ELSEVIER Science Press

Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 2466−2472

Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Liquid drying of BeO gelcast green bodies using ethanol as liquid desiccant

Xiao-feng WANG, Chao-qun PENG, Ri-chu WANG, Yue-hua SUN, Yi-xin CHEN

School of Materials Science and Engineering, Central South University, Changsha 410083, China

Received 25 March 2015; accepted 25 May 2015

Abstract: BeO gelcast green bodies were dried by liquid drying method with liquid desiccant ethanol. Effects of ethanol concentration, solids loading and aspect ratio of green body on the moisture and shrinkage of green bodies were studied through measuring mass and dimension. Additionally, liquid drying stress was analyzed and a model of the initial stage drying stress was established. The results show that higher ethanol concentration, lower solids loading and higher aspect ratio of gelcast green bodies increase the drying rate. Increasing the ethanol concentration decreases the shrinkage rate. Liquid drying stress is generated due to a non-uniform drying rate. During the process of liquid drying, the inner drying stress of the green body changes from compressive stress to tensile stress, while the outer drying stress changes from tensile stress to compressive stress.

Key words: BeO; gelcasting; green body; liquid desiccant; ethanol; drying rate; shrinkage rate; drying stress

1 Introduction

Gelcasting is a near net shape technique for fabricating high-quality complex ceramics developed during the early 1990s [1−4]. This technology integrates the knowledge of polymer chemistry with the traditional ceramic forming techniques to improve the current ceramic gel-forming techniques vastly. In the nearly 20 years since its development, gelcasting has been widely used in areas such as composite materials, porous materials and functional materials, while few practical applications have been found on an industrial scale [5,6]. One of the major reasons for this technique's underuse is that it is difficult to dry the gelcast green bodies [7−9]. Traditionally, the drying of gelcast parts is conducted with controlled temperature and humidity. Also, in order to avoid defects like surface cracking, the drying rate cannot be too fast (especially for a thick-walled body of large size), which results in low efficiency of this drying method [10]. Studies conducted by HARN et al [11,12] have shown that the time required for complete drying of green bodies with this method is at least 24 h.

In order to solve the drying problem of gelcast green body, JANNEY and KIGGANS [8] proposed the liquid desiccant drying method (also known as replacement drying) [13−15], which had previously been used for wood drying. The basic mechanism underlying this method is immersing the green body into a liquid desiccant; the solvent (water) is excluded from the body since the osmotic pressure of the solvent within the liquid desiccant (such as water) is larger than that within the green body [8]. Compared with the traditional heating/drying methods, the liquid desiccant method is more efficient, resulting in more homogeneous drying with fewer drying defects like bending, surface wrinkling, and cracking [8,16−18]. BARATI et al [16] used an aqueous solution of polyethylene glycol (PEG1000) as the liquid desiccant for Al_2O_3 green bodies, which resulted in the removal of 30% moisture in 3 h. TRUNEC [18] investigated the influence of the molecular mass of various polyethylene glycols on the drying efficiency. Researches on wood drying using liquid desiccants have shown that ethanol is a highly efficient, energy-saving, and environmentally-friendly liquid desiccant [19], while few have reported the use of this solvent in liquid desiccant drying of gelcast green bodies.

In the present work, ethanol was used as the liquid desiccant for liquid drying of BeO gelcast green bodies, and the effects of ethanol concentration, solids loading and size of green bodies on the drying rate of BeO gelcast green bodies were studied. The liquid drying stress was analyzed and a drying stress model was

---

Foundation item: Project (51202296) supported by the National Natural Science Foundation of China; Project (20120162120006) supported by the Specialized Research Fund for the Doctoral Program of Higher Education of China

Corresponding author: Ri-chu WANG; Tel/Fax: +86-731-88836638; E-mail: wrc@csu.edu.cn

DOI: 10.1016/S1003-6326(15)63863-8

established for the initial stage of the liquid drying process.

2 Experimental

2.1 Materials

Experimental materials used in this work are listed in Table 1.

2.2 Experimental procedure

BeO green bodies were prepared by typical gelcasting processing. Firstly, BeO powders of high purity were obtained after high-temperature calcination treatment and ball-milled treatment [20]. The powders were then added into a solution that contained amounts of acryl amide monomer (AM), cross-linker N,N′-methylenebisacrylamide (MBAM), and dispersant NH_4PAA was dissolved in deionized water. After 24 h of ball milling (beryllium oxide, 1:1 mass ratio of ball to materials), BeO powder suspensions with different solids loadings were obtained. The suspensions were degassed under vacuum, and added with initiator ammonium persulfate (APS, 10%) and catalyst N,N,N',N'-tetramethylethylenediamine (TEMED) at room temperature (25 °C). The solution was then poured into a mold. After curing reaction within suspensions, the green bodies were removed from the mold and dried.

2.3 Measurement and characterization

Changes in moisture and size of the green body during the drying process were monitored using the gravimetric method and size measurement method, respectively. The green body newly removed from the mold was immersed into the liquid desiccant of ethanol. The body was taken out every 10 min (or 30 min) from the desiccant, and the residual liquid on the surface was absorbed by cotton, after which the mass and the size of the body were measured. An electronic balance (Mettler-Toledo Co., Ltd., China) with an accuracy of 0.001 g was used to measure the mass and a vernier caliper (Harbin Measuring and Cutting Tool Group Co., Ltd., China) with an accuracy of 0.001 mm was used to measure the size.

3 Results and discussion

3.1 Effects of ethanol concentration

Figure 1 shows the effects of ethanol (the liquid desiccant) concentration on moisture and shrinkage of the green body. At a higher ethanol concentration, there

Table 1 Raw materials for experiment

Raw material	Function	Molecular formula	Supplier
BeO	Powder	BeO	Shuikoushan Nonferrous Metals Group Co., Ltd., China
Acrylamide (AM)	Monofunctional monomer	$C_2H_3CONH_2$	Shanghai Chemical Reagent Co., Ltd., China
N,N′,-methylene bis-acrylamide (MBAM)	Difunctional monomer	$(C_2H_3CONH_2)_2CH_2$	Shanghai Chemical Reagent Co., Ltd., China
N,N,N',N'-tetramethy-lethylenediamine(TEMED)	Catalyst	$C_6H_{16}N_2$	Beijing Chemical Reagent Co., Ltd., China
Ammonium persulfate (APS)	Initiator	$(NH_4)_2S_2O_8$	Changsha Organic Chemical Reagent Co., Ltd., China
Ammonium polyacrylate	Dispersant	NH_4PAA	Toagosei Chemical Reagent Co., Ltd., Japan
Ethanol	Liquid desiccant	CH_3CH_2OH	Changsha Organic Chemical Reagent Co., Ltd., China
Deionized water	Solvent	H_2O	Self-produced

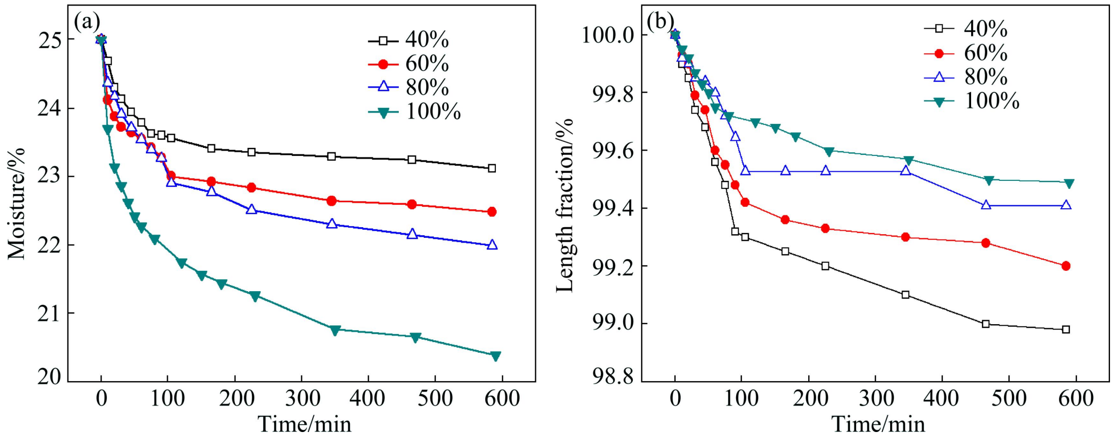

Fig. 1 Effects of ethanol concentration on moisture (a) and length faction (b) of gelcast green body (The solids loading of the green body is 50 % in volume faction)

is a larger moisture gradient between the inside and outside of the green body, as a result, the moisture decreases faster, causing a significant reduction in the moisture. This result is in agreement with that reported by BARATI et al [16] who used PEG1000 solutions with various concentrations to dry Al_2O_3 green bodies. They thought that there was an osmotic pressure gradient between the two media (inside and outside of the green body), and therefore, higher liquid desiccant concentration and larger osmotic pressure gradient would result in a higher drying rate of the body. Figure 1 also shows that at a lower ethanol concentration, the shrinkage of the body is larger. This is because at a lower ethanol concentration, the drying rate is lower, which gives the body a longer time to release the stress generated during the drying process. The polymer network within the body shrinks gradually, resulting in larger shrinkage of the body.

3.2 Effects of solids loading

Figure 2 shows the effects of solids loading on moisture and shrinkage of the gelcast green body using ethanol as a liquid desiccant. Green bodies with higher solids loading have higher initial moisture, which allows for easy replacement of the moisture within the bodies. As a result, the drying rate of the green body is higher, and the reduction in moisture is larger. The shrinkage rate and shrinkage amount also show a corresponding increase. The results obtained are consistent with those obtained by BARATI et al [16].

3.3 Effects of green body size

Figure 3 shows the effects of green body size on moisture and shrinkage during the drying process with ethanol as the liquid desiccant. Compared with green bodies with a height to aspect ratio of 1:1, those with a height to aspect ratio of 5:1 have a larger contact area on the surface with the liquid desiccant, which results in a higher replacement rate of water. Meanwhile, the replacement rate between moisture and liquid desiccant is much higher in the radial direction than in the vertical direction, which gives rise to change in body moisture. Figure 3 also shows that a green body with a height to aspect ratio of 5:1 is comparatively longer and has

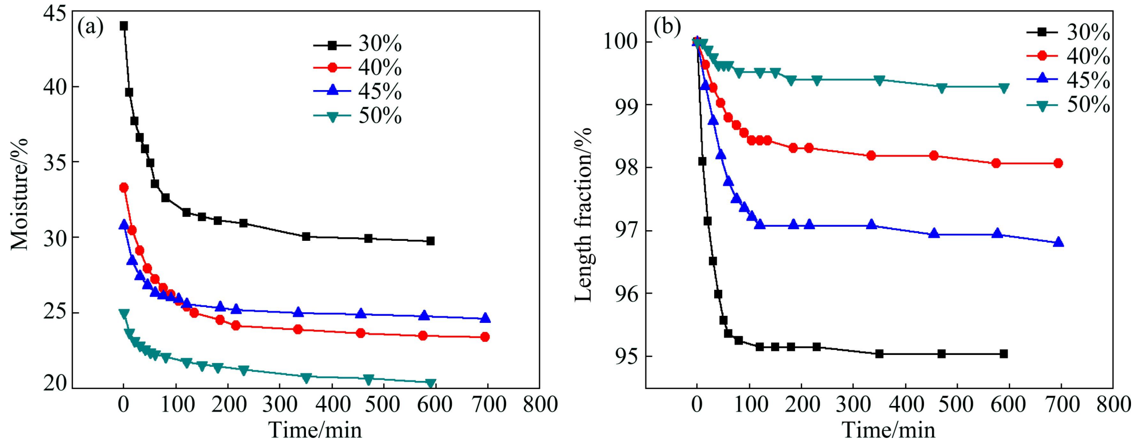

Fig. 2 Effects of solids loading on moisture (a) and length faction (b) in gelcast green body during drying with ethanol (The solids loading of the green body is 50 % in volume faction. The ethanol concentration is 100%)

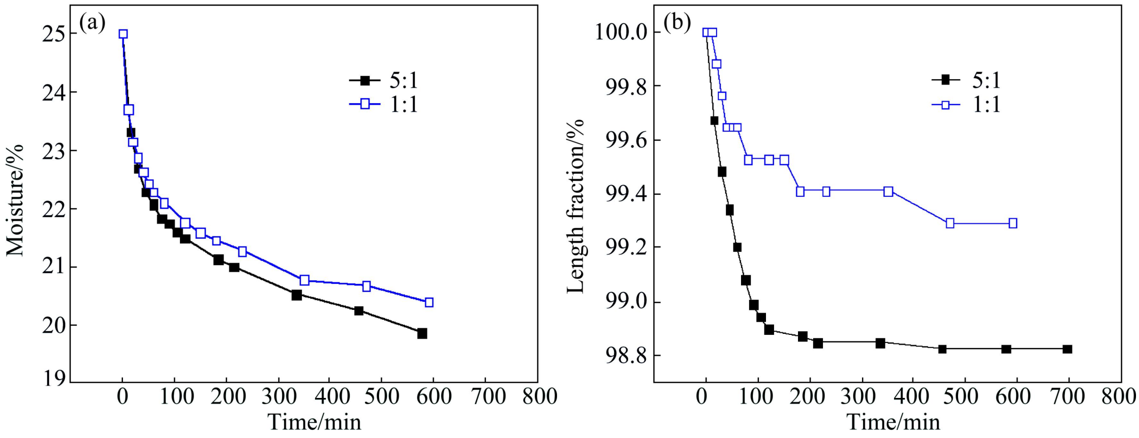

Fig. 3 Effects of size on moisture (a) and length faction (b) in gelcast green body during drying with ethanol (The solids loading of green body is 50 % in volume faction. The ethanol concentration is 100%)

greater shrinkage rate.

3.4 Drying stress in liquid drying

3.4.1 Changes of drying stress during liquid drying process

During the drying process of a ceramic green body, local drying rate is usually uneven, causing uneven distribution of internal moisture of the green body, which results in the development of stress. This leads to the occurrence of phenomena such as warping, surface wrinkles, and even cracking. Therefore, in order to better control the drying process of a green body, it is necessary to assess the stress generated during the liquid desiccant drying process in gelcasting, i.e., the liquid drying stress.

At the moment when a green body is immersed into the liquid desiccant, there is no immediate shrinking or loss of moisture. Therefore, there is no stress within the green body. After a short time, moisture on the surface is lost quickly, which causes the green body to start shrinking. However, due to the suppression by the inner counteraction, shrinkage does not occur. At this time, there is a tensile stress on the surface of the green body that tries to curl up the body surface. At the same time, since the inner body needs to maintain balance, there is a compressive stress in the inner layers of the body that tries to maintain the original status. If the body is cleaved from the middle, deformation occurs where the body bends outwardly (Fig. 4(a)). As the drying proceeds, the moisture of the body decreases gradually, the thickness of the surface anhydrous layer increases gradually, and both the tensile and compressive stresses grow larger. Also, there is a certain elastic-plasticity in the gelcast green body. As a result, residual tensile stress deformation is generated under the tensile stress on the body surface, while residual compressive stress deformation is generated under the compressive stress within the green body. There is a dense layer formed on the body surface, and its thickness increases gradually with an increase in the liquid drying time [21,22]. The dense layer lowers the deformation rate of the body surface, and eventually makes it lower than that within the body. As a result, when the drying process is completed, the shrinkage is larger within the body than that on the body surface, and within the green body compressive stress has been converted to tensile stress. Accordingly, on the surface of the body, the tensile stress is converted to compressive stress. If the green body is cleaved from the middle, deformation occurs where the body bends inwardly (Fig. 4(b)).

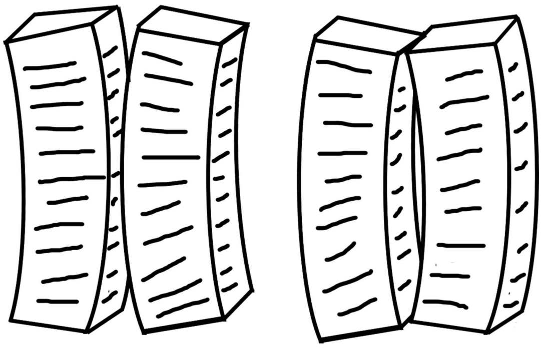
(a) (b)

Fig. 4 Stress in green body during drying: (a) Initial period; (b) Final period

There are two sources for the generation of internal stress of a green body: the wet stress caused by uneven local shrinkage of the body, and the residual stress caused by the residual deformation generated within the green body. Wet stress is time-correlated. When the internal moisture reaches a balance, the wet stress disappears; residual stress is relevant to factors such as uneven gelcast curing reaction [23,24] and residual deformation, but irrelevant to moisture. Residual stress is generated during and after the drying process. Both stresses are generated due to the change in moisture of the green body. Figure 5 shows the change in total stress of the green body dependent on the change in moisture ratio.

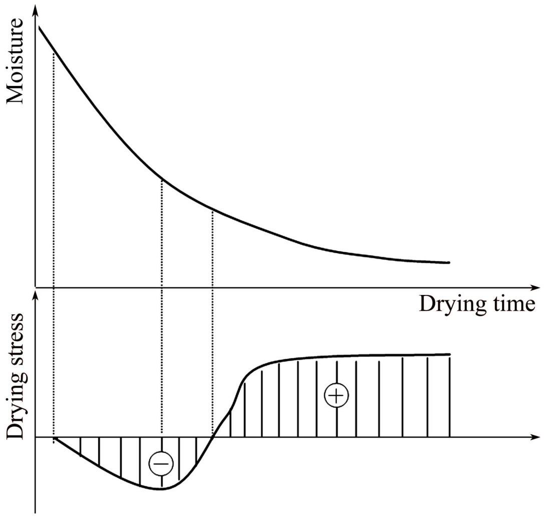

Fig. 5 Schematic representation of evolution of moisture and stress in green body during drying

Based on the analyses above, at a later stage of the drying process, when the shrinkage on the body surface reaches a certain extent, there is only slight shrinkage or even zero shrinkage, while shrinkage within the body continues. Therefore, when the stress difference within and without the green body reaches a certain threshold point, the gelcast green body begins to crack, either internally or externally. This is the drying defect that is most likely to occur, especially during the drying of large-sized, thick-walled green bodies.

3.4.2 Drying stress during initial stage of liquid drying

As described above, during liquid drying of a gelcast green body, the change in internal stress of the body is mainly caused by the change in moisture ratio. Therefore, excluding other factors, the shrinkage of a green body depends primarily on the change in moisture ratio during the initial stage of liquid drying. Figure 6 shows the relationship between the experimentally measured shrinkage rate and change in moisture. As shown in this graph, during the initial stage of liquid drying, there is an approximately linear relationship between these two variables, which are not affected by the type of liquid desiccant and the size of the green body. The linear relationship between the green body drying shrinkage rate and moisture is

$$\frac{L_0-L}{L_0}=K\frac{M_0-M}{M_1}=K\left(W_0-W\right) \qquad (1)$$

where L_0, M_0, and W_0 represent the initial length of the green body, the initial moisture, and the initial moisture, respectively; L, M, and W represent the body length, moisture, and moisture after drying; M_1 represents the dry mass of the green body; K represents the drying coefficient, which is relevant to solids loading of the green body.

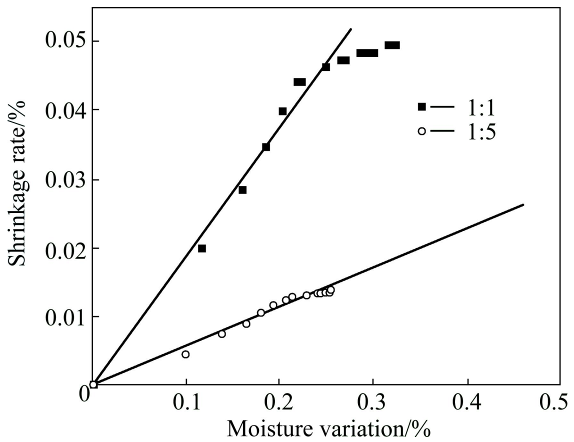

Fig. 6 Relationships between shrinkage rate and moisture variation during drying (The ethanol concentration is 100%. The solids loading of green body is 30% in volume fraction)

Indeed, a similar relationship exists during the wood drying processes [13−15,19], which proves indirectly that there is a linear relationship between shrinkage rate and change in moisture. In wood science, K is called the drying coefficient.

Providing that the cross-section of the body is divided into numerous single layers, the liquid drying of a single layer is similar to an infinite diffusion model, i.e., a single-layer body is dried within infinite liquid desiccant, and the moisture is only released through both sides of the body. If both ends of the single layer body are fixed, there must be an internal stress within the body after the drying process. This stress and the shrinkage obey the Hooke's law:

$$\sigma'=E\delta' \qquad (2)$$

where E represents the elastic modulus of body; δ' represents the theoretical shrinkage rate, and its value is

$$\delta'=\frac{L_0-L}{L_0}=K\left(W_0-W\right) \qquad (3)$$

Moisture is symmetrically distributed across the cross-section of the body, and the moisture W is a function of body thickness:

$$W=f(x) \qquad (4)$$

If both sides of the body are free ends, the body rebalances again, and its internal stress is

$$\sigma''=E\delta'' \qquad (5)$$

where δ'' represents the actual shrinkage rate and its value is

$$\delta''=\frac{L_0-L'}{L_0} \qquad (6)$$

where L' represents the actual length.

Therefore, the actual internal stress of the body is

$$\sigma=\sigma'-\sigma''=E(\delta'-\delta'') \qquad (7)$$

The overall stress of the green body is balanced, and therefore the following equation is satisfied:

$$\int_{-r}^{+r}\sigma \mathrm{d}x=0 \qquad (8)$$

Assuming that the value of the elastic modulus is fixed, then

$$\int_{-r}^{+r}E(K\frac{W_0-W}{W_0}-\delta'')\mathrm{d}x=0 \qquad (9)$$

$$\delta''=K\left[W_0-\frac{1}{r}\int_0^{+r}f(x)\mathrm{d}x\right]=K\left(W_0-\overline{W}\right) \qquad (10)$$

Substitution of Eqs. (3) and (10) into Eq. (7) results in

$$\sigma=EK(\overline{W}-W) \qquad (11)$$

As shown in the equation above, in the initial stage of the liquid drying process, the initial moisture on the body surface is equal to the average moisture of the entire cross-section, $\overline{W}=W$. Therefore, there is no internal stress within the body in this stage. After a period of drying, the moisture of the body surface is lower than the average moisture of the entire cross-section, $\overline{W}>W$, and simultaneously, the moisture within the body is higher than the average moisture of the entire cross-section, $\overline{W}<W$. Therefore, there is a tensile stress on the surface of the body, while there is a

compressive stress within the body. Figure 7 shows the distribution of the moisture of the body's cross-section and the stress.

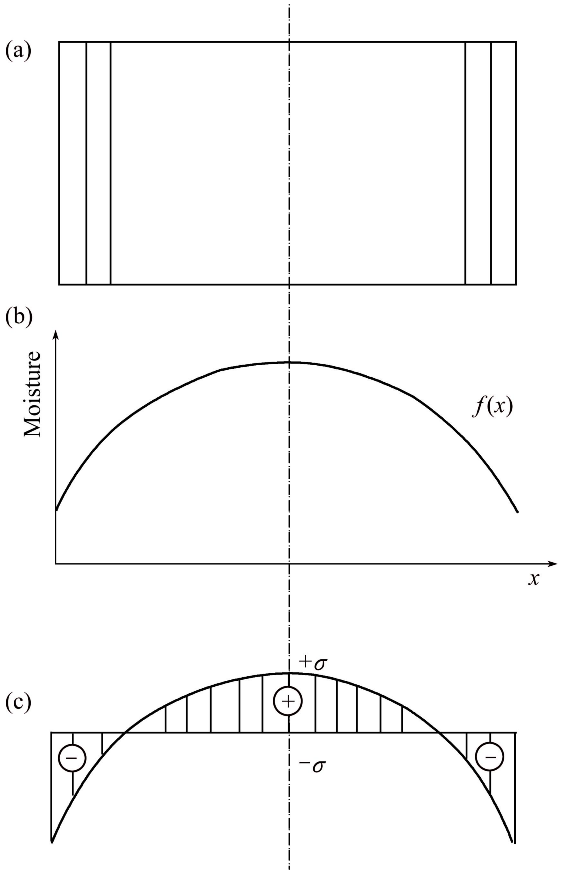

Fig. 7 Distribution of moisture and stress on cross-section of green body in initial drying stage: (a) Cross-section of green body; (b) Distribution of moisture; (c) Distribution of stress

As shown in Eq. (11), the internal stress of a green body is relevant to both the elastic modulus and the drying coefficient. Apparently, both the elastic modulus and the drying coefficient are determined by factors like the relative molecular mass and geometry of the polymer (gel) in the three-dimensional network of the gelcast green body, the type of powder particles, their size and distribution, and solids loading. Also, the drying coefficient is affected by both the body morphology and the size. As a result, the internal stress in liquid drying is also affected by the factors described above.

It must be pointed out that during the middle and later stages of liquid drying, the dense layer formed on the surface of a green body has a great influence on drying. Therefore, there is not a linear relationship between the drying shrinkage rate and change in moisture, which means that Eq. (1) cannot be established, and the stress calculation formula cannot be used (Eq. (11)). The evolution of drying stress during the middle and later stages of liquid drying is very complex, requiring consideration of the dual effects of change in moisture and the dense layer on the surface of the body.

4 Conclusions

1) The moisture of a green body drying with higher concentration of ethanol decreases more while shrinkage rate decreases less. The drying efficacy of a green body containing lower solids loading and higher height to aspect ratio is better.

2) During the liquid drying process, liquid drying stress is generated in the gelcast green body due to an uneven local drying rate. In the initial stage of this process, the relationship among the liquid drying stress, the average body moisture ($\overline{W}$) and the moisture (W) is $\sigma = EK(\overline{W} - W)$.

3) There is no internal stress within the green body in the initial drying stage, while tensile stress is generated on the body surface and compressive stress is generated within the body after a period of drying. As the drying proceeds, the compressive stress within the body is converted to tensile stress, while the tensile stress in the external portions is converted to compressive stress. During the later stage of liquid drying, the shrinkage on the body surface becomes slight or even stops as the shrinkage reaches a certain degree, while the shrinkage within the body continues. When the stress reaches a certain threshold point, the gelcast green body suffers from damages such as internal cracking and external cracking.

References

[1] JANNEY M A, OMATETE O O. Method for molding ceramic powders using a water-based gelcasting: US, 5028362 [P]. 1991−06−02.

[2] YOUNG A C, OMATETE O O, JANNEY M A , MENCHHOFE P A. Gelcasting of alumina [J]. Journal of the American Ceramic Society, 1991, 74(3): 612−618.

[3] WANG Xiao-feng, WANG Ri-chu, PENG Chao-qun, LI Hai-pu, LIU Bing, WANG Zhi-yong. Thermoresponsive gelcasting: Improved drying of gelcast bodies [J]. Journal of the American Ceramic Society, 2011, 94(6): 1679−1682.

[4] YUAN Bo, WU Hai-bo, SUN Xiao-fei, WANG Gang, LI Hong-xia. Fabrication of porous alumina green bodies from suspension emulsions by gelcasting[J]. Materials Letters, 2012, 81(15): 151−154.

[5] OMATETE O O, JANNEY M A, NUNN S D. Gelcasting: From laboratory development toward industrial production [J]. Journal of the European Ceramic Society, 1997, 17(2−3): 407−413.

[6] WANG Xiao-feng, WANG Ri-chu, PENG Chao-qun, LI Ting-ting, LUO Yu-lin, WANG Chao, LIU Bing. Research and development of gelcasting [J]. The Chinese Journal of Nonferrous Metals, 2010, 20(3): 496−509.

[7] OMATETE O O, STREHLOW R A, WALLS C A. Drying of gel-cast ceramics [J]. Ceramic Transactions, 1991, 26: 101−107.

[8] JANNEY M A, KIGGANS J O. Method of drying articles: US, 5885493 [P]. 1999−03−23.

[9] JANNEY M A, WALLS C A. Gelcasting compositions having

improved drying characteristics and machinability: US, 6228299 [P]. 2001−05−08.

[10] ZENG Ling-ke, SHUI An-zhe. Practical drying technologies and illustrations for ceramic industry [M]. Beijing: Chemical Industry Press, 2008: 44−45. (in Chinese)

[11] HARN Y P, GHOSAK S, ARAL G, EMAMI-NAEINI A, DRASKOVICH BARRY S, MAXEY C. Real-time model-based control system design and automation for gelcast drying process [C]//Proceedings of the 1997 IEEE International conference on Control Applications. Hartford: IEEE, 1997: 271−276.

[12] GHOSAL S, EMAMI-NAEINI A, HARN Y P, DRASKOVICH B S, POLLINGER J P. A physical model for the drying of gelcast ceramics [J]. Journal of the American Ceramic Society, 1999, 82(3): 513−520.

[13] PAN Yong-kang, WANG Xi-zhong, LIU Xiang-dong. Modern drying technology [M]. 2nd ed. Beijing: Chemical Industry Press, 2005: 176−180. (in Chinese)

[14] DAVID M. Exploratory study of effect of superheated steam drying on properties of paper [D]. Montreal: McGill University, 1987.

[15] KUDRA T M. Advanced drying technologies [M]. LI Zhan-yong, trans. Beijing: Chemical Industry Press, 2005: 176−180. (in Chinese)

[16] BARATI A, KOKABI M, FAMILI M H N. Drying of gelcast ceramic parts via the liquid desiccant method [J]. Journal of the European Ceramic Society, 2003, 23(13): 2265−2272.

[17] ZHENG Zhi-ping, ZHOU Dong-xiang, GONG Shu-ping. Studies of drying and sintering characteristics of gelcast $BaTiO_3$-based ceramic parts [J]. Ceramics International 2008, 34(3): 551−555.

[18] TRUNEC M. Osmotic drying of gelcast bodies in liquid desiccant [J]. Journal of the European Ceramic Society, 2011, 31(14): 2519−2524.

[19] SALIN J G. Solvent drying of wood-some results [M]. Amsterdam: Elsevier, 1991: 529−534.

[20] LUO Yu-lin, WANG Xiao-feng, WANG Ri-chu, PENG Chao-qun, LI Ting-ting, LIU Bing. Effects of calcination pretreatment on properties of BeO powder for colloidal processing [J]. Materials Science and Engineering of Powder Metallurgy, 2010, 15(2): 151−156. (in Chinese)

[21] GU Xue-rong, ZHU Yu-ping. Gel chemistry [M]. Beijing: Chemical Industry Press, 2005: 57−117. (in Chinese)

[22] FANG Dao-bin, GUO Rui-wei, HA Run-hua. Polymers of acrylamide [M]. Beijing: Chemical Industry Press, 2006: 143−181. (in Chinese)

[23] MA L G, HUANG Y, YANG J L, LE H R, SUN Y. Control of the inner stresses in ceramic green bodies formed by gelcasting [J]. Ceramics International, 2006, 32(2): 93−98.

[24] GUO Jian, SUN Yong-jian, QIU Tai, XUE Wang, YANG Hai-yan. Gelating and drying process of aqueous gelcasting aluminum nitride ceramics [J]. International Journal of Applied Ceramic Technology. 2014. DOI:10.1111/ijac.12355.

采用乙醇为干燥剂的 BeO 凝胶注模坯体的液体干燥

王小锋，彭超群，王日初，孙月花，陈以心

中南大学 材料科学与工程学院，长沙 410083

摘　要：以乙醇为液体干燥剂，研究 BeO 凝胶注模坯体的液体干燥。采用质量称量和尺寸测量等手段，研究乙醇浓度和坯体固相体积分数与尺寸等因素对坯体含水率与收缩的影响规律，分析液体干燥应力并建立干燥初期的应力模型。结果表明：乙醇浓度越高，坯体的含水率下降越多，收缩率越小；坯体的固相体积分数越低，高径比越大，干燥效果越好；坯体因局部干燥速度不均匀而产生液体干燥应力；随着干燥的进行，坯体内部的应力由压应力逐渐转变为拉应力，而坯体外部则由拉应力逐渐转变为压应力。

关键词：BeO；凝胶注模；坯体；液体干燥剂；乙醇；干燥速率；收缩速率；干燥应力

(Edited by Xiang-qun LI)