Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 4595–4601
www.elsevier.com/locate/jeurceramsoc

Ice-mould freeze casting of porous ceramic components

Tassilo Moritz *, Hans-Jürgen Richter

Fraunhofer Institute for Ceramic Technologies and Systems, Winterbergstrasse 28, 01277 Dresden, Germany

Received 13 December 2006; received in revised form 5 April 2007; accepted 14 April 2007
Available online 29 June 2007

Abstract

Porous, hollow ceramic components were produced by freeze casting technique. For this purpose aqueous slurries with high solid contents were prepared which were stable against freezing down to at least −5 °C. Ice cores were made by coating steel components with freezing water which were subsequently dip-coated with the ceramic suspensions. After freeze drying which removes both, the ice core and the frozen suspension liquid, and sintering, ceramic components with a high amount of open porosity including steel parts could be achieved. As an example hydroxyapatite was used for showing the opportunities of the freeze casting technology among others for applications in the field of bone replacement. The influence of the solid content of the hydroxyapatite slurries on the ice crystal growth has been investigated by means of compact hydroxyapatite bodies which were prepared by freeze casting using ice moulds with cylindrical cavities.

Keywords: Shaping; Porosity; Freeze casting; Apatite

1. Introduction

Freeze casting which is known as a shaping technique for refractories for about 60 years[1] did not lose its attractiveness for shaping advanced ceramic materials till this day. The freeze casting technique involves the preparation of a ceramic slip that is poured into a mould which is then frozen and subjected to sublimation drying of the solvent. The frozen solvent acts temporarily as a binder holding the part together for demoulding.[2,3] A variation of the freeze casting technology[4–7] uses sols which form gels when frozen below 0 °C as a form of chemical bonds between the powder particles. The ceramic powders and sol are mixed into a paste which is fed into a mould. This is then frozen to temperatures below −20 °C. The frozen component is released from the mould and allowed to warm back up to ambient temperature afterwards. Although it still has the original water content the component is solid and now simply needs to be dried out.

The advantages of this shaping method can be seen in its environmental friendliness,[8] because of the minimized organic additive concentration and the use of water as suspension liquid, in the elimination of drying stresses such as in the exclusion of shrinkage during freeze drying. Because of the almost zero shrinkage the authors described, this variation of the freeze casting process can be called a near net shape process. Furthermore, this shaping technique offers the possibility to adjust a certain amount of open porosity with interconnecting pore channels[9] or pore size gradients in ceramic bodies.[3] In several publications[9–12] freeze casting is used for achieving porous ceramic structures for applications as biocatalysts or biosensors, separation filters, catalyst supports, gas distributors, preforms for metal-impregnated ceramic-metal composites, and implantable bone scaffolds. Sintered bodies of Al_2O_3 and Si_3N_4 with aligned channels have been fabricated by unidirectional freeze casting of conventional aqueous ceramic slurries[11,13] or silica-sol containing ceramic slurries.[14] For attaining pore structures in ceramic bodies, slips with lower solid contents are first frozen to obtain vehicle ice crystals which are often connected with each other in dendritic shapes, surrounded by frozen concentrated ceramic slurry. After freeze drying channels are created replicating the shape of the interconnected crystals.[9] The greatest influence on the porosity and the pore size distribution of the ceramic body can be exerted by the solid content of the suspension, the temperature gradient and the ice crystal growth rate over the thickness of the sample. With increasing freezing rate and larger temperature gradients the pore sizes become smaller.[15] Thereby, the thermal isolation of the already frozen

---

* Corresponding author. Tel.: +49 351 2553 747; fax: +49 351 2554 197.
E-mail address: Tassilo.Moritz@ikts.fraunhofer.de (T. Moritz).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.04.010

part of a sample causes a decrease of the crystal growth rate. Since large pores decrease the mechanical strength of the freeze cast ceramic bodies drastically, the freezing behaviour of aqueous slurries was controlled by using hydrogen bond forming compounds, such as glycerol, to reduce the size of ice crystals during solidification of water.[16] In most cases silicon rubber,[2,7] polyurethane,[9] fluorocarbon polymer[11] or metals are used as mould materials for freeze casting. In 1991 a casting technology which was patented by Yodice[17] has demonstrated the possibility and advantages of freeze casting with ice patterns. This technology, called Freeze Cast Process (FCP), was developed by DURAMAX Co. It started with the building of solid master and silicone moulds. Then ice patterns were made with the mould and dipped into refrigerated ethyl silicate slurry and stuccoed. After repeating the dipping and drying processes, a ceramic shell was made and then it was put in room temperature and allowed the ice pattern to melt, drain, and dry.[18]

Due to its chemical and crystallographic structure similar to that of bone mineral hydroxyapatite has been widely used as a bone replacement material in restorative dental and orthopaedic implants.[19] It shows excellent biocompatibility with hard tissues, skin and muscle tissues, because it does not exhibit any cytotoxic effects and can be bonded to the bone directly. Hydroxyapatite as the basic mineral in mature bone is the most used material for bioactive fixation.[20] Once hydroxyapatite is implanted, it is bonded to the bone directly, enhancing the fixation in a shorter time and reducing healing time.[19] A synthetic scaffold for bone tissue engineering requires an inner structure with interconnecting pores. Pore sizes with diameters above 300 μm are recommended to promote good vascularisation and attachment of bone cells to guide their growth into all three dimensions.[21] As critical minimum pore size needed for the formation of a vital new bone 100 μm are necessary.[20] Duan et al.[22] produced biphasic porous hydroxyapatite/tricalcium phosphate ceramics with interconnecting pores. The porosity of the materials was 50–60%.

The goal of this article is to show the opportunities of ice-mould freeze casting for shaping of porous ceramic components with individual and complex geometries without complicate demoulding. Moreover, this novel technique allows producing closed porous ceramic shells with encapsulated components. The material combination hydroxyapatite/steel was chosen as an example for encapsulation of two completely different kinds of materials by this shaping technique. Furthermore, the components made by ice-mould freeze casting shall emphasize the potential of this method for producing porous ceramic parts for a variety of applications, for instance as filters, supports for catalysts, sensors or bone scaffolds. Beside hydroxyapatite also alumina and zirconia were used as materials for ice-mould freeze casting,[23,24] but the results of these investigations are not described in this article.

2. Experimental procedure

In this work ice was used as mould and as core material for preparation of compact hydroxyapatite parts such as of hydroxyapatite shells including steel components. The steel parts acted as a demonstrator showing the feasibility of encapsulating different materials in porous ceramic shells. Hydroxyapatite has been chosen as a suitable material for which freeze casting could be used to adjust a desired porosity of 50–60% with pore sizes up to 100 μm. As a component with individual and complex shape for demonstrating the opportunities of ice-mould freeze casting 3D data of a human jaw-bone had been used for producing a stereolithographic model which served as initial part.

In contrast to the state of the art, the ice cores were removed by sublimation drying without melting. No sol–gel transition was used for mechanical strengthening of the ceramic scaffold in the green state, but ice was the only binding phase in the frozen slip.

2.1. Materials

Hydroxyapatite powder (Merck KGaA, Darmstadt, Germany) with a median particle size (d_{50}) of 2.04 μm and a specific surface of 72.7 m^2/g has been used. For adjusting the necessarily high solid contents in the slurries of at least 70 wt.%, a commercially available dispersant (Dolapix CE 64, Zschimmer & Schwarz, Lahnstein, Germany) was used. Furthermore, glycerol (Sigma–Aldrich, Seelze, Germany) was added to the suspensions as a cryoprotectant for lowering the freezing point and for influencing the ice crystal growth.

As steel parts which should be encapsulated in a hydroxyapatite shell, cylindrical profiles (5 mm in diameter, 30 mm in length) made of ferritic stainless steel type 430 were used.

2.2. Fabrication procedure

For producing hollow hydroxyapatite bodies ice cylinders (diameter 40 mm, height 5–7 mm) were made by freezing deionized water in silicon rubber moulds. The steel parts which should be encapsulated in hydroxyapatite shells must be encased in ice previously. Initially, the steel rods were equipped with thin textile filaments. Afterwards, the steel parts were cooled in liquid nitrogen and dipped into water which was at a temperature close to its freezing point. For achieving a certain thickness of the ice coating, the steel rods were dipped alternately into liquid nitrogen and into water. In this way a dense and thick ice shell with adjustable thickness could be fabricated. It must be taken into account that the hydroxyapatite shell shrinks during sintering, whereas the steel rod elongates simultaneously. For preventing cracking of the hydroxyapatite shell the thickness of the ice coating must act as a spacer to enable both, shrinkage of the ceramic powder and thermal expansion of the steel rod. The ice cylinders and the ice-coated steel rods were stored in a refrigerator at −20 °C before use. Furthermore, ice moulds had been prepared showing a cylindrical cavity (40 mm in diameter and 10 mm in height) for achieving compact discs of hydroxyapatite.

For stabilising the surface charge the initial hydroxyapatite powder was thermally treated at 800 °C for 1 h previous to the slip preparation. The zeta potential of the initial powder and of the heat treated powder was measured in dependence on the pH of the suspension liquid by means of Zetamaster S (Malvern Instruments GmbH, Worcestershire, UK). The slips for the freeze casting process were produced by stirring the powders into water in an ultrasonic bath. Since hydroxyapatite is soluble in acidic milieu the pH of the suspension media must be in the basic range. According to the results of the zeta potential measurements the pH was adjusted to 11 to achieve a sufficient surface charge of the powder particles for electrostatic stabilisation. The electrostatic stabilising effect was additionally improved by adding the dispersant Dolapix CE 64. In a last step 8–10 vol.% glycerol were added to the suspensions as a cryoprotectant. For achieving high solid contents and for maintaining a viscosity which was suitable for the casting process, the slips were treated meanwhile by an ultrasonic sonotrode (UW 2200, Bandelin, Germany). Alternatively, the slips were treated in a planetary ball mill (Pulverisette, Fritsch, Germany) for 4 h. To investigate the influence of the solid content on the pore size distribution of the freeze cast parts suspensions with solid contents of 25.5, 32, and 42.5 vol.% had been prepared. The prepared slips were cooled down to −2 °C for avoiding melting of the ice core when getting into contact with a relatively warm slip. This cooling step was done in a double wall glass vessel. A sodium chloride/ice water mixture with a temperature of approx. −19 °C was used as cooling liquid for this purpose. The initially prepared ice cores were dipped into the cold suspensions which enclosed the ice completely. For avoiding an excessive ice crystal growth in the hydroxyapatite shell due to a low temperature gradient, the ice cores were dipped into liquid nitrogen previous to the contact with the suspension. Moreover, cooled suspension was poured into the ice mould with the cylindrical cavities for producing cylindrical discs. After the instantaneous freezing step of the hydroxyapatite shell, the formed bodies were put into a freeze drier (Gamma 20, Martin Christ GmbH, Osterode, Germany) and dried at 25–40 °C at a vacuum pressure of 2.5 mbar for 48 h.

The shrinkage of the samples during drying could be neglected. After complete removal of the suspension liquid, the ice cores, and the ice moulds, the green hydroxyapatite bodies could be handled carefully. The residual organic material was burnt out at 500 °C for 1 h. Sintering was done at 1350 °C for 2 h. The sintering step was carried out in hydrogen atmosphere for protecting the steel against oxidation. In the case of the compact hydroxyapatite discs sintering was done in air.

2.3. Characterisation

Rheometric measurements were carried out for characterizing the viscosity of the slips in dependence on the solid content with an annular gap system (Rheolab MC 10, Physica, Germany). The solid content of the slips was measured by drying at 110 °C (Halogen Moisture Analyzer HR 73, Mettler-Toledo, Germany). The pore size distribution of the ceramic parts in the green state was estimated by mercury intrusion (AutoPore IV 9500, micromeritics). Archimedes principle was used for the density measurements. Sintered samples were cut and prepared for light microscopic and FESEM investigations.

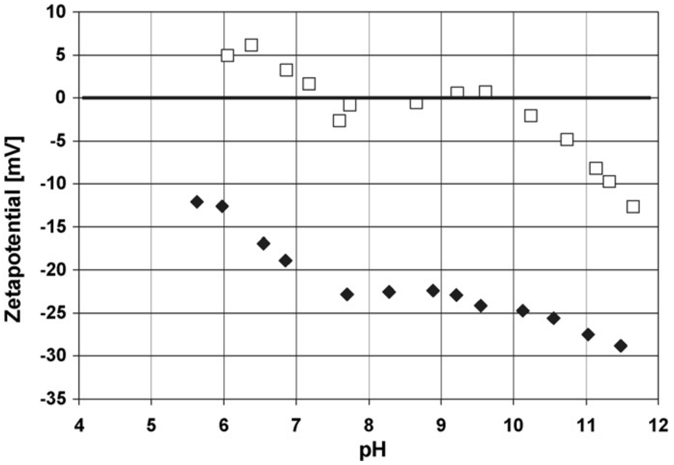

Fig. 1. Dependency of the zeta potential of the initial hydroxyapatite powder (□) and of the powder after a heat treatment at 800 °C for 1 h (♦) on the pH value of the dispersion media.

3. Results and discussion

Fig. 1 shows the dependency of the zeta potential of the initial hydroxyapatite powder (□) and of the powder after a heat treatment at 800 °C for 1 h (♦) on the pH value of the dispersion media. The diagramme emphasized the necessity of this thermal treatment for achieving a sufficient surface charge and a high zeta potential which are prerequisites for the preparation of a suspension with sufficiently high solid content. After the thermal treatment the dispersing behaviour of the hydroxyapatite powder was improved remarkably. Simultaneously, the specific surface of the powder was decreased from 72 to 25 m^2/g by this heat treatment.

Fig. 2 shows the dependence of the viscosity in ceramic suspensions with different solid contents on the shear rate. All suspensions of hydroxyapatite showed shear thinning. Solid contents larger than 28 vol.% caused a remarkable increase in the dynamic viscosity. However, for the freeze casting experiments with hydroxyapatite also suspensions with solid contents up to 45 vol.% had been used.

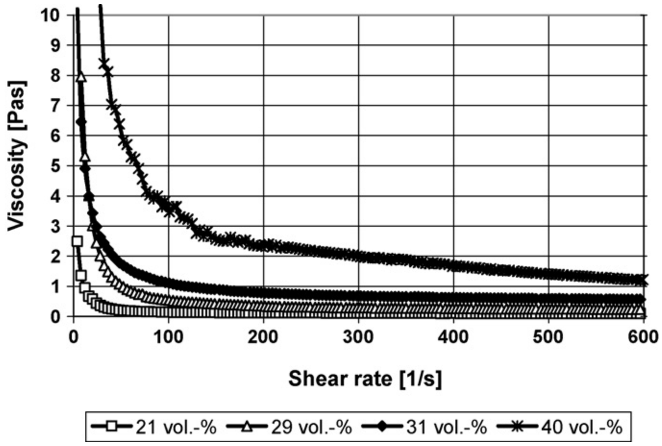

Fig. 2. Dependency of the suspension viscosity from the shear rate measured at suspensions with different solid contents of hydroxyapatite powder.

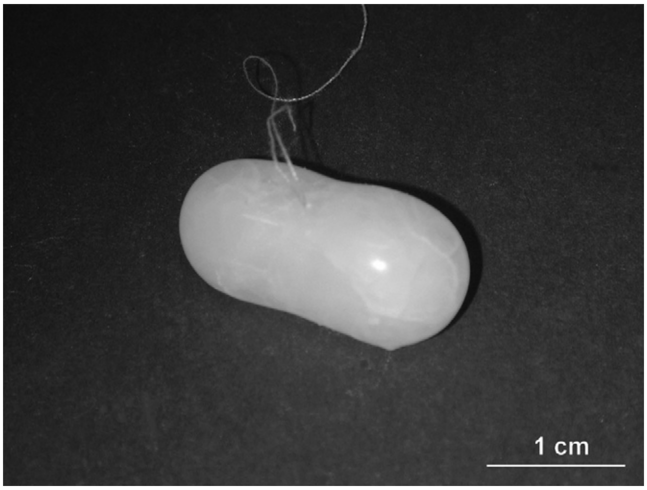

Fig. 3. Steel rod coated with ice (the textile filament was fixed to the steel rod for convenient handling during the coating step).

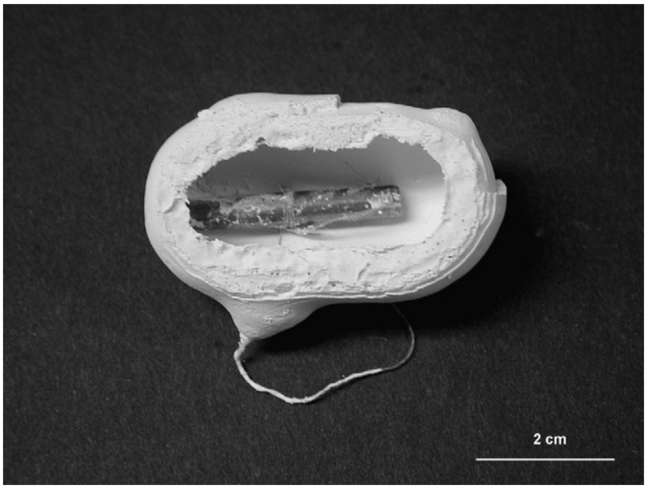

Fig. 5. Opened hydroxyapatite shell encapsulating a steel rod after freeze drying.

Encapsulation of a steel rod in an ice core with adjustable thickness is quite simple, especially if the temperature of the water is not far from the freezing point. An encapsulated steel rod is shown in Fig. 3. This ice core was dipped into the cold hydroxyapatite suspension for coating. The temperature of the ice core and the duration of the coating step influenced the thickness of the frozen slip layer. Fig. 4 shows a cylindrical ice core after coating with hydroxyapatite slip. The textile filament sticking out of the frozen slip shell enabled a convenient handling of the ice core during dip-coating. The filament remained in the sample after removal of the ice core by sublimation, but it disappeared during the burning out of the organic additives at 500 °C. The remaining small hole in the shell was closed during the sintering step.

Fig. 5 allows looking into a hydroxyapatite shell enclosing a steel rod after removing the ice core by sublimation drying. By adjusting the ice core thickness the distance between the ceramic shell and the encapsulated part can be varied. After sintering a closed shell enclosing a component of another material can be achieved in this way. An optical microscopic image of a cross-section of a hydroxyapatite shell with a steel rod inside can be seen in Fig. 6. It is necessary to emphasize here that the chosen material combination only served as a demonstrator. The goal of this experiment was to show that a component of a certain material can be encapsulated in a shell of another material in this way. In future applications such porous ceramic shells could act for instance as thermal or mechanical protection of encapsulated components which simultaneously enable an exchange of gaseous components.

The influence of the solid content of the suspension on the ice crystal growth and the resulting pore structure of cylindrical hydroxyapatite bodies which were produced by shaping in ice moulds can be seen in Figs. 7–9. With increasing solid content the volume of ice in the frozen part such as the size of the ice crystals was reduced. The direction of the ice crystal growth follows the temperature gradient in the freezing suspension. A strong gradient in temperature at the interface between ice mould and suspension caused the formation of many small ice crystals (Fig. 7), whereas a weak gradient in the centre part

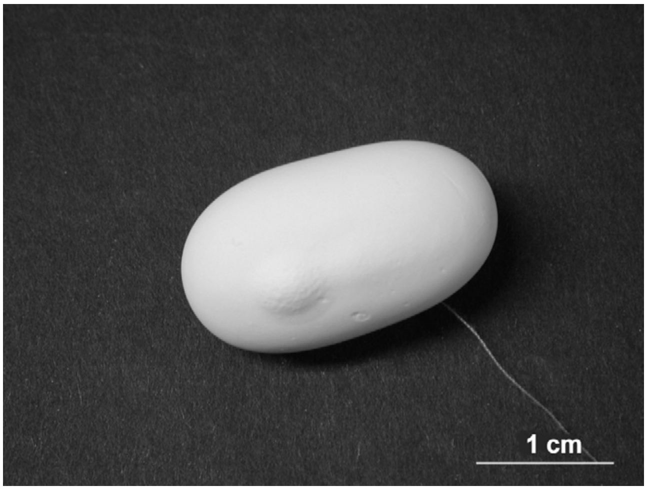

Fig. 4. Hydroxyapatite shell after sublimation of the ice core and the suspension liquid.

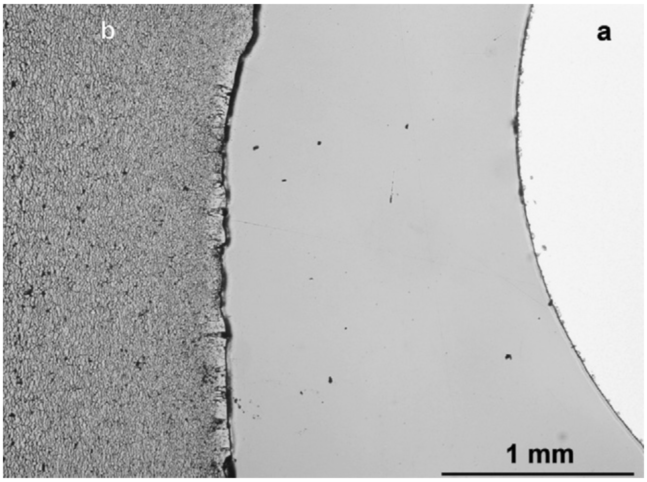

Fig. 6. Optical microscopic image of the cross-section of a steel rod (a) encapsulated in a hydroxyapatite shell (b) after sintering.

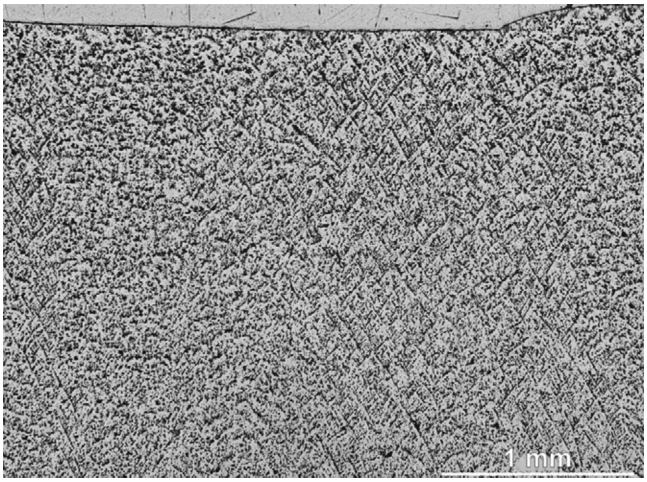

Fig. 7. Optical microscopic image of a polished cross-section of a sintered hydroxyapatite part produced from a suspension with 42.5 vol.% solid content.

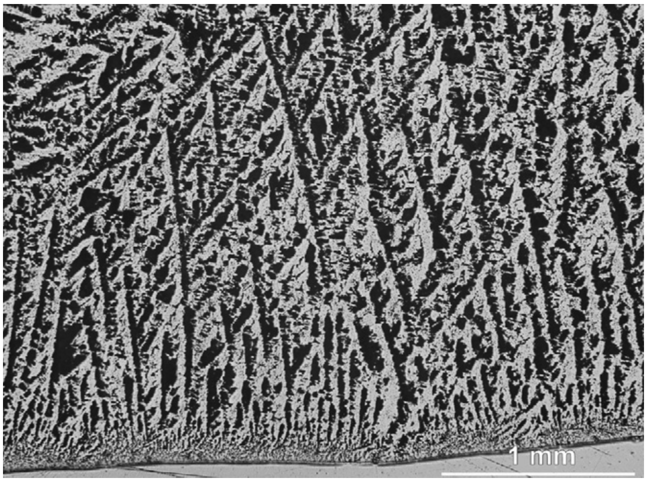

Fig. 8. Optical microscopic image of a polished cross-section of a sintered hydroxyapatite part produced from a suspension with 32 vol.% solid content.

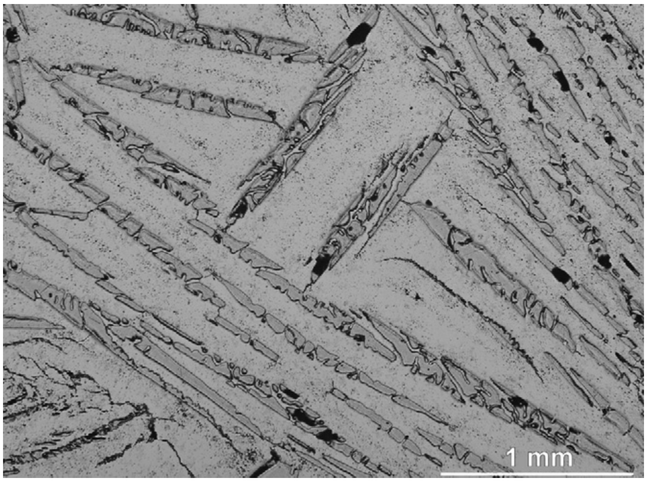

Fig. 9. Optical microscopic image of a polished cross-section of a sintered hydroxyapatite part produced from a suspension with 25.5 vol.% solid content.

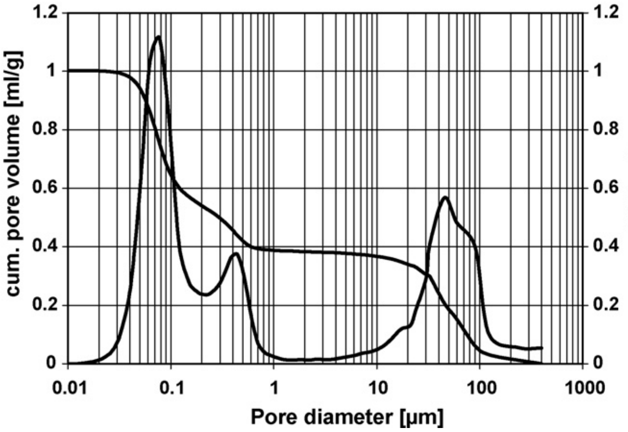

Fig. 10. Pore size distribution and cumulative pore volume of a hydroxyapatite part in the green state produced from a suspension with a solid content of 25.5 vol.%.

of the shaped bodies allows few ice crystals to grow very strong (Fig. 9).

Fig. 10 shows the multi-modal pore size distribution of a hydroxyapatite part in the green, i.e., unsintered state which was prepared using a suspension with a solid content of 25.5 vol.%. Whereas the peak at 70 nm can be attributed to the pores between the powder particles in a relatively dense package, the peak at 400 nm and the peak between 20 and 100 µm are caused by ice crystals. The porosity of the sample was 76%. After sintering the smaller pores disappeared and the open porosity decreased to 25%. For comparison, Fig. 11 shows the pore size distribution of a green, freeze cast hydroxyapatite part made of a suspension with a solid content of 42.5 vol.%. In contrast to the pore size distribution shown in Fig. 10 at higher solid contents only the pores attributed to the particle package could be detected. The larger pores arising from the ice crystal growth are distributed over a large size range and consume only a quarter of the entire pore volume, whereas in the case of the part made of the suspension with 25.5 vol.% almost 60% of the pore volume is caused by ice crystals. The porosity of the part made of the suspen-

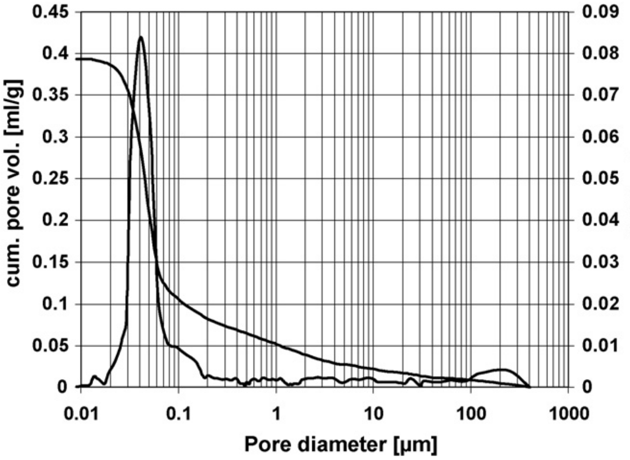

Fig. 11. Pore size distribution and cumulative pore volume of a hydroxyapatite part in the green state produced from a suspension with a solid content of 42.5 vol.%.

Fig. 12. Human jaw-bone made of hydroxyapatite by freeze casting in ice moulds.

sion with 42.5 vol.% was 51% in the green state and 13% after sintering.

The component shown in Fig. 12 is a human jaw-bone which was made from a model produced by stereolithography, subsequent reshaping of the component in an ice mould and freeze casting of a hydroxyapatite suspension. This part demonstrates the opportunity of producing complex and individually shaped components made of ceramic materials by using ice as mould material.

4. Conclusions

Freeze casting of components from aqueous suspensions by means of ice moulds and ice cores combines a number of advantageous aspects arising from the ice itself. Ice can act as a very strong binder between the powder particles in the frozen component. Ice can be used as mould material and can be machined for this purpose. It may encapsulate components and transfect them into closed shells, because the ice core can be removed by sublimation. Moreover, ice can be used as a pore forming agent by adjusting the solid content of the powder suspension. The shape of the ice crystals and their aspect ratio can be influenced by so-called cryoprotectants. Ice is a non-expensive, available and environmental-friendly material. The experiments have shown that completely closed hydroxyapatite shells can be produced using ice cores which were removed subsequently by freeze drying. Furthermore, other materials, for instance steel, can be transfected into such closed shells by encapsulating them in ice cores. The distance between the core material and the shell can be adjusted simply by the thickness of the ice core. The sublimation process causes an open pore structure of the cast material, because the shape and the size of the ice crystals determine the shape and the size of the resulting pores. Ice volume and the size of the ice crystals can be influenced by the solid content of the initial suspension. Moreover, the size of the ice crystals depends on the freezing rate, caused by the temperature gradient. The direction of the ice crystal growth follows the temperature gradient.

Ice mould freeze casting may be a suitable shaping technique for producing individually shaped ceramic components with complex geometry, like dental parts or bone scaffold.

Acknowledgement

Financial support of the German Research Foundation (DFG) is gratefully acknowledged.

References

1. Maxwell, W. A., Gurnick, R. S. and Francisco, A. C., Preliminary investigation of the freeze-casting method for forming refractory powders, *NACA Research Memorandum E53L21*, 1954, pp. 1–19.
2. Sofie, S. W. and Dogan, F., Freeze casting of aqueous alumina slurries with glycerol. *J. Am. Ceram. Soc.*, 2001, **84**(7), 1459–1464.
3. Donchev, D., Andresen, L., Koch, D., Grathwohl, G. and Ulrich, J., Einstellen einer gezielten Porosität in keramischen Grünkörpern über das kontrollierte Kristallisieren der wässrigen Phase (Setting of a desired porosity in ceramic green bodies via controlled crystallization of the aqueous phase). *Chemie Ingenieur Technik*, 2004, **76**(11), 1688–1690.
4. Jones, R. W., Near net shape ceramics by freeze casting. *Ind. Ceram.*, 2000, **20**(2), 117–120.
5. Schmedders, T., Hesse, T., Andresen, L., Koch, D. and Grathwohl, G., Porous ceramic materials by freeze-casting. In *Proceedings Materials Week 2001, International Congress on Adv. Materials, their Processes and Applications*, 2001, pp. 1–6.
6. Laurie, J., Bagnall, C. M., Harris, B., Jones, R. W., Cooke, R. G., Russell-Floyd, R. S., Wang, T. H. and Hammett, F. W., Colloidal suspensions for the preparation of ceramics by a freeze casting route. *J. Non-Cryst. Solids*, 1992, **147–148**, 320–325.
7. Yodice, A., The freeze casting process. In *SAE 2000 World Congress, Casting Solutions for the Automotive Industry, 1504*, 2000, pp. 11–14.
8. Höhne, J., Vollweiler, L. and Hausner, H., Die Herstellung keramischer Formkörper über die Gefrierspritzgusstechnik (Manufacturing of ceramic bodies via freeze injection moulding technique), *Symposium DKG*, 1989; *Fortschrittsberichte DKG*, 1990, **5**(2), 83–92.
9. Araki, K. and Halloran, J. W., Porous ceramic bodies with interconnected pore channels by a novel freeze casting technique. *J. Am. Ceram. Soc.*, 2005, **88**(5), 1108–1114.
10. Araki, K. and Halloran, J. W., New freeze-casting technique for ceramics with sublimable vehicles. *J. Am. Ceram. Soc.*, 2004, **87**(10), 1859–1863.
11. Fukasawa, T., Deng, Z.-Y., Ando, M., Ohji, T. and Kanzaki, S., Synthesis of porous silicon nitride with unidirectionally aligned channels using freeze-drying process. *J. Am. Ceram. Soc.*, 2002, **85**(9), 2151–2155.
12. Soltmann, U., Böttcher, H., Koch, D. and Grathwohl, G., Freeze gelation: a new option fort he production of biological ceramic composites (biocers). *Mater. Lett.*, 2003, **57**, 2861–2865.
13. Fukasawa, T., Ando, M., Ohji, T. and Kanzaki, S., Synthesis of porous ceramics with complex pore structure by freeze-dry processing. *J. Am. Ceram. Soc.*, 2001, **84**(1), 230–232.
14. Koch, D., Andresen, L., Schmedders, T. and Grathwohl, G., Evolution of porosity by freeze casting and sintering of sol–gel derived ceramics. *J. Sol-Gel Sci. Technol.*, 2003, **26**, 149–152.
15. Kemper, S., Kühn, M., Poehnitzsch, S., Koch, D., Kuntz, M. and Grathwohl, G., Etnwicklung und Charakterisierung poröser keramischer Werkstoffe (Development and characterization of porous ceramic materials), *Fortschritte in der Metallographie*, *35. Metallographie-Tagung*, *Neu-Ulm, 2001*, 2002, **33**, 355–360.
16. Dogan, F. and Sofie, S. W., Microstructural control of complex-shaped ceramics processed by freeze casting. *cfi/Ber. DKG*, 2002, **79**(5), E35–E38.
17. Yodice, D. B., *Investment Casting Process*, U.S. Patent No. 5,072,770, December 17, 1991.
18. Zhang, W., Leu, M. C., Feng, C., Ren, R., Zhang, R., Lu, O., Jiang, J. and Yan, Y., Investment casting with ice patterns made by rapid freeze prototyping. In *Solid Freeform Fabrication Proceedings*, 2000, pp. 66–72.

19. Oh, I.-H., Nomura, N., Chiba, A., Murayama, Y., Masahashi, N., Lee, B.-T. and Hanada, S., Microstructures and bond strengths of plasma-sprayed hydroxyapatite coatings on porous titanium substrates. *J. Mater. Sci.: Mater. Med.*, 2005, **16**, 635–640.
20. Popa, C., Simon, V., Vida-Simiti, I., Batin, G., Candea, V. and Simon, S., Titanium-hydroxyapatite porous structures for endosseous applications. *J. Mater. Sci.: Mater. Med.*, 2005, **16**, 1165–1171.
21. Leukers, B., Gülkan, H., Irsen, S. H., Milz, S., Tille, C., Schieker, M. and Seitz, H., Hydroxyapatite scaffolds for bone tissue engineering made by 3D printing. *J. Mater. Sci.: Mater. Med.*, 2005, **16**, 1121–1124.
22. Duan, Y. R., Zhang, Z. R., Wang, C. Y., Chen, J. Y. and Zhang, X. D., Dynamic study of calcium phosphate formation on porous HA/TCP ceramics. *J. Mater. Sci.: Mater. Med.*, 2005, **16**, 795–801.
23. Moritz, T. and Richter, H.-J., Ceramic bodies with complex geometries and ceramic shells by freeze casting using ice as mold material. *J. Am. Ceram. Soc.*, 2006, **89**, 2394–2398.
24. Moritz, T. and Richter, H.-J., Freeze casting of ceramic components using ice cores and ice moulds. *Adv. Sci. Technol.*, 2006, **45**, 391–396.