Novel Functional Structures and Structural Combinations by Additive Manufacturing

Additive manufacturing methods open the door to a completely new freedom in design. This is due to the fact that components are built up layer by layer, tool-free, and basing only on a CAD file [1]. The present expectations in the field of additive manufacturing can be called a hype. Everybody is talking about “3D Printing”. For polymers and for metals several methods and devices for real production of components already exist. Especially for polymers printing devices are available to reasonable costs, also for private use. In the field of ceramic materials the situation is much more differentiated

Introduction

On the one hand side in ceramics is a rapidly growing interest in individualized or customized products, in efficient single components or small scale production of ceramic parts with complex geometry, and also in avoiding waste of expensive materials, e.g. from green machining of isostatically pressed components. On the other hand side, there are versatile methods for additive manufacturing of ceramic components which can be divided roughly into powder-based and suspension-based methods. The latter additionally include techniques using thermoplastic feedstocks and wires, inks or pastes. However, concerning ceramics, often the material determines the process since not all methods are suited for each ceramic powder, i.e. some powders decompose in contact with a laser beam and others cannot be processed by exposure due to the absorption of visible or UV light. This is aggravated by the fact that there are only a few devices commercially available for additive manufacturing of ceramic components which provide ceramic parts with sufficient density, homogeneity and surface quality in acceptable size and tolerances. The versatile opportunities offered by additive manufacturing technique and the demands from the industry on one side and the present state of development of additive manufacturing in the field of ceramics on the other side, will open up an exciting and promising field of research and development work in the very next future [1].

In this contribution some novel ceramic components with innovative functional structures made by Lithography-based Ceramic Manufacturing (LCM) and by combination of LCM with a new direct-foaming method, the so-called Freeze Foaming [2], will be introduced. The examples will show some outstanding features which cannot be obtained with any other shaping technique but additive manufacturing.

Keywords
lithography-based ceramic manufacturing (LCM), freeze foaming, functional structures, structural combinations

Motivation

Today, microreaction technology is one of the most innovative branches in chemical syntheses and chemical engineering. Users of micro reaction technology are convinced, in particular, of achieving enhanced product selectivity and yields, improved process safety and an access to new products and processes, resulting in an accelerated “time-to-market”. So far, ceramic microfluidic devices had been made by assembling planar components with inner channel structures manufactured by conventional shaping techniques like injection moulding, multilayer technique, pressing and green machining or casting techniques. Insufficient tightness of the microreactors and inner leakiness, especially at higher fluidic pressures, often cause problems for manufacturing and application. Today, additive manufacturing allows to build up components with inner channel structures without any parting planes or joining zones. All major operational units of a processing plant (mixers, reactor units, heat exchangers, and analyzers), for use in different reaction environments, can be constructed. Moreover,

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additive manufacturing techniques allow a much functionality-oriented than production-oriented designing of microreactors.
A second motivation is the combination of different porous structures for mimicking individualized bone replacement components. By combining additive manufacturing with conventional shaping routes components with a combination of both, individual outer shape and an inner pore structure for enhanced ingrowth of blood vessels and cells, are becoming reality. Apart from that, a process combination between additive manufacturing and large series production techniques like tape casting or injection moulding would allow the production of customized or personalized products with interesting application fields in jewellery, medicine, sports or lifestyle.

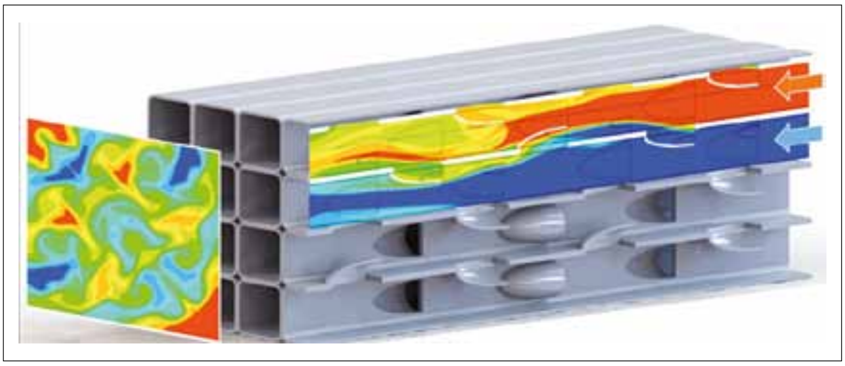

Fig. 1
Schematic view of the mixing simulation result of a mixer with inner spoilers and openings in the separation walls

Lithography-based ceramic manufacturing (LCM)

For producing dense material structures with a high level in mechanical properties additive manufacturing methods have to be used basing on suspensions and pastes instead of a powder bed, allowing a very homogeneous distribution of ceramic particles and a possibly high volume content of powder in the suspension media. A very promising method for attaining dense ceramic components with properties comparable to conventionally produced parts is the Digital Light Processing (DLP). The ceramic powder is dispersed initially in a photo-curable organic binder system homogeneously. Via selective exposure of this suspension by means of a micromirror array a ceramic green body according to the CAD model is built. This DLP principle is applied by a device from Lithoz GmbH/AT (CeraFab 7500) which is also used at Fraunhofer IKTS. This method especially developed for additive manufacturing of ceramic components is called lithography-based ceramic manufacturing (LCM). In this device the layer thickness of the suspension can be varied between 25 and 100 µm, the lateral resolution is 40 µm. As known from stereolithography a radical polymerization of the binder system is initiated with blue light by means of the DLP-modulus. All regions of a layer necessary for constructing the desired component are cured simultaneously by this method. In this way the productivity of this technique is increased in comparison to the dot-wise exposure by means of a UV-laser beam in stereolithography.
The working group “Shaping” of Fraunhofer IKTS used the LCM method for the development of novel microreactor components as well as for the development of bone-mimicking structures by combining LCM technique with freeze foaming.
The suspensions used for LCM have relatively high solid contents allowing green densities of the components of up to 55 % relative density. Since the components are made upside down in hanging position in the LCM method, the suspension volume necessary for the production process is relatively low. This is important for resource-efficient processing. After curing the bottommost layer close to the bottom of the glass vessel containing the suspension, the component is raised by a specific distance corresponding to the thickness of the next layer. A novel suspension layer is then applied by a doctor-blade and exposed in the next processing step. At present, three different ceramic materials are commercially available for the LCM process: alumina, zirconia, and tricalciumphospate. Fraunhofer IKTS uses commercial suspensions as well as own suspension compositions. Densities achieved after sintering of the debindered green bodies are 99,4 % th. D. in the case of alumina [3], and 99,0 % th. D. for zirconia. To achieve an efficient curing of the binder whilst exposed to blue light, it is imperative for the ceramic particles dispersed in the binder not to absorb the radiation. For that reason, dark ceramic powders are strongly limited for use in the LCM process.

Microreactors with function-oriented design

By using the advantages of additive manufacturing, i.e. the layer-by-layer construction of components, novel functionalities and add-ons in multichannel structures can be constructed such as openings in separating walls, channels with changing cross-sections and spoilers for influencing the flux velocity. Simulation software tools like ANSYS Fluent 14.5 and COMSOL 4.5 have been applied for simulating the mixing efficiency of two liquids in different mixing structures. Fig. 1 shows the component with the most efficient mixing result – a multichannel structure with inner spoilers and openings in the separation walls for a more intensive exchange of the liquids on shorter mixer length.
Fig. 2–3 show two further ceramic microreactor components made by LCM technique. The component in Fig. 2 has two inlets for fluids which will be intensively mixed and split into manifold partial fluxes. In Fig. 3 a component is shown with changing channel cross-sections which will lead to changing velocities of the fluid fluxes inside the channels.
Very important for future microreactors and an outstanding advantage of addi-

Fig. 2
Ceramic (alumina) micromixer with two inlets and manifold inner channels

Fig. 3
Ceramic (alumina) multichannel component with changing cross-sections of the channels and openings in the walls

Fig 4
Schematic view of a micromixer with fluidic connections for distribution of the initial fluids

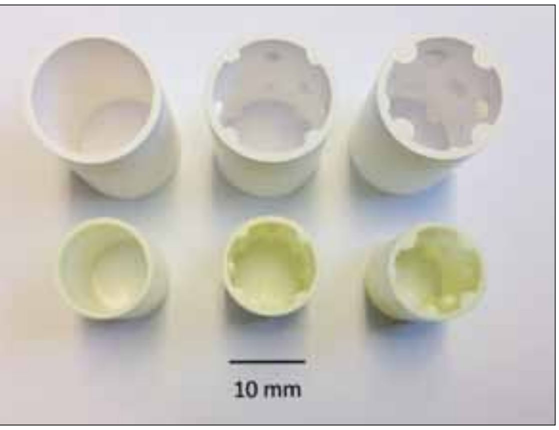

Fig. 5
Tubular zirconia shell structures made by LCM in the green (upper row) and sintered state (lower row) ready to be filled with a suspension for freeze foaming

tive manufacturing techniques is that the micro-fluidic connections or lids can be built together with the reactor components without subsequent joining steps as inherent risk of leakage.

Fig. 4 schematically shows an example of a micromixer with changing cross-sections of the micro-channels and two micro-fluidic connections distributing two fluids on the micro-channels for subsequent intensive mixing.

Bone-mimicking structures by combination of LCM with freeze foaming

Combining additive manufacturing methods with conventional or new shaping techniques offers the opportunity to attain either an individualization of series parts and/or a combination of outstanding product properties. This was done in the special case of a combination between freeze foaming and additive manufacturing. The structural advantages of a so-called freeze foam typically are high mechanical strength due to filled foam ligaments on the one hand and a bimodal pore size distribution due to an open-cell structure and an ice crystal growth in the ligaments (due to a freezing process) on the other hand. By combining these features with given AM possibilities patient-specific bone geometries can be achieved. However, a requirement for any combination of shaping technology is the precise adjustment of the shrinkage of the components for a common sintering step. In our case the shrinkage of the ceramic foam structure had to be adjusted to the shrinkage of the component made by LCM. The most common way for doing this is equalizing the solid content of both green components.

The challenge for making bone-mimicking structures is to obtain a part consisting of an open-porous core, enabling a fast in-growth of bone cells and blood vessels, and a shell with much smaller pores, a higher mechanical strength and the bone-specific shape. The approach was, firstly, to make tubular testing parts with a thin, but load bearing shell structure by the LCM method and secondly, shell structures from CAD data taken from a real human femur bone (www.grabcad.com/library "human-femur-bone-1") in a scale of 1 : 2. Zirconia powder TZ-3Y-SE (TOSOH Corp.) had been chosen as material for the bone-mimicking structures showing a high mechanical strength and bioinertness.

The tubular testing shells can be seen in Fig. 5. The differently shaped inner surfaces of the tubes shall support a sufficient fixing of the foam structure during and after debinding and sintering.

The foam suspension was made by means of a planetary mixer ARV-310CE (Thinky Corp.). The solid content of the aqueous-based suspension was adjusted to approx 40 vol.-% which is comparable to the solid content of the LCM suspension. Subsequently the well-dispersed suspension was poured into the testing tubes and the bone-mimicking shells, respectively. The LCM parts have to be partially sintered prior to the suspension filling in order to prevent crack formation. The partially filled structures were then placed in a freeze drying device Alpha 2-4 LSCplus (Martin Christ GmbH). With falling ambient pressure inside the vacuum chamber the foam inflates.

Fig. 6 a–b
A computed tomography image of a bone-mimicking part,
b bone-mimicking part made by combined additive manufacturing of the outer shell and freeze foaming of the porous inner core (CAD data derived from a human femur)

Simultaneously, the equilibrium temperature in the suspension drops down. When reaching the triple point of water the foam structure freezes suddenly. After a freeze drying step of about 12 h the dried foam structures were removed from the vacuum chamber, debindered and co-sintered with the surrounding shell structure.

The sintering step provided the desired bone-mimicking composite parts with a dense shell and an open-porous core (Fig. 6). As expected, a quite homogeneous microstructure between the core and the shell had been attained (Fig. 6a and 7).

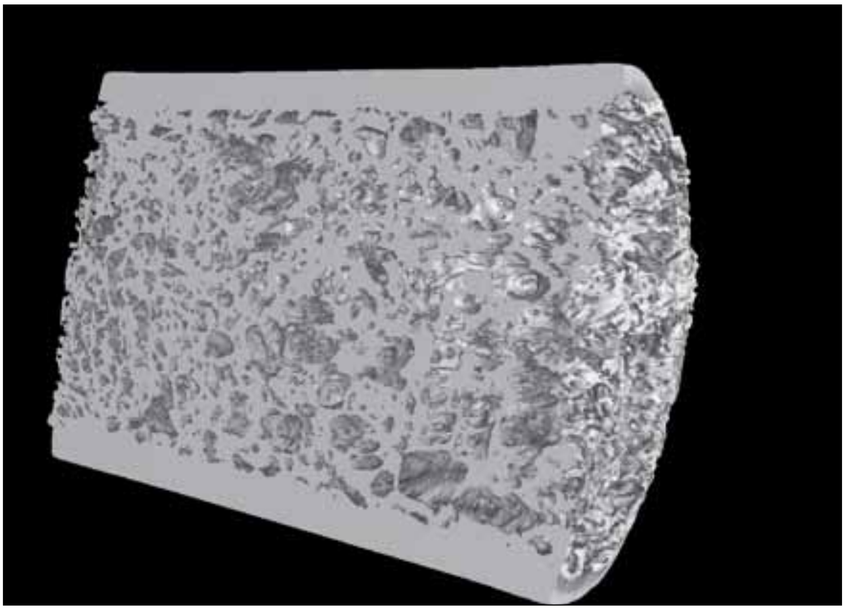

Fig. 7
3D computed tomography image of a tubular testing part in the sintered state

Conclusions

For production of ceramic components, additive manufacturing (AM) technologies can be seen as an excellent "add-on" to the conventional shaping technologies presented by dry-pressing, (thermo-)plastic shaping and suspension-based routes. Additive manufacturing will be used if the complexity of the components would not allow any other shaping method or if injection moulding or green machining of dry pressed components would be too expensive due to either tooling costs or waste of expensive material.

Furthermore, additive manufacturing will be favoured if single, individual parts or limited editions of components are desired. For using freedom in design in full width, ceramic component manufacturers and designers have to think "additive". Totally new components can be invented and existing parts can be optimized or functionalized and can be pushed to ultimate perfection.

Beside the "simple" application of additive manufacturing methods for making novel complex-shaped parts, promising solutions for technical challenges lie in the combination of conventional shaping techniques with AM technologies, either for individualization of large series components and multi functionalization or, for the combination of outstanding properties of each single shaping method.

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