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Original Article

Evaluation of the pore morphology formation of the Freeze Foaming process by *in situ* computed tomography

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ABSTRACT

The so-called Freeze Foaming method aims at manufacturing ceramic cellular scaffolds for diverse applications. One application is dedicated to potential bone replacement material featuring open, micro and interconnected porosity. However, the main challenges of this foaming method is to achieve a homogeneous pore morphology. In a current project, the authors throw light on the bubble/pore and strut formation of this process by *in situ* computed tomography. This allows for evaluating varying process parameter's effects on the growth of the ceramic foam during the foaming process. As first result and basis for CT analysis, a stable and reproducible model suspension was developed which resulted in reproducible foam structures. In dependence of selected process parameters like pressure reduction rate or air content in the ceramic suspension resulting Freeze Foams became adjustable with regard to their pore morphology. Pore size and distribution data as well as the porosity were characterized and evaluated accordingly.

1. Introduction

1.1. The Freeze Foaming process

There is a variety of foaming techniques of ceramic suspensions. The two largest industrially relevant techniques are based on poly urethane (PU) foam replication (Replica/Schwartzwalder approach [1]) and pore forming substances like *e.g.* starch, wax, polymeric beads, carbon black or sawdust [2,3]. PU scaffold and pore formers later need to be burned out in order to achieve the desired porous body. By a third relevant technique, the direct foaming, suspensions are foamed either by turbulent mixing with surfactants [4] or by *in situ* gas and vapour developing reactions [5,6].

In contrast to these foaming techniques that are based on the burnout of organic volatile pore formers and polymer scaffolds, the so-called Freeze Foaming is the direct foaming of almost any desired material (diverse ceramics, metals, *etc.*) prepared as aqueous suspension. Without foaming agents or deliberately injected gas into a suspension, the Freeze Foaming process is triggered by ambient pressure reduction of an aqueous suspension in a freeze dryer. Through the applied vacuum, the suspension medium inflates by rising processing air and water vapour. Further pressure reduction drives the aqueous system along the vapour-liquid equilibrium line towards the triple point (p,T-diagram of water, Fig. 1II). When that point is crossed, the generated proto foam freezes instantaneously and subsequently dries *via* sublimation (Fig. 1III and IV) [7,8]. Thus, the Freeze Foam's pore formers are rising bubbles of processing air and water vapour as well as sublimated frozen water.

Those structures are then debinded and sintered. Resulting Freeze Foams typically exhibit filled struts and a high proportion of open porosity, micro porosity and interconnectivity. An example of a highly porous sintered hydroxyapatite foam is shown in Fig. 2.

Especially these are properties, which demonstrably predestine such cellular structured Freeze Foams for a possible use as biocompatible components when made of Hydroxyapatite (HAp) or ZrO_2; even as composite mixture [9–11]. In addition, Freeze Foaming offers near-net shaping capabilities and was also applied to develop porous refractory bricks made of mullite [12,13]. In recent contributions, the Freeze Foaming's advantages were used to fill the inside of 3-dimensional, complex-shaped hollow shell geometries. Those shell structures can be manufactured either by conventional or by Additive Manufacturing processes. In that way, porous and cellular features provided by the Freeze Foaming have been connected to dense and complex features provided by LCM (Lithography-based Ceramic Manufacturing). Demonstrators in form of a femoral bone model were successfully co-sintered to one composite part. This hybrid shaping technology

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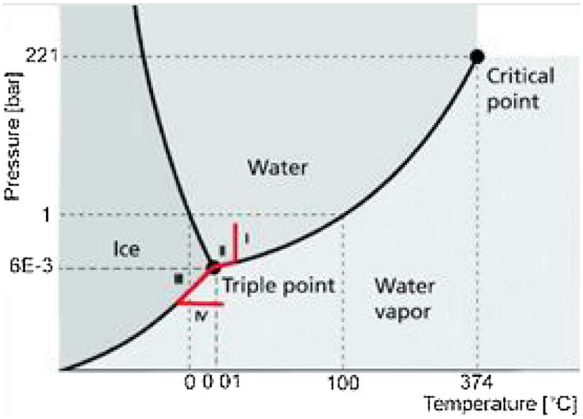

Fig. 1. Exemplary p,T-phase diagram of water including Freeze Foaming process [8].

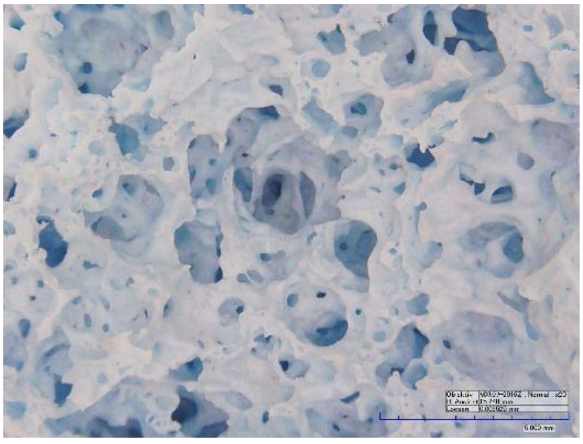

Fig. 2. Optical microscopic image of an open porous sintered hydroxyapatite Freeze Foam.

therefore offers a wide range of application potential for personalized and surface customizable implant structures to be applied in the field of biomedical technology and engineering [14,15] (Fig. 3).

The above mentioned examples so far were made only on a laboratory scale. An upscaling of the Freeze Foaming process requires larger batches of ceramic suspensions. Suspension and Freeze Foaming need to be reproducible and robust. Industry often requires foamed scaffolds to have either a closed or open as well as a homogeneous pore morphology in order to guarantee and provide the targeted properties. For instance, refractories require homogeneously distributed small pores (mainly closed porosity) in the range of 100 nm to 1mm for proper isolation capability [16]. With regard to bioceramic scaffolds for bone replacement material, a porosity greater than 70–80%, interconnectivity [17] and sufficiently large pores (at least 100–500 µm) for cell attachment [18,19] as well as micro porosity is required [20]. Like depicted above, Freeze Foaming indeed allows producing open porous, interconnected and microporous scaffolds. However, on the example of Figs. 2 and 3b a completely heterogeneous pore morphology becomes obvious. That makes estimations and assessment concerning the reproducibility of biocompatibility and even mechanical strength very difficult.

Therefore, intense research is needed with regard to establishing a material preparation and process approach that firstly, allows a controlled tuning of the pore morphology and secondly, provides real time data acquisition of the foaming process, the strut and bubble/pore formation itself.

1.2. *In situ* computed tomography

In situ analyses allow insights into processes that have an influence on materials, for instance during preparation, occurring reactions or under load. One solution is being provided by computed tomography (CT) and *in situ* computed tomography which has become a sophisticated tool for improved damage and degradation analyses in the field of material sciences [21–25]. An additional and important advantage is the allocation of 3-dimensional (3D) volumetric pore morphology information. Software tools like MAVI [26] or VGStudio Max [27] give access to volume-based data like porosity, pore size and distribution or pore shape. This contribution reports about the use of *in situ* CT to acquire and clarify occurring Freeze Foaming phenomena and to derive the vey principles of foaming process. The results shall allow the production of 3D scaffolds with targeted pore size and distribution.

Within the frame of a DFG-funded project (“Erarbeitung der Gesetzmäßigkeiten der Schaumstrukturbildung im Gefrierschäumprozess biokompatibler Keramikschäume”) CT analyses are provided by the project partner *Technical University Dresden, ILK (Institute for Lightweight Engineering and Polymer Technology), TUD-ILK*. The analyses of the evolving foam structure by X-ray measurements will be conducted by two methods: the first is real-time foaming monitoring by X-ray radiography (2D), the second method, allowing the evaluation of foam structuring phenomena, is computer-aided reconstruction of areal image information by means of RµCT (3D) [28,29]. In order to gather 3D foam volume information by CT scan (usually 3–10 min for one measurement) the foaming process itself needs to be stopped at certain points. Accordingly,

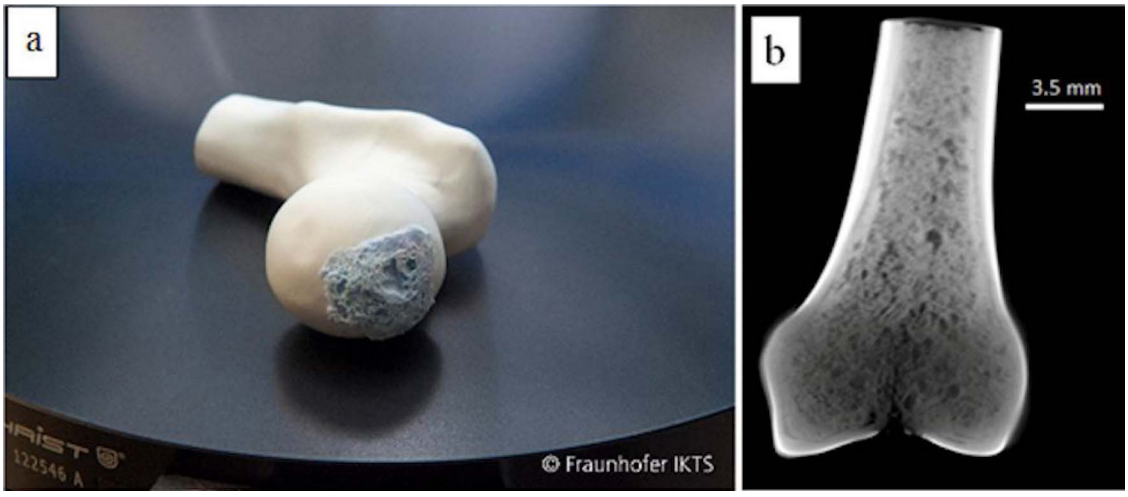

Fig. 3. Hybrid shaping approach to bone-mimicking scaffolds: (a) femoral bone model of HAp, (b) CT reconstruction images of a bone model made of ZrO_2.