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Short communication

Functionally graded porous ceramics with dense surface layer produced by freeze-casting

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Abstract

Graded and porous Al_2O_3 ceramics with dense surface layer were fabricated by camphene-based freeze-casting process. The Al_2O_3/camphene/dispersant slurries were prepared by ball-milling at 60 °C for 24 h, before pouring into silicone rubber die. The warm slurry was cast into a mold at 25 °C, where the top surface of the cast body was exposed to air to allow for the controlled evaporation of molten camphene, and the bottom was attached to a copper plate before being placed on the top of a metal plate immersed in a water bath which can be cooled by ice-water (°C) and liquid nitrogen (−196 °C). This processing method can produce a graded porosity and pore structure distribution. A typical four pore structure, that is surface dense layer, transition layer, aligned pore distribution region and inner porous region is formed between the top surface and bottom surface. This technique is considered potentially useful in fabricating novel porous ceramics with special structure.

Keywords: B. Porosity; B. Microstructure-final; D. Al_2O_3; Freeze-casting

1. Introduction

Highly porous ceramics, due to their large surface area, high porosity, low thermal conductivity and high-temperature resistance, were widely used in many fields, such as supports for ceramic filters, artificial bones, high temperature insulator and active cooling parts [1–3]. To meet these requirements, various fabricating methods have been adopted to produce highly porous ceramics. These processing methods include the replication of polymer foams by ceramic dip coating, the foaming of aqueous ceramic powder suspensions, the pyrolysis of preceramic precursors, partial sintering by pressureless sintering, and the firing of ceramic powder compacts with pore-forming fugitive phases [5–8].

Freeze-casting has attracted considerable attentions as a simple, versatile, low-cost and environmentally friendly fabrication method for porous structures and generally offers a wide range of pore distributions compared to conventional fabrication technique [6,9]. Especially, for freeze-casting method, the pore structure and the pore size can be tailored in a certain range by adjusting the parameters in the processing easily, such as slurry concentration, freezing temperature and cooling rate.

Special pores can be produced during freeze-casting by removing the dendrites composed of the freezing vehicle (e.g. water [9], tert-butyl alcohol [10] and camphene [11,12]). Compared with water and tert-butyl alcohol, camphene can be frozen and easily sublimed near room-temperature compared with other frozen vehicles. Camphene-based freeze-casting can produce special pore channels in a tailored manner, e.g. aligned and interconnected pore channels on a scale of several microns, which offers superior mechanical properties and functions [13–15]. For example, Ren et al. [16] fabricated gradient pore TiO_2 sheets by freeze-tape-casting process and pore structure with different solid loading was discussed. Chen et al. [17] investigated the unidirectional ordered and gradient porous structures using tert-butyl alcohol(TBA)/acrylamide(AM)/alumina slurries by freeze-gelcasting technique. Macchetta et al. [4] used camphene-based freeze-casting to fabricate HA/TCP ceramic scaffolds with aligned, interconnected and graded porosity, and the initial solid loading played an important role in the resulting porosity of the scaffolds. Sofie [18] prepared functionally graded and aligned porosity in thin ceramics

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substrates using TBA-based slurries by freeze-tape casting. The effects of solids loading, freezing temperatures, and solvent type on pore structure were investigated.

The purpose of the present work is to fabricate porous Al_2O_3 ceramics with functionally graded microstructure including dense surface layer, aligned channel, interconnected porous structure, using a camphene-based freeze-casting process under different cooled conditions. The pore formation mechanism and pore distribution regularity were investigated and analyzed.

2. Materials and methods

Fine Al_2O_3 powder (CT3000, Alcoa Chemical, Qingdao, China) was used as the starting materials. Camphene ($C_{10}H_{16}$) (95% purity, Guangzhou Huangpu Chemical Factory, Guangzhou, China) was used as the freezing vehicle without any further purification. In addition, Texaphor 963 (Guangzhou Haichuan Co. Ltd., Guangzhou, China) was used as dispersant and binding agent (density at 25 °C of 0.89–0.91 g cm^{-3}). The concentration of Texaphor 963 was 1.5 wt.% of the ceramic–camphene slurry for all 10, 15 and 20 vol.% of solid loadings.

The solidification of the slurry was monitored by preparing an Al_2O_3/camphene slurry at 60 °C with a solid loading of 10 vol.% and placing a drop into a pre-heated slide glass (about 60 °C for both top and bottom) in order to avoid rapid freezing. The size of drops for camphene-based slurry is about 4 mm in diameter. After dropping onto the prewarmed slide glass, it was then covered rapidly by another slide glass. Simultaneously the central position of the two slide glasses was covered by silicone rubber insulation. The drop was left to freeze at room temperature, after which the structure formed was examined using optical microscopy, with particular emphasis on observing the presence of primary and secondary dendrites.

The slurry was stirred via the use of a motor and stirrer with a cap on the top to prevent any camphene vapor escaping. Al_2O_3/camphene/dispersant slurries with various solid loadings were prepared by ball-milling at 60 °C for 20 h, before pouring into silicone rubber die which the bottom was attached to copper plate. The slurry was left to cool at 25, 0 (ice-water) and −196 °C (liquid nitrogen) environment for 30 min.

After 24 h sublimation, sintering of the green body at 1400 °C/3 h enabled the densification of the samples and concomitant improvements in mechanical strength. The sintering regime entailed heating the samples at 0.5 °C/min up to 500 °C followed by 1 h of dwell time. They were then heated at 1 °C/min up to final sintering temperature and held at this temperature for 2 h, prior to cool down to room temperature at the same rate of 20 °C/min. After solidification, the green body was removed from the moulds and left to sublime (optimized to 48 h) at room temperature in order to remove the camphene entirely and achieve a highly porous structure. Following sublimation, sintering of the green body at 1400 °C/3 h enabled the densification of the samples and concomitant improvements in mechanical strength. The sintering regime entailed heating the samples at 0.5 °C/min up to 600 °C followed by 1 h of dwell time. They were then heated at 2 °C/min up to final sintering temperature and held at this temperature for 2 h, prior to cooling down to room temperature at the same rate of 20 °C/min.

The fabricated samples were investigated by evaluating their pore structures, including pore size and porosity using scanning electron microscopy (SEM, Model S-4700, Japan). Pore size

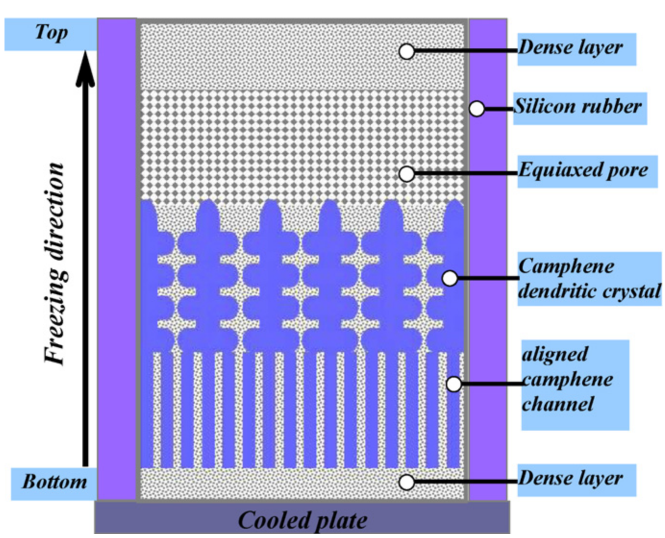

Fig. 1. Schematical illustration of freeze casting system and pore structure formation during freeze casting.

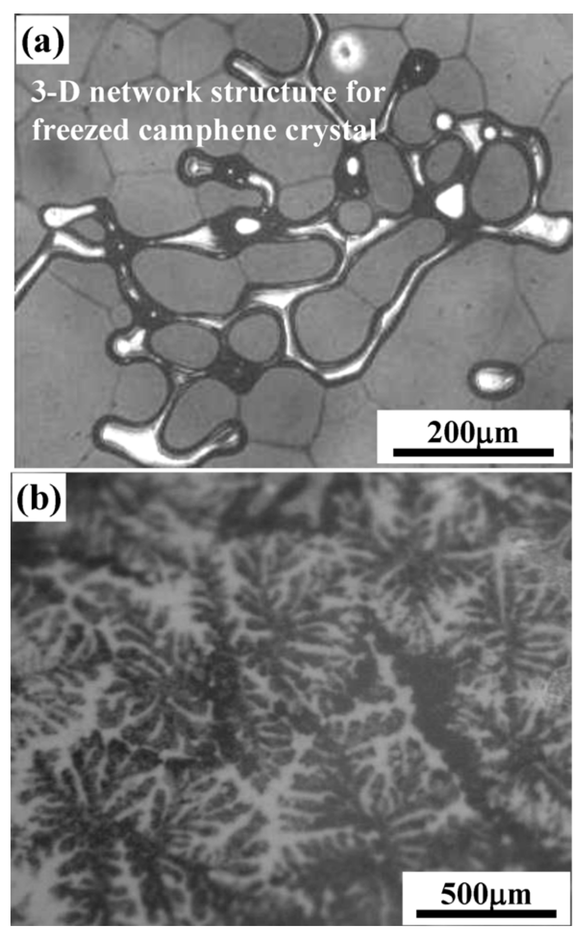

Fig. 2. Typical dendritic growth and particle rejection phenomenon for (a) camphene and (b) camphene–ceramic mixed slurry.

distribution was analyzed by a mercury intrusion porosimetry on certain parts of the sample with different freezing environment. Bulk density of the sintered samples was measured from sample mass and dimension, and relative density thus porosity was determined from the ratio of the measured bulk density to the theoretical one of the Al_2O_3 material. Three samples were used to determine the average porosity.

3. Results and discussion

Freeze casting of Al_2O_3/camphene slurry was employed to produce porous Al_2O_3 ceramics with graded and porous structure using different freezing temperature (i.e., liquid nitrogen, ice-water and room-temperature environment). Fig. 1 shows the schematical illustration of freeze casting system and pore structure formation during freezing casting. The system mainly consists of the camphene aligned channel, camphene dendritic crystal, the ceramic walls and the dense layer near the bottom and upper surface. This processing exploits the fact that camphene normally forms aligned channel, dendritic and equiaxed structure when solidified under a certain freezing temperature. During freeze casting, camphene gradually crystallized to form unidirectionally aligned channel, dendritic and equiaxed pore structure parallel to the freezing direction, running from low temperature of the bottom to high temperature of the top. Meanwhile, the ceramic particles were repelled by the growing camphene crystal to cohere together and form strong porous ceramic walls.

The solidification behavior of camphene and camphene/ceramic slurry was studied to understand the geometry and characteristics of camphene dendrite formation. Fig. 2(a) shows the development of dendritic branches along the freezing plane, which, in the image, runs towards the top left corner (indicated by the arrow). Although preheating of both the top and bottom slide glass was used to facilitate two-dimensional dendritic formation, there was still a difference in the temperature gradient posed by the low conductivity of the glass which could explain the difficulty in the development of secondary dendrites. Fig. 2(b) reveals a typical dendritic growth of camphene as well as Al_2O_3 ceramic particle rejection from the warm slurry. It can be found that the development of dendritic branches along the freezing plane, which, in the image, runs towards the top right corner. The particles are not only pushed along ahead of the advancing macroscopic solidification front composed of tips of growing dendrites, but are also connected on the spot after being rejected by dendrite arms.

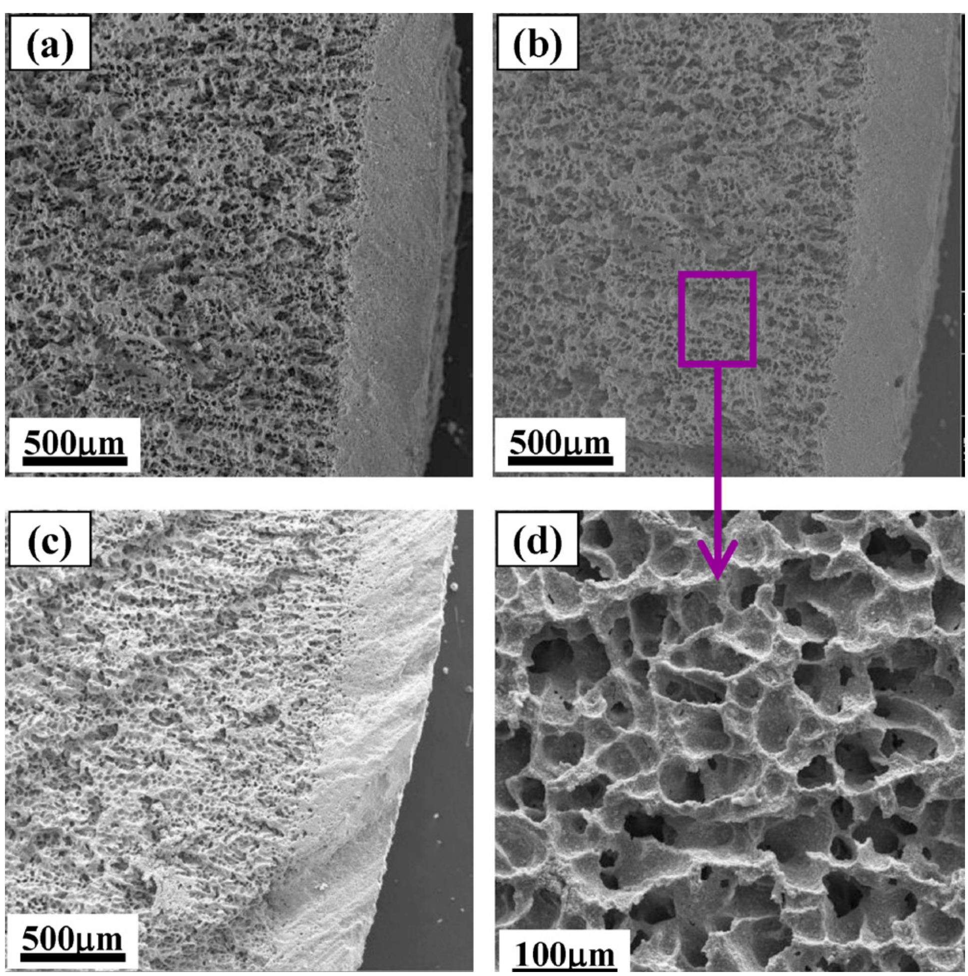

Fig. 3. Microstructure porous Al_2O_3 ceramics on cross-section near the upper surface. All samples fabricated by freeze-casting route having a dense/porous structure for different initial solid loadings. (a) 10 vol.%, (b)15 vol.% and (c) 20 vol.%.

Fig. 3(a)–(c) shows the typical microstructure prepared by camphene-based freeze-casting. It can be seen there is in situ formation of a dense/porous bi-layered Al_2O_3. A 0.5-mm-thick surface dense layer on the porous layer was successfully formed after sintering at 1400 °C for 2 h in air without any noticeable defects (e.g. interfacial cracking or debonding). The dense layer maintained identical thickness whether or not the initial solid content increased or reduced.

Generally, two evaporation stages will occur during the solidification of the ceramic/camphene slurry. In the early stages there is a rapid increase in weight loss which the evaporation of the molten camphene near the sample surface. The second stage is dominated by sublimation as the rate of evaporation is decreased and remains relatively constant [19]. In this study, warm slurry was cast at 60 °C, where the top surface of the cast body was exposed to air at 30 °C. Camphene has a relatively high-vapor pressure of 2×10^3 Pa at 55 °C [20], so the camphene near the surface in the cast body can evaporate readily until significant solidification has occurred, and it can increase the solid content on the surface.

As the warm Al_2O_3 ceramic/camphene slurry is cast into the mold that the bottom attached to copper plate mold at 0 °C, it experiences a temperature gradient, and therefore affects its solidification behavior. The heat is transferred from the solid, while the solidification of the slurry begins at the bottom surface and advancing towards the center of the cast body. A

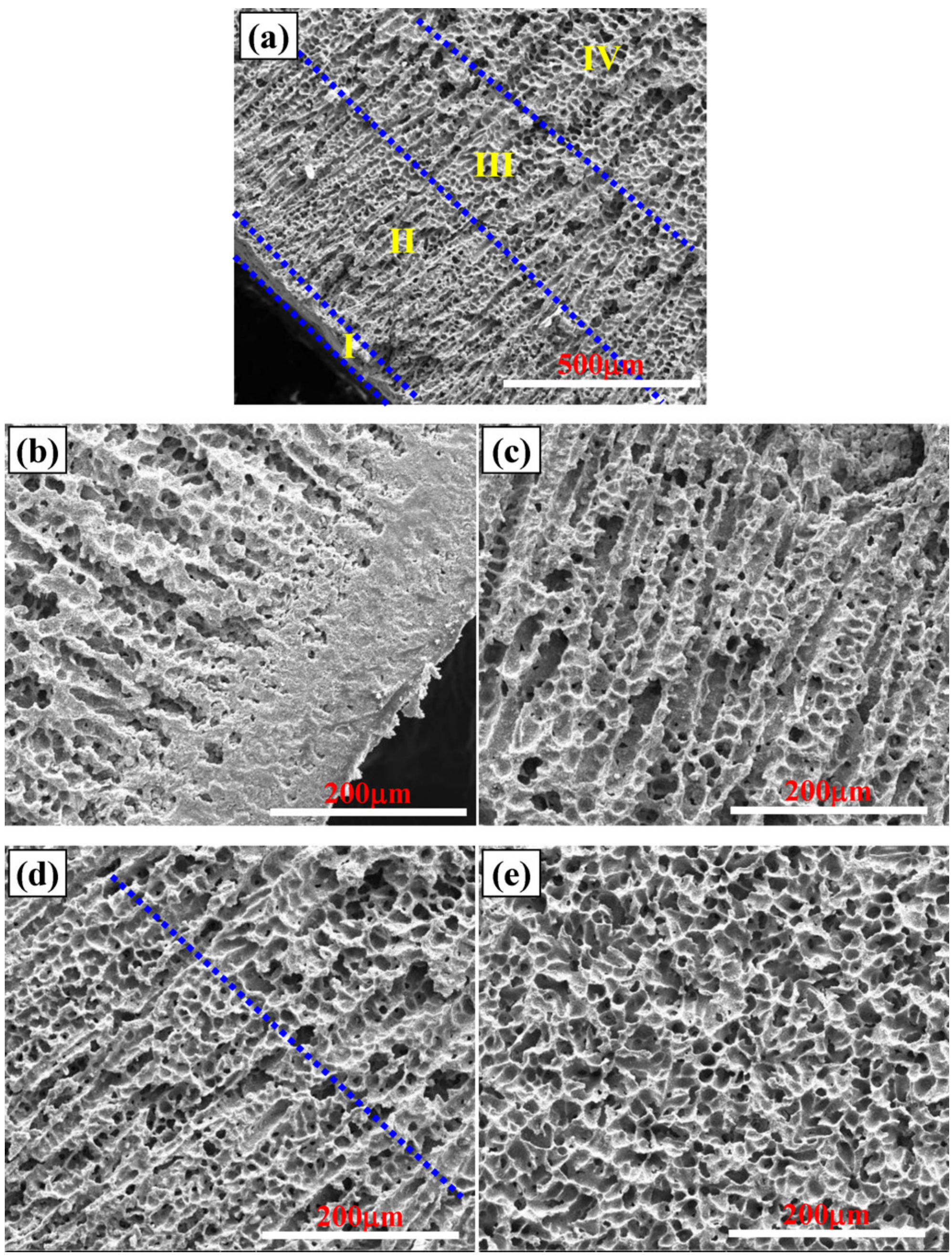

Fig. 4. Micro-morphology from the bottom surface to the central region frozen at ice-water environment for 15 vol% initial Al_2O_3 solid loading.

typical microstructure of the sample produced using ice-water as freezing condition is shown in Fig. 4(a).The samples prepared herein exhibited four different region (regions I–IV), each showing a different pore structure.

Fig. 4(b) shows a dense layer near the bottom surface with a thickness of ~200 μm formed uniformly onto the surface of the porous core, revealing that the dense layer are almost fully densified with negligible pores. It might be noticeable that the dense layer formed near the bottom surface because of the rapid solidification of the slurry near the cooper plate without overgrowth of the camphene dendrites and a concentration of the ceramic particles. It is proposed that a model based on 2-dimensional growth of the camphene from the bottom plate and a concentrated ceramic particles layer as the surrounding skin of the sample. More specifically, immediately after freeze casting, many camphene crystals nucleate on the mold wall and grow towards the center of the cast body, which pushes the ceramic particles into the remaining slurry.

Near the outer dense layer, the inner regions (zone II) were found to have aligned pore channels, as shown in Fig. 4(b). It is indicated that the possibility of controlling pore orientation by controlling parameters such as the heat transfer gradient and direction of freezing. Since the chilled mold was suddenly cooled with ice-water about 0 °C, the camphene rapidly cooled below its solidification temperature, and thus many nuclei of the camphene then form and begin to grow into the warm slurry. Under these conditions, most of the nuclei do not have a preferential orientation that corresponds to the direction of the heat conduction. Therefore, these camphene crystals cannot overgrow dendritically, and this results in the formation of long straight channels in the sintered sample.

Beyond the zone II, the temperature gradient near the die wall decreases and the camphene crystals began to grow dendritically in certain crystallographic directions. Those crystals with a preferential orientation close to the direction of heat flow, i.e., parallel to the mold wall, grow faster and can lead to their secondary dendritic formation. Fig. 4(d) shows a transition zone, which the pore structure changed from aligned pore channel to dendritic or equiaxial pore structure.

The morphologies of the pores formed in the central zones (zone IV) were distinctively different from those formed in zones I, II and III, as shown in Fig. 4(e). In the center of the cast body, some of the dendrite side arms might be melted off and then act as seeds for new dendrites, resulting in the formation of equiaxed pore structures. This unique pore structure in the center of the cast body might be related to the breakaway of the side arms from the primary dendrite of the camphene.

Fig. 5 shows the microstructure of the pore distribution in the freeze-casted porous Al_2O_3 ceramics at different locations from the cooled plate under different freezing temperature of −196, 0 and 25 °C. A greater alignment of the pores was observed (Fig. 5(a) and (b)) at lower freezing temperatures due to the larger driving force of the camphene dendrites during the solidification process as a direct consequence of heat transfer gradient.

The directionality of the solidification is critical in regards of the desired directionality of the porosity. When the slurries are solidified without any temperature gradient, i.e., for freezing environment at 25 °C, the camphene crystals can nucleate at any place and have no preferred growth direction, and thus no aligned pore channel appeared in the final structure (shown in Fig. 5(c)). This results in structures with a random orientation of the porosity. However, when the experimental setup allows imposing a defined temperature gradient (i.e., solidified at 0 and −196 °C), the solvent crystals are forced to grow along the temperature gradient. Provided the temperature field is carefully controlled,

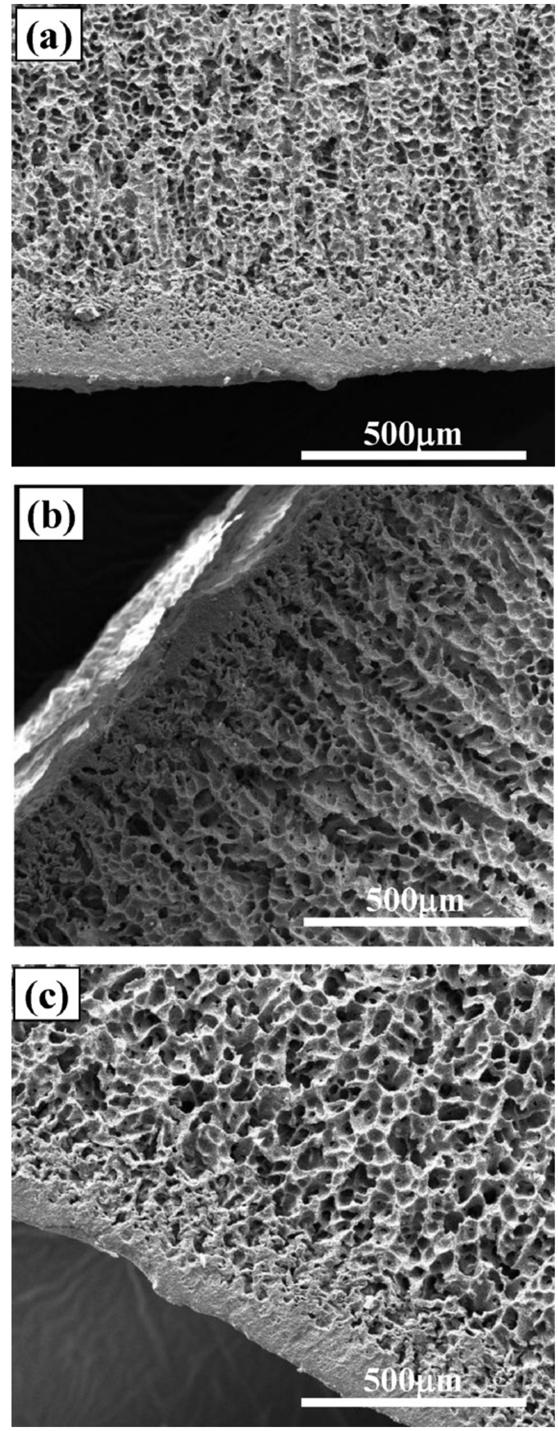

Fig. 5. Microstructure of freeze-casted porous Al_2O_3 ceramic with 15 vol% solid loading under different freezing environment at (a) liquid nitrogen (−196 °C); (b) ice-water (0 °C) and (c) 25 °C environment.

camphene crystals and hence resulting pore channels can run through the final sample, reaching dimensions of a few centimeters.

4. Conclusions

Highly porous Al_2O_3 ceramics with graded and porous structures have been fabricated by a camphene-based freeze-casting method. The typical pore structure includes surface dense layer, aligned channel, dendritic and equiaxed pore using ice-water and liquid nitrogen as cooled agent. The formation of dense surface layer is attributed to the evaporation of camphene, due to its high-vapor pressure during solidification. For the dense layer on the bottom side, it is mainly due to the rapid solidification rate, accordingly, allowed no overgrowth of the camphene dendrites and a concentration of the ceramic particles.

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References

[1] S. Deville, E. Saiz, A.P. Tomsia, Freeze casting of hydroxyapatite scaffolds for bone tissue engineering, Biomaterials 27 (2006) 5480–5489.
[2] S.F. Liu, Y.P. Zeng, D.L. Jiang, Fabrication and characterization of cordierite-bonded porous SiC ceramics, Ceram. Int. 35 (2009) 597–602.
[3] L.F. Hu, C.A. Wang, Effect of sintering temperature on compressive strength of porous yttria-stabilized zirconia ceramics, Ceram. Int. 36 (2010) 1697–1701.
[4] A. Macchetta, I.G. Turner, B.C.R. owen, Fabrication of HA/TCP scaffolds with a graded and porous structure using a camphene-based freeze-casting method, Acta Biomater. 5 (2009) 1319–1327.
[5] D.C. Clupper, J.J. Mecholsky, G.P. LaTorre, D.C. Greenspan, Bioactivity of tape cast and sintered bioactive glass–ceramic in simulated body fluid, Biomaterials 23 (2002) 2599–2606.
[6] M. Boaro, J.M. Vohs, R.J. Gorte, Synthesis of highly porous yttria stabilized zirconia by tape-casting methods, J. Am. Ceram. Soc. 86 (2003) 395–400.
[7] Y.H. Koh, E.J. Lee, B.H. Yoon, J.H. Song, H.E. Kim, Effect of polystyrene addition on freeze casting of ceramic/camphene slurry for ultrahigh porosity ceramics with aligned pore channels, J. Am. Ceram. Soc. 89 (2006) 3646–3653.
[8] H. Schmidt, D. Koch, G. Grathwohl, Micro-/macroporous ceramics from preceramic precursors, J. Am. Ceram. Soc. 84 (2001) 2252–2255.
[9] S. Deville, E. Saiz, R.K. Nalla, A. Tomsia, Freezing as a path to build complex composites, Science 311 (2006) 515–518.
[10] R.F. Chen, Y. Huang, C.A. Wang, J.Q. Qi, Ceramics with ultra-low density fabricated by gelcasting: an unconventional view, J. Am. Ceram. Soc. 90 (2007) 3424–3429.
[11] B.H. Yoon, W.Y. Choi, H.E. Kim, J.H. Kim, Y.H. Koh, Aligned porous alumina ceramics with high compressive strengths for bone tissue engineering, Scripta Mater. 58 (2008) 537–540.
[12] Y.H. Koh, J.J. Sun, H.E. Kim, Freeze casting of porous Ni–YSZ cermets, Mater. Lett. 61 (2007) 1283–1287.
[13] T. Waschkies, R. Oberacker, M.J. Hoffmann, Control of lamellae spacing during freeze casting of ceramics using double-side cooling as a novel processing route, J. Am. Ceram. Soc. 92 (2009) S79–S84.
[14] K. Araki, J.W. Halloran, Porous ceramic bodies with interconnected pore channels by a novel freeze casting technique, J. Am. Ceram. Soc. 88 (2005) 1108–1114.
[15] E. Cadirli, N. Marasli, B. Bayender, Dependency of the microstructure parameters on the solidification parameters for camphene, Mater. Res. Bull. 35 (2000) 985–995.
[16] L.L. Ren, Y.P. Zhen, D.L. Jiang, Fabrication of gradient pore TiO_2 sheets by a novle freeze-tape-casting process, J. Am. Ceram. Soc. 90 (2007) 3001–3004.
[17] R.F. Chen, C.A. Wang, Y. Huang, L.G. Ma, W.Y. Lin, Ceramics with special porous structures fabricated by freeze-gelcasting: using tert-butyl alcohol as a template, J. Am. Ceram. Soc. 90 (2007) 3478–3484.
[18] S.W. Sofie, Fabrication of functionally graded and aligned porosity in thin ceramic substrates with the novel freeze–tape-casting process, J. Am. Ceram. Soc. 90 (2007) 2024–2031.
[19] Y.H. Koh, I.K. Jun, J.J. Sun, H.E. Kim, In situ fabrication of a dense/porous bi-layered ceramic composite using freeze casting of a ceramic-camphene slurry, J. Am. Ceram. Soc. 89 (2006) 763–766.
[20] C.Q. Hong, X.H. Zhang, J.C. Han, J.C. Du, W.B. Han, Ultra-high-porosity zirconia ceramics fabricated by novel room-temperature freeze-casting, Scripta Mater. 60 (2009) 563–566.