Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 718−722
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effects of alcohol additives on pore structure and morphology of freeze-cast ceramics

Jing ZENG, Yan ZHANG, Ke-chao ZHOU, Dou ZHANG

State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

Received 17 April 2013; accepted 11 October 2013

Abstract: The porous alumina ceramics with lamellar structure were fabricated successfully by freeze casting. The viscosities of alumina slurries, pore structures, porosities and mechanical properties of the sintered ceramics were investigated by introducing both types of alcohols as water solidification modifier into the initial slurries, such as ethanol and 1-propanol. With the addition of ethanol or 1-propanol, the viscosities of slurries increased and porosities of sintered ceramics decreased. The compressive strengths of the sintered porous alumina ceramics were improved due to a good connectivity between lamellae with the addition of both types of alcohols. The lowest porosities of 68.52% and 73.72% and highest compressive strengths of 18.2 MPa and 15.0 MPa were obtained by the addition of 30% ethanol in mass fraction and 1-propanol, respectively.

Key words: alumina ceramic; lamellar porous material; ethanol; 1-propanol

1 Introduction

Porous materials have attracted much attention due to their superior functions and a wide range of applications varying from bone substitutes to part for the automotive industry including ceramic filters, catalyst support, porous electrode, gas distributors, biomaterials and insulators [1−3]. Nowadays, various fabrication techniques of porous ceramics have been developed such as gel casting [4], direct foaming [5], polymer foam replication [6] and freeze casting [7]. Freeze casting as a simple, versatile, low-cost, environmentally friendly and complex-shape-forming method is widely used to prepare porous materials with aligned pores [4,8]. During the freeze casting process, the solvent is frozen under a certain freezing temperature to push the ceramic particles into spaces between adjacent frozen lamellaes, followed by freeze drying under vacuum by sublimation of ice to prevent the generation of cracks, shrinkage and warp which usually exist in common drying of the green body [9].

Recently, many researches on alumina porous material by freeze casting with the addition of additives were investigated, exhibiting a strong correlation between the kind and concentration of the employed additives and the morphology and mechanical properties of ice-templated porous ceramics. KOH et al [10] investigated the effect of polystyrene (PS) addition as organic binder on the freezing behavior of a very dilute alumina/camphene slurry for the fabrication of ceramics with aligned pore channels and found that the addition of PS can result in the formation of porous ceramic with ultra-high porosities more than 88%, and no collapse was observed in the porous structure. It is known that many cryoprotectants, also known as antifreeze agents, show considerable decrease of freezing points [11] and several possible cryoprotectants have been considered to modify the formation of green bodies for obtaining different porous structure [12]. For example, SOFIE and DOGAN [4] reported that the glycerol additive resulted in uniform pore channels of the alumina ceramics.

Since ethanol or 1-propanol can act as cryoprotectants or water solidification modifier [13], our work was to add different alcohols as additives and explore their influence on the rheological properties of aqueous slurries and the microstructures of freeze-cast ceramics, and to characterize the mechanical properties of porous ceramics.

Foundation item: Projects (20110162130003, 20110162110044) supported by the PhD Programs Foundation of Ministry of Education of China; Projects (51172288, 51072235) supported by the National Natural Science Foundation of China; Project (11JJ1008) supported by Hunan Provincial Natural Science Foundation of China
Corresponding author: Ke-chao ZHOU; Tel: +86-731-88836418; E-mail: zhoukc2@csu.edu.cn
DOI: 10.1016/S1003-6326(14)63116-2

2 Experimental

2.1 Materials

Commercially available alumina powder (AES-11, Sumitomo Chemical Co., Ltd., Tokyo, Japan) with an average particle size of 0.5 μm and purity of 99.8% and the deionized water were used as the start material and freezing vehicle, respectively. Ammonium polyacrylate (Hydro Disper A160, Shenzhen Highrun Chemical Industry Co., Ltd., China) and PVA (420, Kuraray Co., Ltd., Japan) were used as the dispersant and binder, respectively. In addition, ethanol (Tianjin Hengxing Chemical Industry Co., Ltd., China) and 1-propanol (Tianjin Kermel Chemical Industry Co., Ltd., China) were used as additives.

2.2 Preparing processing

The deionized water, ammonium polyacrylate (1% of alumina powder in mass fraction), a certain amount of alumina powder, PVA binder (1% of alumina powder in mass fraction), ethanol or 1-propanol with different concentrations (10%, 30% of the deionized water in mass fraction) was added to the mixing container and ball-mixed at room temperature for 24 h with zirconia balls, followed by being de-aired through stirring in a vacuum desiccator to remove air bubbles completely. The initial solid concentration of alumina slurry was kept as 10% in volume fraction. The slurry containing same solid content without any alcohols was also prepared for the comparison purpose. Then the slurry was poured into a transparent cylindrical polydimethylsiloxane (PDMS) mould with 10 mm in diameter and 15 mm in height. Then the mould was transported to a copper cold finger placed in a liquid nitrogen container. The frozen bodies were then taken out of the mould and put into a vacuum chamber of a freeze-drier (FD-1A-50, Beijing Boyikang Medical Equipment Co., China) under 10 Pa and −53 °C to be free-dried for 24 h. The dried bodies were sintered at 1500 °C in air for 2 h, with heating rate of 5 °C/min and cooled to room temperature in furnace naturally.

2.3 Characterization

The viscosities of the ceramic slurries were investigated by a rheometer (AR 2000, TA Instrument, New Castle, DE) at a shear rate from 1 to 500 s^{-1} at 25 °C using a stainless steel parallel-plate configuration (diameter: 40 mm; gap: 500 μm). The sintered density, which was measured through Archimedes principle, was divided by the theoretical density of alumina, 3.98 g/cm^3, to obtain the relative density and the total porosity. Every point was measured at least three times. Environmental scanning electron microscope (ESEM, Quantan 200, JEOL, Tokyo, Japan) was used to measure the microstructures on fracture surfaces of the sintered bodies coated with a thin layer of gold. To determine the compressive strength of the sintered body, an electronic universal testing machine (KD11-2, Shenzhen KEJALI Technology Co. Ltd., China) was used at a crosshead speed of 0.2 mm/min.

3 Results and discussion

3.1 Viscosities of slurries

Figure 1 shows the effects of the alcohol concentrations on the viscosities of 10% solid loading slurries at the shear rate from 1 to 500 s^{-1}. All viscosities of alumina slurries were in a range of additive concentrations from 0 to 30%. With the increase of the shear rate, the viscosities of all slurries decreased and showed the shear thinning behavior. It is obvious that the slurries with ethanol or 1-propanol showed higher viscosities than those without the addition of alcohols, similar to the trend obtained by ZHANG et al [14]. At the same shear rate, the viscosities of slurries increased with the increase of the concentration of both types of alcohols from 0 to 30%. The slurries without and with the addition of 1-propanol showed little difference in viscosity at all shear rates. The viscosity of slurry with 30% ethanol was nearly 5−10 times that without additive.

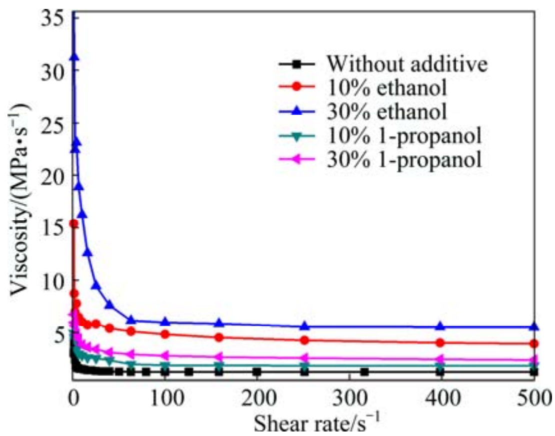

Fig. 1 Viscosities of alumina slurries prepared using 10% solids and various concentrations of different alcohol additives at shear rate of 1−500 s^{-1}

3.2 Microstructure

Figure 2 shows the SEM micrographs of sintered porous Al_2O_3 ceramics prepared from 10% solids loading slurries with different concentrations of ethanol ranging from 10% to 30%. The porous architecture with lamellar channels of long-range order as the replica of the ethanol−water mixture dendrites can be approximately found parallel to the macroscopic ice growth direction, as

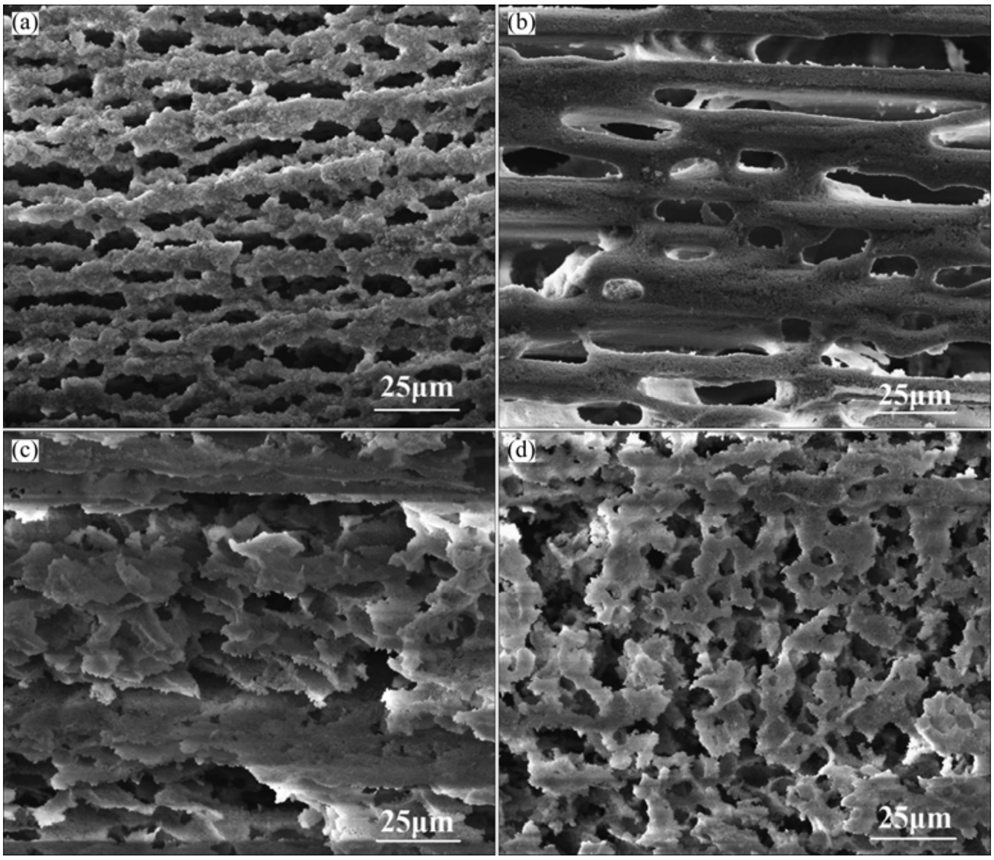

Fig. 2 SEM images of porous alumina ceramics prepared by various ethanol concentrations of 10% (a, b) and 30% (c, d) (The left and right images show the pores formed parallel and perpendicular to the ice front, respectively)

shown in Figs. 2(a) and (c). With the increase of the ethanol concentration, the lamellar pore width decreased as a result of variation of viscosity, which corresponds well to our previous report using hydroxyapatite as the raw material [15]. During the solidification of the aqueous slurry with the addition of ethanol, most ceramic particles in the slurry were rejected by the growing dendrites and became intensive between the dendrite arms or the neighboring dendrites. In the direction perpendicular to the ice top (Figs. 2(b) and (d)), this phenomenon can be observed more directly. Connections in a small bonding area between the ceramic adjacent lamellae with pore size of 10−80 μm were observed with the addition of 10% ethanol. When the concentration was up to 30%, a nearly dense ceramic wall with the pore size of 5−10 μm was achieved.

Figure 3 shows the SEM images of sintered porous Al_2O_3 ceramics prepared from 10% solids loading slurries with different concentrations of 1-propanol ranging from 10% to 30%. With the addition of 10% 1-propanol, the long-range ordered pore structure as the replica of the 1-propanol-water mixture dendrites is more easily observed in the direction both parallel and perpendicular to the ice front, as shown in Figs. 3(a) and (b). With the increase of 1-propanol concentration, the well aligned pore structure disappears but the adjacent ceramic lamellae joints together. Meanwhile, a twist due to the growing of 1-propanol-water mixture dendrite and a nearly dense structure can be obtained.

In our previous work [17], the long-range ordered lamellar architecture can be clearly observed from the sintered porous Al_2O_3 ceramic without any alcohol additives. However, with the addition of 30% alcohol, the ceramic walls surrounding pore channels are almost fully dense for both types of alcohol additives. The differences in microstructures may be caused by the equilibrium among the diffusion rate of alcohol, ice crystal growth rate and the alumina particle expelling rate. On the other hand, high viscosity of the slurry also inhibited the expelling of alumina particles from the growing ice crystals on a certain extent [14]. Due to the higher viscosity of the suspensions prepared by 30% both types of alcohols, the freezing front experienced higher resistance in the freeze-casting process and obtained a relatively dense structure, as shown in Fig. 2(c) and Fig. 3(b). After the unidirectional process, sublimation of the ice bonds between ceramic particles would result in many small-pore structures in the ceramic wall which were not eliminated by the following sintering process. Moreover, the addition of

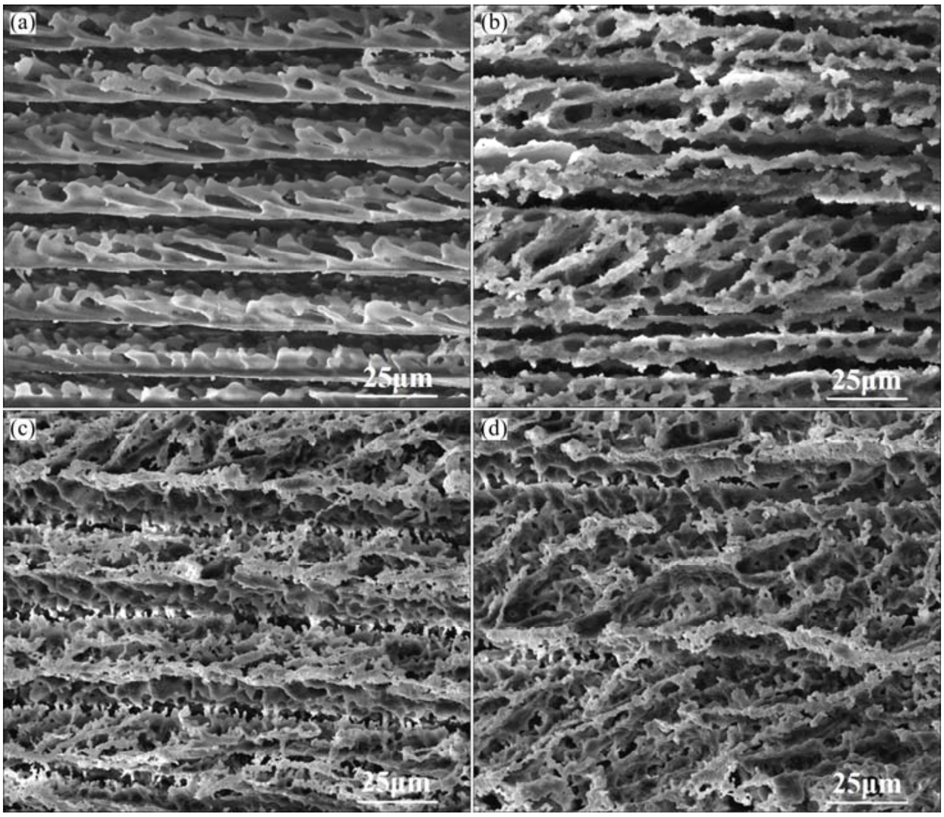

Fig. 3 SEM images of porous alumina ceramics prepared by various 1-propanol concentrations of 10% (a, b), 30% (c, d) (The left and right images show the pores formed parallel and perpendicular to the ice front)

alcohol changed the hydrogen bonding of water. It is known that in the ethanol−water mixtures and 1-propanol−water mixtures, both the hydroxyl hydrogen and oxygen play the roles of proton donor and acceptor in the formation of hydrogen bonds, respectively. Furthermore, the hydrogen bonds between the hydroxyl hydrogen and oxygen became strong with the increase of alcohol concentration, resulting in the strong hydrogen-bonding interactions between alcohol and water molecule, meanwhile water molecules in the mixtures were present around the hydroxyl group of alcohols to form hydrogen bonds with the hydroxyl groups [13], which may disrupt the crystallization of ice and result in the differences in the microstructure of porous alumina ceramic[4]. The mechanism of the interaction between the hydrogen bonding in water and ice, however, was not clearly understood and required further investigation. In addition, as shown in Table 1, the addition of ethanol or 1-propanol had different effect on the freezing points of alcohol−water mixtures, which may result in different microstructures of sintered porous alumina ceramics.

3.3 Porosity and compressive strength

Figure 4 shows the effects of different concentrations of both types of alcohols prepared from 10% solids loading slurries on the compressive strength and porosities of porous Al_2O_3 ceramics. With the addition of ethanol ranging from 0 to 30%, the porosity decreased from 74.35% to 68.52% and the corresponding compressive strength increased from 13.4 MPa to 18.2 MPa. The porosity decreased from 74.35% to 73.72% and the corresponding compressive strength increased from 13.4 MPa to 15.0 MPa with the addition of the 1-propanol in the same range. The addition of ethanol resulted in a lower porosity than the samples with 1-propanol for all the concentrations of 10% solids loading. For the compressive strength, the trend was reversed. The compressive strength of the porous ceramics prepared by the ethanol was around 1.1 times that of the ceramics prepared by the 1-propanol additive at the same concentration, as shown in Fig. 4. The increase of compressive strength may be attributed to the varying of the connection between ceramic lamellaes, exhibiting a great potential in the loading biological application [18].

Table 1 Freezing points of alcohol−water mixture [16]

Additive concentration/%	Freezing point/°C	
	Ethanol-water mixture	1-propanol-water mixture
10	−4.0	−2.3
30	−14.0	−8.3

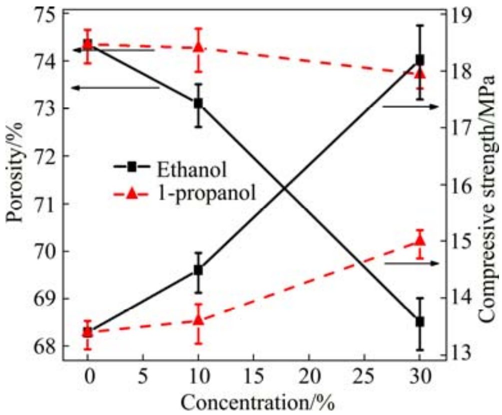

Fig. 4 Porosity and compressive strength of porous Al_2O_3 ceramic as function of concentration of both types of alcohols

4 Conclusions

The effects of the addition of ethanol or 1-propanol on the rheological properties of alumina ceramic slurries, microstructure, porosity and compressive strength of the porous alumina by freeze casting the aqueous alumina slurries with 10% solid loading were investigated. With the increase of alcohol concentrations from 0 to 30%, the viscosities of the slurries increased. Ethanol addition with concentration ranging from 0 to 30% resulted in change in the viscosity, or up to 5−11 times. The strong hydrogen bonding interactions between alcohols and water molecules may disrupt the crystallization of ice, cause a good connectivity between lamellaes of porous alumina ceramic and thus result in a higher compressive strength. With the addition of 30% ethanol and 1-propanol, the lowest porosities of 68.52% and 73.72% and the highest compressive strengths of 18.2 MPa and 15.0 MPa were obtained, respectively. The result demonstrates a great potential in the loading biological application.

References

[1] GAO Hai-yan, HE Yue-hui, ZOU Jin, XU Nan-ping, LIU C T. Tortuosity factor for porous FeAl intermetallics fabricated by reactive synthesis [J]. Transactions of Nonferrous Metals Society of China, 2012, 22: 2179−2183.

[2] MORITZ T, RICHTER H J. Ice-mould freeze casting of porous ceramic components [J]. Journal of the European Ceramic Society, 2007, 27: 4595−4601.

[3] OH S T, CHANG S Y, SUK M J. Microstructure of porous Cu fabricated by freeze-drying process of CuO/camphene slurry [J]. Transactions of Nonferrous Metals Society of China, 2012, 22: s688−s691.

[4] SOFIE S W, DOGAN F. Freeze casting of aqueous alumina slurries with glycerol [J]. Journal of the American Ceramic Society, 2001, 84: 1459−1464.

[5] BARG S, SOLTMANN C, ANDRADE M, KOCH D, GRATHWOHL G. Cellular ceramics by direct foaming of emulsified ceramic powder suspensions [J]. Journal of the American Ceramic Society, 2008, 91: 2823−2829.

[6] FU Q, RAHAMAN M N, BAL B S, BROWN R F, DAY D E. Mechanical and in vitro performance of 13-93 bioactive glass scaffolds prepared by a polymer foam replication technique [J]. Acta Biomater, 2008, 4: 1854−1864.

[7] DEVILLE S, SAIZ E, NALLA R K, TOMSIA A P. Freezing as a path to build complex composites [J]. Science, 2006, 311: 515−518.

[8] HONG C Q, DU J C, LIANG J, ZHANG X H, HAN J. Functionally graded porous ceramics with dense surface layer produced by freeze-casting [J]. Ceramics International, 2011, 37: 3717−3722.

[9] DEVILLE S. Freeze-casting of porous ceramics: A review of current achievements and issues [J]. Advanced Engineering Materials, 2008, 10: 155−169.

[10] KOH Y H, LEE E J, YOOH B H, SONG J H, KIM H E, KIM H W. Effect of Polystyrene addition on freeze casting of ceramic/camphene slurry for ultra-high porosity ceramics with aligned pore channels [J]. Journal of the American Ceramic Society, 2006, 89: 3646−3653.

[11] LOTTIN O, EPIARD C. Dependence of the thermodynamic properties of ice slurries on the characteristics [J]. International Journal of Refrigeration, 2001, 24: 455−467.

[12] HUGGINS C E. Frozen blood [J]. Freeze Drying and Advanced Food Technology, 1975, 160: 51−60.

[13] MIZUNO K, MIYASHITA Y, SHINDO Y. NMR and FT-IR studies of hydrogen bonds in ehanol-water mixture[J]. Journal of Physical and Chemistry, 1995, 99: 3225−3228.

[14] ZHANG Y M, HU L Y, HAN J C, JIANG Z H. Freeze casting of aqueous alumina slurries with glycerol for porous ceramics [J]. Ceramics International, 2010, 36: 617−621.

[15] ZHANG Y, ZHOU K C, BAO Y X, ZHANG D. Effects of rheological properties on ice-templated porous hydroxyapatite ceramics [J]. Materials Science and Engineering C, 2012, 33: 340−346.

[16] MU Guang-zhao. Practical solvents handbook [M]. Shanghai: Science and Technology Press, 1990: 153−157. (in Chinese)

[17] ZHANG D, ZHANG Y, XIE R, ZHOU K C. Freeze gelcasting of aqueous alumina suspensions for porous ceramics [J]. Ceramics International, 2012, 38: 6063−6066.

[18] DEVILLE S, SAIZ E, TOMIA A P. Freeze casting of hydroxyapatite scaffolds for bone tissue engineering [J]. Biomaterials, 2006, 27: 5480−5489.

醇类添加剂对冷冻浇注陶瓷的多孔结构及形貌的影响

曾 婧，张 妍，周科朝，张 斗

中南大学 粉末冶金国家重点实验室，长沙 410083

摘 要：采用冷冻浇注法制备具有层状多孔结构的氧化铝陶瓷。通过添加乙醇和正丙醇两种类型的醇类来改变水的凝固点，研究醇类的添加量及浆料的固态含量对水基氧化铝浆料的黏度、多孔陶瓷的微观结构、孔隙率和力学性能的影响。结果表明：随着浆料中乙醇和正丙醇含量的增加，浆料的黏度增加，氧化铝陶瓷的孔隙度降低；醇类的加入会使片层之间具有较好的连接从而增加多孔氧化铝陶瓷的抗压强度；当乙醇或正丙醇的添加量为 30%(质量分数)时，对应的孔隙度最低，分别为 68.52 %和 73.72%，而抗压强度最高，分别为 18.2 MPa 和 15.0 MPa。

关键词：氧化铝陶瓷；层状多孔材料；乙醇；正丙醇

(Edited by Hua YANG)