Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 5906–5910

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effects of sintering temperature and holding time on porosity and shrinkage of glass tubes

Dongliang Yang, Yong Zhang*, Xiaozhen Song, Yongzhou Chen, Ziqin Shen, Chong Yang

Beijing Key Laboratory of Fine Ceramics, State Key Laboratory of New Ceramics and Fine Processing, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

Received 17 November 2015; received in revised form 16 December 2015; accepted 24 December 2015
Available online 1 January 2016

Abstract

The influences of sintering temperature and holding time on porosity and shrinkage of glass tubes have been studied by optical microscope. It is evident that there exists three stages for the sintering process of glass. At the first stage, both increasing temperature and prolonging the holding time contribute to lowering the porosity and to intensifying the shrinkage greatly. At the second stage, the glass further densifies and the voids among particles become smaller and less. Finally, at the third stage the shrinkage rate almost keeps unchanged to sintering temperature and holding time.

Keywords: A. Sintering; B. Porosity; D. Glass; Shrinkage

1. Introduction

Glass-to-metal seal technology is used extensively to provide a robust hermetic seal between a metal conductor and a metal body. A typical glass-to-metal seal consists of three elements, that is, a metal body, a pin conductor, and a piece of preformed glass tube to fit between the pin and the metal body [1]. During sealing processing, these three components are placed on a fixture which holds them in position. This entire assembly is placed in an oven configured to maintain a controlled atmosphere. At the sealing temperature, the glass melts and fills the space between the pin and the metal body. Thus glass-to-metal seal technology can provide hermeticity and pressure resistance around electrical contacts. Nowadays this technology is used in the electronic packaging [2], solar cell [3], solid oxide fuel cell (SOFC) [4] and in the manufacture of medical equipments like heart pacemakers [5].

However, for these types of applications the glass-to-metal seal technology is successful and relatively easy to make. In other sectors, like the nuclear and the fusion one [6], the glass-to-metal joints are still difficult to make and certainly not fully understood. A joint between glass and metal for a nuclear or fusion application has to resist high temperatures, high pressures, and high neutron fluence and must be leak tight. These characteristics are difficult to obtain. Therefore, there are more and more investigations needed to cast light on these difficulties for making good glass-to-metal sealing.

The manufacture of the preformed glass tube is a prerequisite for the production of good glass-to-metal seals. On sealing glass to metal, the presence of voids in the glass tube causes bubbles to form at the glass-to-metal interface or within the sealing glass. These bubbles cause blistering and therefore a poor seal and a bad insulation [7]. To remove the voids from the preformed glass tube, and hence the bubbles during the sealing operation, the glass parts are usually sintered before the sealing. However, limited work is available in the literature concerning the sintering process of the preformed glass tubes. The effects of sintering temperature and holding time on sintering behavior are needed for further investigation of the glass tubes, in terms of porosity, linear shrinkage, and pore size.

In this work, a silicate borate glass was selected and sintered in the temperature range of 640–680 °C. And the holding time of sintering was varied in the range of 60–180 min. After

*Corresponding author. Tel.: +86 10 80194055; fax: +86 10 89796022.
E-mail address: yzhang@tsinghua.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.ceramint.2015.12.138
0272-8842/

sintering, the microstructures of the specimens were examined. The objective of this paper is to study the influences of sintering temperature and holding time on the porosity and shrinkage properties of the silicate borate glass system.

2. Experimental procedures

2.1. Sample preparation

A glass with the composition of $60SiO_2$–$6B_2O_3$–15BaO–10CaO–$3TiO_2$–$6K_2O$ was prepared from reagent-grade SiO_2, B_2O_3, $BaCO_3$, $CaCO_3$, TiO_2, K_2CO_3. Well-mixed powder containing appropriate amounts of the above chemicals was melted in a platinum crucible at 1500 °C for 5 h and then rapidly poured into a container filled with distilled water. The obtained glass powders were milled in a milling container with ethanol.

For the preparation of the preformed glass tube, a finely pulverized glass powder was mixed with organic binder and pressed into the glass tubes with dimensions of 12 mm outer diameter, 10 mm inner diameter, and 6 mm axial thickness at a pressure of 10 MPa. The following binder burnout was performed at 600 °C for 6 h. After that, the glass tubes were sintered at 640, 645, 650, 655, 660, 665, 670, 675, and 680 °C, respectively. The holding time of sintering were 60, 120 and 180 min, respectively.

2.2. Characterization

The linear shrinkage rate Y of the glass tube can be obtained through the equation

$$Y = \frac{D_1 - D_2}{D_1} \times 100\% \quad (1)$$

in which D_1 is the outer diameter of the glass tube before sintering, and D_2 is the outer diameter of the glass tube after sintering. The cross sections of the sintered glass tubes were polished and observed by an optical microscope. The program Image J, a public domain image analysis software designed to be adapted for different roles, was used to analysis the porosity and pore size. Image J is a fast and effective tool to measure porosity, which is often applied to count cells [8] and to measure porosity of many materials in different fields, such as cortical bone in medicine [9], fruit in food engineering [10], stone in geoscience [11,12], etc. The microstructure image is converted into a binary image through "Binary" command that specifies each pixel with zero or one. In such images, pore spaces are shown by black pixels (zero) and other parts of the image are shown by white pixels (one). The porosity value of each image is obtained through dividing the number of black pixels to total number of the image pixels. By the commands of thresholding, edge detection and particle analysis, the average pore size can be obtained [13]. In order to give an objective description, the average values of porosity and pore size were calculated from 4 to 6 photos.

3. Results and discussion

3.1. Effect of sintering temperature

Optical microscopy studies were performed on the glass tubes to better illustrate the sintering behavior. Fig. 1(a)–(i) shows optical micrographs that illustrate the sintering temperature dependence of the glass tubes. Fig. 1(a) shows a representative image of the samples sintered at low sintering temperature. This image revealed a large number of void area coexisted with a small number of real contact area. The void area decreased gradually with increasing temperature, leaving more contact area. At 650 °C, the real contact area associated with glass particles was increased to a continuous state, as shown in Fig. 1(c). Further increase in the sintering temperature resulted in a gradual reduction in the void area, and above 665 °C, the void area associated with pores decreased significantly. After this period, the number of the pores kept almost unchanged with the increase of sintering temperature, as shown in Fig. 1(g)–(i). The microstructural aspects of the loose-to-dense transformation were observed with the increase of sintering temperature.

3.2. Effect of holding time

Fig. 2 shows the optical micrographs of the glass tubes sintered at 650 °C for 60, 120, and 180 min, respectively. A large amount of void area appears for the sample with the holding time of 60 min (Fig. 2(a)). Moderate amounts of void area are found for the sample with the holding time of 120 min; however, small amounts of void area remain for the sample with the holding time of 180 min. These results indicated that the real contact area increased and the void area decreased with the increase of holding time. This trend indicates that the transformation from loose state to dense one occurs gradually with increasing holding time.

Fig. 3 shows the porosity change as a function of sintering temperature for the glass tube samples sintered for various holding time. The porosity tended to rapidly decrease with increasing sintering temperature up to 665 °C and then to slightly decrease. At and above the sintering temperature of 665 °C, the porosity below 2.5% was obtained for all the specimens. Another important feature in Fig. 3 is the variation of diminishing tendency with holding time. When these tendencies at the sintering temperatures lower than 660 °C are compared, it is evident that the decrease are rapid for the samples with the holding time of 60 min, whereas it is slow for the samples with the holding time of 180 min.

The effects of sintering temperature and holding time on linear shrinkage rate of the glass tube samples are shown in Fig. 4. An increasing tendency in linear shrinkage rate with sintering temperature was observed. The linear shrinkage rate is sensitive to the sintering temperature below 655 °C. It increases rapidly with increasing sintering temperature up to 655 °C and then slightly increases. When the sintering temperature is above 660 °C, a plateau was observed, demonstrating that there is no further increase in shrinkage with