



Innovative and novel manufacturing methods of ceramics and metal-ceramic composites for biomedical applications



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ABSTRACT

Recently, the so-called freeze-foaming method, for achieving open porous and mainly interconnected foam structures, was combined with the Additive Manufacturing technique Lithography-based Ceramic Manufacturing which provides personalized and complex 3D structures. After a co-sintering step, composite structures, combining the advantages of dense and porous features in one single part were achieved. These novel potential bone replacement structures might serve as possible next-generation bioceramics/-composites used for personalized implants which, additionally, allow a structural adaption according to the customer's needs. In other current projects, metal-ceramic composites were obtained by tape-casting technologies and reshaping methods like lamination and deep drawing. After final co-sintering demonstrators of a bipolar scissor and a miniature button-sized device for medical application were developed. These composites provide biocompatible and isolating properties given by zirconia and at the same time, conductive properties given by steel layers. Thus, they are applicable to prevent bleedings and initiate a localized tissue vaporization respectively.

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1. Introduction

The topic of biomedical engineering represents a vast field of possible applications. According to the desired shape, porosity and application, research activities range from (porous) bone replacement materials to medical devices. As wide as the applications differ as manifold the manufacturing technologies are. Well-known conventional techniques like compression methods or MIM/PIM (Metal/Powder Injection Molding) are applied to achieve mostly dense parts.

In contrast, especially for achieving porous structures appropriate foaming methods (e.g. Replica, Placeholder, and Direct-Foaming methods) are executed, as well as the so called tape casting for achieving layers of a desired material with thicknesses of a few microns to several hundreds of microns. Recent activities often

favor novel Additive Manufacturing (AM) approaches (e.g. Selective Laser Sintering: SLS, Lithography-based Ceramic Manufacturing: LCM, Selective Laser Melting: SLM, Fused Deposition Modeling: FDM, etc.) to achieve complex three-dimensional dense or porous structures. This variety of technological approaches is mirrored by its equally wide application-specific and required choice of materials from polymers to metals to ceramics. Especially in medical engineering biocompatible and highly corrosion-resistant materials are of importance. Depending on operating conditions they need to have specific electrical properties and/or defined mechanical properties. More and more the use of composite materials which combine the properties of each class of material as well as the need for proper co-manufacturing routines becomes interesting and even essential on the path toward novel tools and structures.

1.1. Freeze Foaming

Concerning porous materials, previous works dealt with a novel approach to porous ceramic structures by the so-called direct “Freeze Foaming”. Commonly used foaming techniques are based on the burnout of often environmentally harmful organic volatile pore formers or even whole polymer scaffolds. The resulting structures either feature closed porosity or unfilled struts allowing only limited mechanical loading, for instance. These foams have to be

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Table 1

Additive contents for the zirconia and steel suspension (wt.% relative to the powder quantity).

Material	Binder (wt%)	Plasticizer (wt%)	Dispersing and defoaming agent (wt%)
TZ-3Y-E	10.0	14.0	1.1
17-4PH	2.0	2.5	0.3

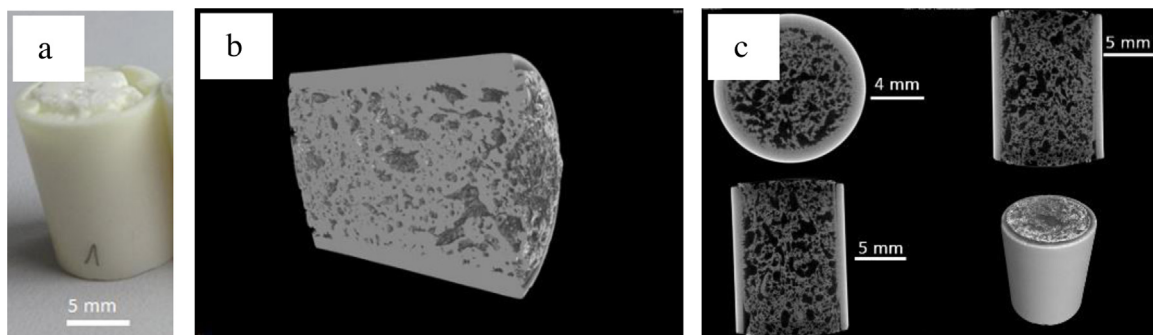
**Fig. 1.** Process scheme to co-manufacture Freeze Foam-filled LCM parts.

infiltrated or coated to achieve higher compressive strength values. Freeze Foaming on the other hand, is the direct foaming of almost any desired material (diverse ceramics, metals) dispersed as aqueous suspension. In contrast to other direct-foaming techniques based on environmentally harmful foaming agents, *in-situ* bubble formation through chemical reactions or deliberately injected gas in a suspension, the freeze-foaming process is the result of an ambient pressure reduction on an aqueous suspension. The occurring pore formers are mostly rising water vapor, air and the sublimation of frozen water. After debinding and sintering freeze-foamed structures exhibit filled struts *ergo* higher mechanical strength *per se* and a high proportion of open porosity, microporosity and interconnectivity. These are apparently properties which demonstrably predestine these cellular Freeze Foams for a possible use as biocompatible or bioinert products when made of hydroxyapatite (HAp) or zirconia (ZrO_2) and even as composite mixture [1–3]. Since Freeze Foaming offers the possibility of near-net shaping it was also applied to develop porous refractory bricks made of mullite [4,5].

However, this near-net shaping possibility of porous materials can also be applied to fill geometries of a particular shape from the inside or to provide a porous shell around any given part. This leads to novel composite tools and structures. The parts which are to be combined with a Freeze Foam can be manufactured either by conventional or by AM processes, and thus offer a wide range of application potential for personalized and surface customizable implant structures to be applied in the field of medical technology. In a recent Master's Thesis Freeze-Foam filled additive manufactured (via LCM) parts were co-manufactured and co-sintered to a next generation of biocomposites [6].

1.2. Metal-ceramic composites

Partially stabilized zirconium oxide and stainless steel are excellent materials for meeting the requirements of certain surgical instruments like bipolar scissors. Both materials are used already in medicine, especially in surgical and minimally invasive areas and the prosthetic technology. The austenitic chromium-nickel steel 17-4PH (AISI 1.4542) is also known as surgical steel and preferably used for mono- or bipolar instruments. A high frequency alternating current is passed through monopolar or bipolar instruments in order to selectively damage or to cut human tissue. In contrast to the monopolar, the current of the bipolar instruments flows only through a small area of the human body. By two separate electrodes with an insulating layer, the current can feed in and also bleed off in one instrument. In contrast to an insulation made of a polymer a ceramic material has advantages in the long-term and corrosion resistance. Zirconia is a common implant material in dentistry and as joint replacement. While polymers often show aging phenomena under surgical conditions, ceramics are much more resistant without impairment of the insulation effect. By using a multi component tape casting approach, metal-ceramic laminate components are manufactured in the shape of bipolar scissors and other surgical instruments like gripper, tweezers or electrodes [7]. A coating technology which is derived from the paper industry allows to apply a very thin insulating layer of a few microns between the electrodes [8,9]. The insulating properties remain. Until now, bipolar surgical instruments are on the market which are produced by mechanical joining of steel and ceramic [10]. This joining step can lead to stresses in the sensitive ceramic material and leaves fine gaps that are not preventable except with a pure force fit and/or form fit. Both

**Fig. 2.** Co-manufactured Freeze Foam-filled LCM specimen (a), reconstructed CT images (b and c).

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