investigation of the hot casting slip provides important information on the dewaxing process. During the debinding of an Al_2O_3 feedstock as obtained by a thermogravimetric/differential scanning calorimetry (TG/DSC) study, an endothermic peak of the DSC signal appears at about 65 °C. This peak corresponds to the melting of paraffin. In a multistage reaction with decomposition and oxidation processes overlapping each other the organic additives are released in the temperature range 200–500 °C, depending on the heating rate used. It is revealed by the TG signal that dewaxing is completed at about 500 °C. The total measured weight loss of 12 % corresponds to the original quantity of organic additives. To remove the organics, the green bodies are put onto porous plates and heated slowly to an end temperature of 500 °C in a chamber furnace with air circulation. The dewaxing program has been adapted from a decomposition process observed at 0.5 K/min. Heating rates and dwell times are strongly dependent on the geometry and design of the components. Large or thick-walled components have to be dewaxed much more slowly than small or thin-walled parts. Edges or corners should be avoided in the design, if possible, as here increased stresses occur during thermal treatment. These stresses may cause cracks. The ceramics are sintered in a conventional manner. For example, sintering of aluminum oxide takes place at temperatures of up to 1700 °C. After sintering, a density of 95 % of theoretical density was reached in the components. This value corresponds to the material data specified by the manufacturer. Linear shrinkage of the parts amounts to about 13 %. Total duration of the thermal treatment is in the range 20–30 h.

3. Precision and Limits of the Process

In this section, the accuracy of molding and limits of the process are discussed and illustrated with some examples. As a whole, the replication steps of the rapid prototyping process chain exhibit very high precision and accuracy in the micrometer range. Measurements with regard to the reproducibility of the dimensions of structural details yielded a standard deviation of only 0.2 %. The quality of the original polymer mold is of decisive importance for the reproducibility of the ceramics. The achievable resolution and surface quality of the ceramic components are mainly limited by the layer structure of the polymer mold, where each sloping part of the component is approximated by steps. The layered structure of the original mold is also reflected by periodic depressions on the vertical walls of the original mold. The higher the selected layer thickness, the coarser the reproduction of contours in the ceramic component. As compared to this effect, the grain size in the sintered ceramic part may be neglected in most cases.

The molding quality of the rapid prototyping process chain becomes obvious when comparing the replication stages. In Figure 1, the original polymer mold, the silicone mold, and the ceramic component are represented based on the example of a medium distributor structure with 500 μm wide channels designed for a chemical microreactor. For a better comparison, the representation of the silicone mold in the center has been mirrored. The ascending bottom part of the channels is approximated by steps that are clearly visible in all three molding stages. In the front section of media supply, minor defects can be observed in the ceramic material. However, these defects have already been contained in the original mold. They are attributed partly to the unprecise laser control and partly to insufficient cleaning of the polymer mold upon exposure.

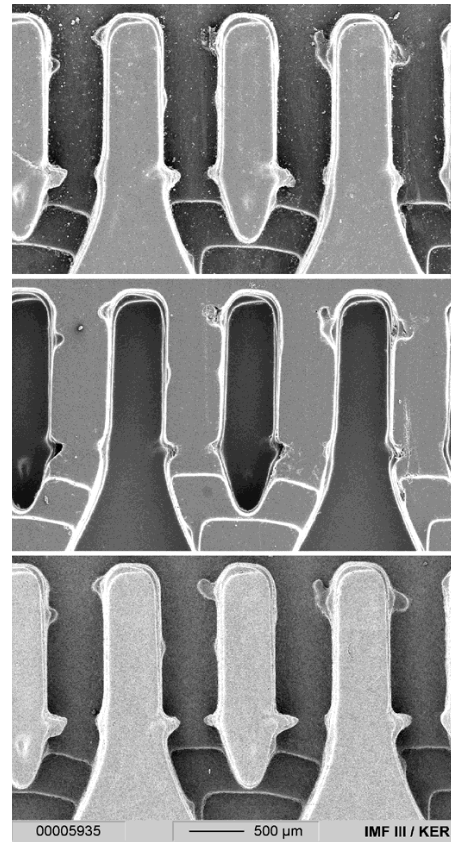

Fig. 1. Comparison of the three replication stages of polymer (top), silicone (center, mirrored), and ceramics (bottom). The small defects contained in the original mold are also molded into the ceramic part.

Figure 2 shows some examples of components made of Al_2O_3, manufactured by the rapid prototyping process chain. In all components with inclined areas, these slopes that are approximated by steps in the original mold produced by stereolithography are clearly visible in the ceramic parts. The fluid distributor structure with a constantly decreasing size of the channels in Figure 2a is characterized by a high molding and surface quality. The 100 μm steps existing in the original mold are clearly visible at the bottom of the channels. The layer structure of the original mold is reproduced very precisely on the vertical walls.

Besides the laminar setup of the original mold, data processing may also cause some inaccuracy of the final component. The detailed view of a fluidic component shows good molding also in the round medium passages (Figure 2b). At some points, however, the rounded-off areas are seen to be approximated by planar areas. This does not result from an insufficient precision of stereolithography, but from the relatively low resolution chosen for the triangulation during data conversion from the CAD system to stereolithography.

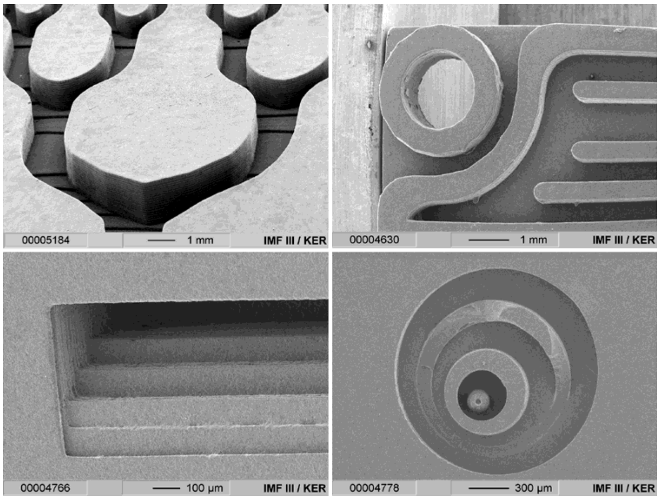

Fig. 2. a) Detailed view of a fluid distributor structure of Al_2O_3 with branching channels of decreasing size. The depressions visible on the vertical walls result from the layered structure of the original mold. b) Partial view of a fluidic ceramic component with a medium passage. The not-exactly-circular hole results from the inaccuracy of data processing. c) Detailed view of an Al_2O_3 test structure with about 80 µm wide steps of variable height, molded using an original RMPD mold. d) Section of an Al_2O_3 test structure with rings of variable depth, molded using an original RMPD mold. The defects result from the partial destruction of the original acrylate mold during repeated molding in silicone.

For components that are to have a larger precision and a higher level of detailing, the RMPD technique was used for the fabrication of the polymer molds, e. g. a medium distributor structure with 250 µm wide channels in the front section. Both the surface of the component and the bottom area of the channels are inclined slightly and have been approximated by 25 µm steps in the original mold. The ceramic component was molded with high accuracy. The layered structure of the original mold is not only visible on the inclined areas, but also on the walls of the channels. If necessary, layer thickness can be further reduced down to 1 µm in RMPD technology. However, it should be taken into account that any reduction of layer thickness leads to an increase in the layer number and, hence, in the time required and costs incurred for the production of the original mold.

The aspect ratios that can be achieved in ceramic molding by low-pressure injection molding also depend on the original mold used. When applying original molds of high surface quality (e.g., LIGA components) aspect ratios of more than 10 can be reached. In contrast to this, the much rougher surfaces resulting from the layered structure of the polymer molds considerably aggravate demolding at vertical walls with aspect ratios > 5 due to the relatively high friction forces. This may cause problems not only when demolding the ceramic green compact, but also when molding in silicone. To identify the limits of molding, a test structure with aspect ratios of up to 5 and smallest structural details of 50 µm was produced by means of the RMPD mask technique. While molding the ceramics, no problems occurred due to the filling of the mold and the details exhibited a high sharpness of the edges (Fig. 2c and Fig. 2d). Due to the brittleness of the acrylates used, however, the fine, free details of the polymer mold are very fragile and may be destroyed easily during repeated silicone molding processes. The ceramic ring structure represented in Figure 2d, for instance, exhibits certain defects that can also be observed in the polymer mold after repeated molding.

The rapid prototyping process chain with its rapid, flexible, and inexpensive production of original molds with its rapid supply of new ceramic functional models saves much time when designing and developing new parts. An example is the development of a ceramic microreactor for use in microreaction technology (Fig. 3).[27] Whereas metal microreactors have already been demonstrated to work successfully, comparable ceramic components for very high temperatures or corrosive conditions are still lacking. For ceramic microreactors a novel design had to be established. For design development and due to the desired modular character of the reactor, various molding tools were needed. As the final design cannot be verified on design models, but only under operating conditions, the manufacturing of functional models was indispensable. Moreover, a fabrication technique had to be chosen that met the requirements for the molding of the relatively large reactor housings as well as of the micropatterned details of the modular components. Without the use of the rapid prototyping process chain, this development would not have been possible within a reasonable period of time and at acceptable costs.

Fig. 3. Modular ceramic microreactor for use in microreaction technology. All components have been produced by means of the rapid prototyping process chain. (L, 68 mm; W, 25 mm).

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4. Outlook

When developing ceramic components, repeated adaptation of the molds is necessary in the design development. For any change of the feedstock, the dimensions of the molding tool have to be adapted accordingly, as a change of the shrinkage behavior may result. While in the past, feedstock development had to be completed before an expensive molding tool was ordered, the combination of rapid prototyping processes and low-pressure injection molding allows simultaneous adaptations of feedstock and design and allows the production of new prototypes within a period of a few days. Further developments of the stereolithography process (e.g., the RMPD technique) allow a rapid fabrication of polymer molds with internal structural details in the micrometer range. Due to this rapid and flexible fabrication of molds, it is also possible to produce components whose original molds presently cannot be produced at all or in an economically reasonable way by mechanical micromachining and LIGA molding. In contrast, e.g., to the LIGA technique or a silicon etch process, that is suggested elsewhere[28] as a fabrication process for the original parts there is virtually no limitation for the stereolithographic components in *z*-direction.

By means of the rapid prototyping process chain combining microstereolithography and low-pressure injection molding, ceramic microparts can be manufactured rapidly, at low cost, and with high precision. Furthermore, modifications of the design may be implemented within a short period of time. This results in a considerable reduction of the development and redesign costs, while commercialization of the components is accelerated. The process may be used to produce preliminary series with good reproducibility. Consequently, problems of upscaling, which usually occur during the transition from prototyping to production of larger series, are avoided. For very large series, when the tool costs play a minor role only, use of the high-pressure injection molding process appears reasonable. Due to the similarity of the processes, most experiences gained in low-pressure injection molding can be utilized.

If an increased resolution is reached by the direct, generative processes for the production of ceramic components, they may represent an interesting alternative to the process for the production of micropatterned ceramic prototypes, which is presented here. As the time-determining step of both processes is thermal treatment, however, time reduction will be relatively small, since only silicone molding and low-pressure injection molding would no longer be necessary. Furthermore, the direct processes hardly allow for any economically efficient production of larger series of components.

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