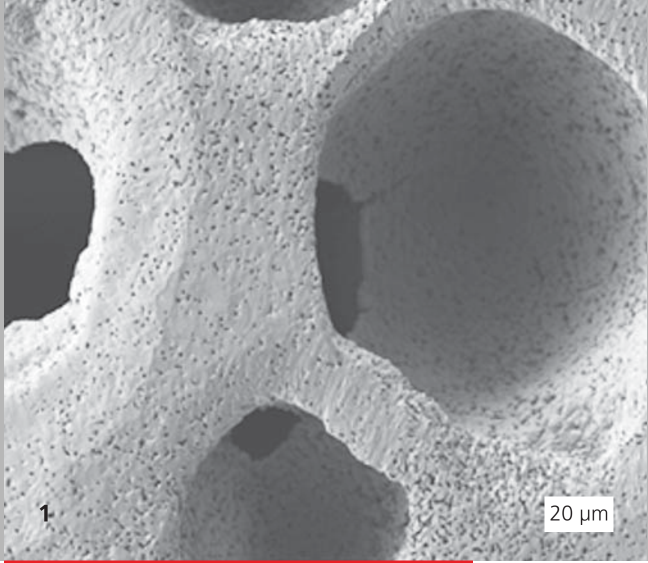

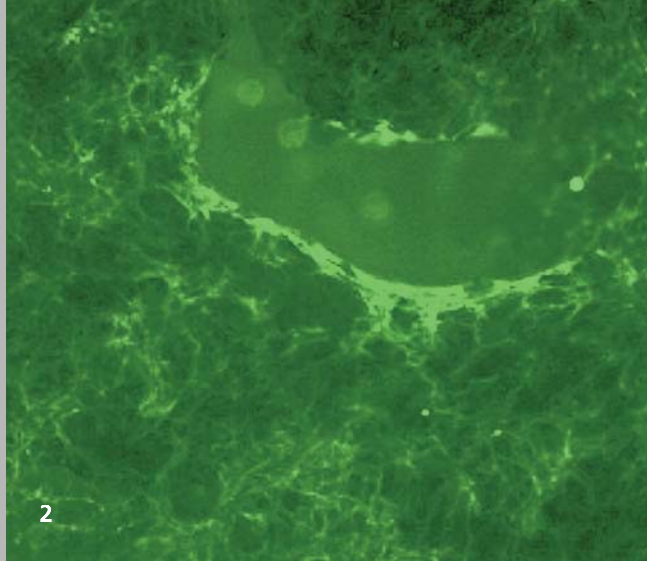

CERAMIC FOAMS AS BONE REPLACEMENT MATERIAL

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In general, bones in a human organism have a pore size of approx. 100–700 µm that seems to be favorable for cell cultivation. The pore structure consists of macropores as well as micro/mesopores. The inorganic component of bones mainly consists of apatite, a calcium phosphate. Therefore, hydroxyapatite powder (HAp, $Ca_5(PO_4)_3(OH)$) is a suitable material for producing an artificial bone. For the generation of porosity different methods can be used (e.g. replica or placeholder technique, direct foaming).

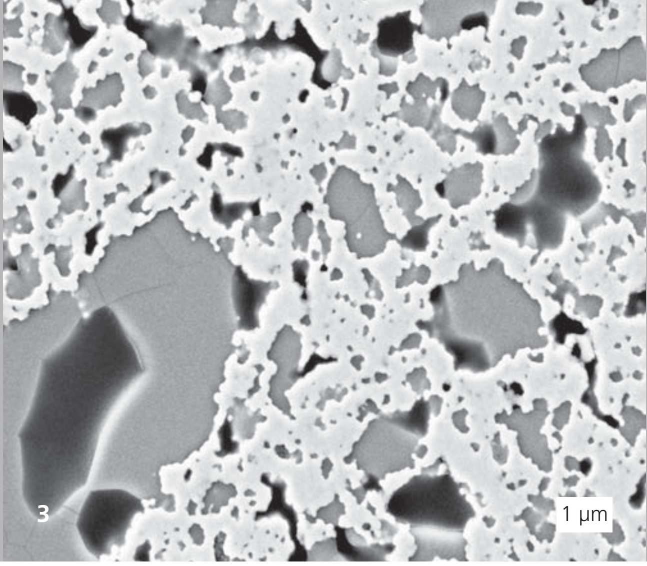
The ceramic foams presented in this article were produced by the so-called freeze foaming method where the ambient pressure around an aqueous, ceramic suspension in a freeze dryer (Christ GmbH, Gamma 1-20) is reduced. As a result, the suspension swells. If the pressure falls below the triple point, liquid water turns to ice (at approx. 6 mbar). Thus, the generated foam is stabilized. Then, the structure dries due to sublimation, the so-called freeze-drying process. After thermal treatment, a solid ceramic foam is obtained which may serve as potential bone replacement material.

Generally, typical freeze-foamed biomaterial structures have a mainly open porosity between 70 and 90 %, pore sizes ranging from micro/meso (0.1–20 µm) to macropores (100–1000 µm) and an interconnectivity. The pore-connecting struts are filled and microporous. So, they contribute to the structure's stability (Figure 1). In cooperation with the Fraunhofer Institute for Biomedical Engineering IBMT, live and dead staining tests with fluorescein diacetate (FDA) were carried out on murine (mouse) fibroblasts to verify the biocompatibility. Alkaline phosphatase (ALP) provides a first indication of a beginning osteogenic differentiation of human mesenchymal stem cells of bone marrow origin succeeds. As immunocytochemical collagen I-staining were detected in and on the porous structures, proliferation was validated. The hMSCs differentiate, i.e. they are able to form different types of cell/tissue (Figure 2).

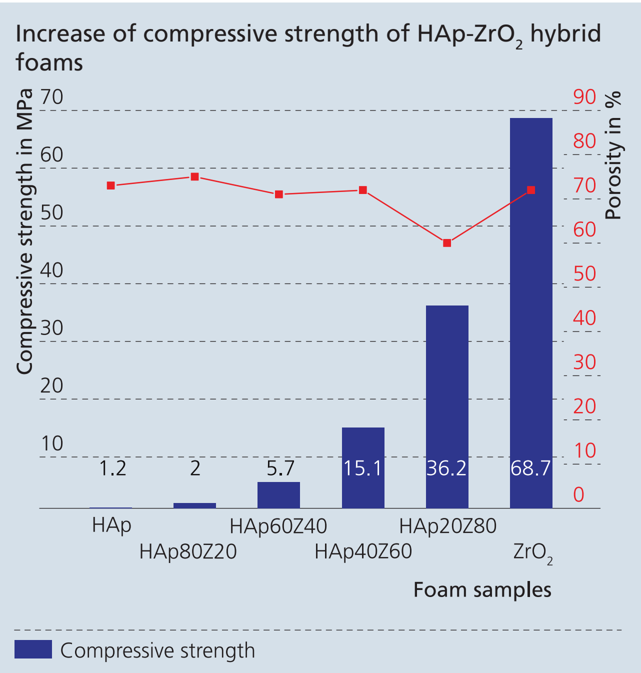
A natural bone withstands relatively high compressive strengths. In contrast, artificial hydroxyapatite per se shows a much lower load tolerance and mechanical strength. This is similar to materials like tricalcium phosphate or bioglass®, all of them suitable non-metallic biomaterials. Accordingly, the compressive strength of highly porous structures is lower.

However, freeze foaming allows not only for foaming completely different materials (e.g. metals) but also for processing two or more materials at the same time, time-shifted and/or interpenetrating or as layers on each other.

Therefore, non-load bearing hydroxyapatite (e.g. by MERCK or SIGMA-ALDRICH) was paired with the likewise biocompatible and provably load-bearing zirconia (ZrO_2, TZ3-Y-E, by TOSOH) in a hybrid mixture. The mixing ratios were varied starting at 20 vol% ZrO2 in HAp up to 100 vol% pure ZrO_2 in order to evaluate the effect of zirconia on the compressive strength of the porous freeze foams. It was demonstrated that the structural compressive strength can be increased to approx. 15 MPa at the ratio of 60 : 40 vol% (ZrO_2:HAp). That effect corresponds to the reached percolation threshold of zirconia in hydroxyapatite. Connected, filigree ZrO_2 scaffolds (white), which enclose solid HAp clusters (grey), lead to the observed increase of strength (Figure 3). A ratio of up to 80 vol% zirconia results



in porous structures which are able to withstand compressive strength of almost 40 MPa (see diagram).



Follow-up procedures of the biocompatibility of the porous structures confirm: all ceramic foams are not cytotoxic and thus biocompatible. Preliminary experiments on osteogenic differentiation deliver positive results for these new, strength-enhanced ceramic hybrid foams.

The use of similar or newly developed materials in combination with near-net shaping by freeze foaming (Figure 4) as well as further process optimization provide a possible scenario for an application as implant.

Services offered

- Development of suspensions for freeze-technological shaping methods like:
  - Freeze foaming
  - Freeze casting
- R&D projects/feasibility studies for producing artificial bone replacement materials and components

1 SEM images of a HAp foam.

2 Collagen I proof on a HAp foam.

3 HAp-ZrO_2 hybrid foam.

4 Freeze-foamed thumb bone replica of HAp.

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