JOURNAL OF MATERIALS SCIENCE 17 (1982) 2845–2849

Fabrication of hollow glass microspheres in the Na_2O–B_2O_3–SiO_2 system from metal alkoxides

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Hollow glass microspheres (HGS) for laser fusion targets were fabricated in the system Na_2O–B_2O_3–SiO_2 from $NaOCH_3$, $B(OCH_3)_3$ and $Si(OC_2H_5)_4$. Gel powders prepared from metal alkoxides and urea liberate H_2O, CO_2 and NH_3 gases, evolution of which takes place completely at about 500° C. The precursor of HGS is formed by the encapsulation of these gas components in the glass layer formed at the surface of the powder. HGS are produced from the gel powders having both a melting temperature lower than about 1000° C and a viscosity at that temperature lower than 10^5 P. In the Na_2O–B_2O_3–SiO_2 system, the compositions from which HGS are produced are those containing 55–75 wt % SiO_2 and 0–20 wt % B_2O_3. HGS ranging from 100–500 μm diameter and 0.5–7.0 μm wall thickness are obtained by change of urea content.

1. Introduction

Hollow glass microspheres (HGS) typically with diameters 100–500 μm and 0.5 to several μm wall thickness are the principal fuel containers for inertial fusion research. For HGS to be useful for the targets, they almost always exhibit good wall uniformity, sphericity and surface finish. Furthermore, the strength, permeability of the gases contained and the chemical durability of the HGS are also important properties.

HGS are produced from solutions or powders. Hendricks produced HGS using droplets of silicate solutions [1]. On the other hand, the fabrication of HGS from powders was adopted by Budrick *et al.* [2] and Hendricks *et al.* [3]. We have directed our efforts to the fabrication of high quality HGS with the desired sizes from metal alkoxides. In the previous paper, HGS were fabricated with the composition $20Na_2O \cdot 10B_2O_3 \cdot 70SiO_2$ (wt%) using powders prepared from $NaOCH_3$, $B(OCH_3)_3$ and $Si(OC_2H_5)_4$, which were about 100 μm diameter and about 1.0 μm wall thickness [4]. It was estimated that the gases effective for the formation of HGS were those contained within a third of the radius of powders, and the expansion rate of the HGS was governed by the pressure of gases encapsulated and the viscous relaxation of the glass shell.

In this paper, the formation of HGS from metal alkoxides is examined in the Na_2O–B_2O_3–SiO_2 system. The effects of gas amounts and glass composition on the size of HGS are also examined.

2. Experimental methods

2.1. Preparation of HGS

Fig. 1 shows the glass composition of HGS examined in this experiment. The glass composition is indicated with the number shown in Fig. 1. The metal alkoxides used as the starting materials are $Si(OC_2H_5)_4$, $B(OCH_3)_3$ and $NaOCH_3$. Metal alkoxides corresponding to the ultimate oxide composition with a weight of 100 g were reacted in the vessel for 2 h at room temperature. After 20 g urea was dissolved in this solution, 150 ml of $0.15\,mol\,l^{-1}$ HCl solution was slowly added, stirring continuously to produce hydrolysis of the metal alkoxide solution. The resultant gelled mass was gradually heated to 120° C and maintained at that temperature for 15 h. Approximately 8 wt % water and 5 wt % urea were observed to be contained in

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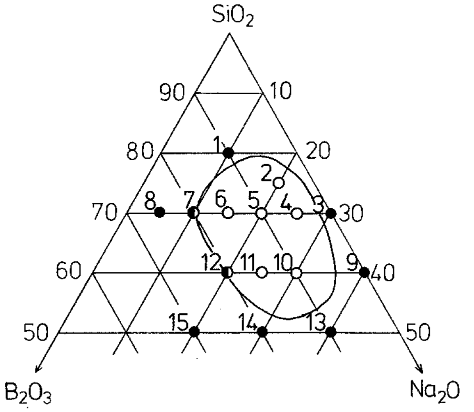


Figure 1 Compositions of the HGS and HGS-forming region. ○; HGS ◐; partially HGS ●; beads.

the dried gel. The gel was crushed and sieved into fractions from 44 to 250 μm with about 20 μm intervals, using a screen. The furnace used for the production of HGS is described in detail elsewhere [4]; it was a vertical type of alumina tube, 70 mm diameter and 1500 mm long which had a heating zone of about 1000 mm. The HGS collecter was connected to the bottom of the tube. The transit time (4 to 6 sec) of HGS through the furnace was controlled by pumping.

2.2. Measurement of properties

The average diameter and wall thickness of the HGS were determined by measuring 50 HGS, selected at random from each batch, with an Interphako interference microscope.

Gel powders transfer to HGS for only a few seconds while dropping through the furnace. To develop a better understanding of the HGS forming process, the change of gel to glass and the gas evolution from the gel were examined by thermal gravimetric analysis (TGA), differential thermal analysis (DTA) and evolution gas analysis (EGA). The heating rate of the samples was 20° C min^{-1}. The evaporated gases were analysed by gas chromoatography connected to the furnace for TGA–DTA. The column was parapak N, 1 m long at a temperature of 100° C.

Glasses of the same composition as the HGS were prepared by melting the mixtures of SiO_2, H_3BO_3 and Na_2CO_3 in a Pt crucible. The viscosity of the glass was measured with a rotor-type viscometer. The temperature dependence of the viscosity of glass was obtained. Observation by SEM and measurement of pore volume of the gels by mercury porosimeter were also performed.

3. Results and discussion

3.1. Composition range of HGS

The metal alkoxide solutions containing less than ~ 40 wt% Na_2O were transfered into the gelled masses by hydrolysis. However, solutions which contained more than about 40 wt% Na_2O, such as samples 9 or 13, did not eventually gel, even if heated to 120° C. Typical SEM photographs of powders are shown in Fig. 2. Powders containing B_2O_3 are always porous, consisting of small particles (Fig. 2a). Their pore volumes are ~ 0.3–1.0 cm^3 g^{-1}. In the powders in the binary Na_2O–SiO_2 system, gel particles were not observed (Fig. 2b).

The sieved powders were dropped through the furnace kept at 1200–1400° C. Three kinds of products are observed, which are shown in Fig. 3. The powders with high SiO_2 content, such as sample 1, partially foam and do not become hol-

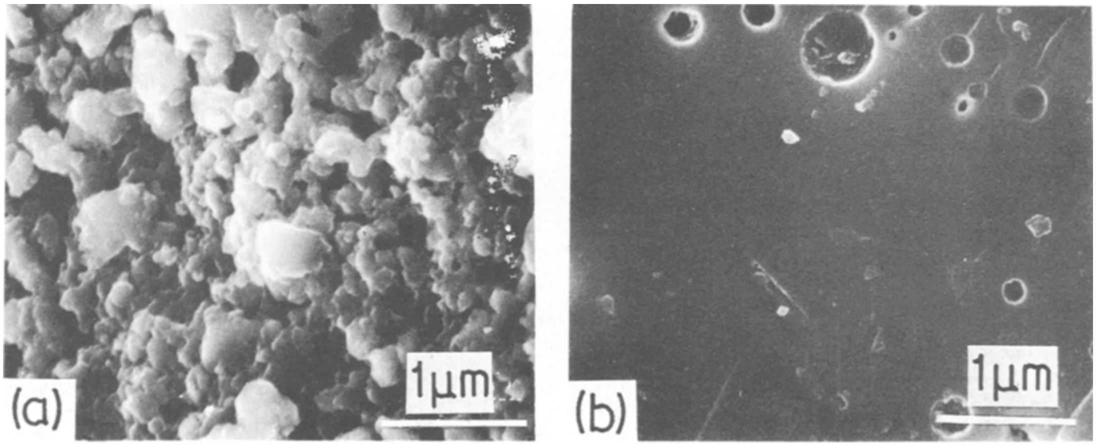


Figure 2 Scanning electron micrographs of gel powders. (a) Sample 5, (b) sample 3.

low spheres (Fig. 3a). On the other hand, from powders containing less than 55 wt% such as samples 14 or 15, glass beads are obtained (Fig. 3c). Furthermore, powders not containing B_2O_3, such as sample 3, also produce glass beads. HGS are produced in the glass composition region containing both 55–75 wt% SiO_2 and 0–20 wt% B_2O_3, as shown in Fig. 1. Fig. 3b shows an example of HGS produced from powders of sample 5, 105–125 μm in size at a furnace temperature of 1300° C. The HGS shown in Fig. 3b have a diameter of $\sim 200\,\mu$m and a wall thickness of $\sim 3\,\mu$m. Using powders of variable sizes HGS 100–500 μm diameter and 0.5–0.7 μm wall thickness can be currently fabricated. Their sphericity and wall uniformity are satisfactory for the target requirements.

3.2. Formation process of HGS in the Na_2O–B_2O_3–SiO_2 system

3.2.1. Gas evolution from the gel and vitrification of the gel

Typical examples of TGA and EGA curves are shown in Fig. 4 for sample 5. The gas amount shown in Fig. 4b is arbitarily plotted as the peak area of gas chromatographs. Two large weight losses are observed around 150 and 400° C. They are due to the evaporation of water and CO_2 and NH_3, respectively. The amounts of NH_3 and the major part of CO_2 are those due to the pyrolysis of urea added as the blowing agent. CO_2 gas produced by decomposition of residual organic compounds is only traced up to 700° C. The evolution of large amounts of gases effective for the formation of HGS takes place completely at about 500° C. These features are similar to those observed in gels having different compositions. Therefore, for the powders to transfer to HGS, the gases evaporated from water and urea and air which occupies the cavities in the porous powder must be encapsulated in the HGS.

Fig. 5 shows a DTA curve of sample 5, which indicates that the endothermic peak at about 150° C is due to the evaporation of water, followed by a small exothermic peak around 400° C.

After the endothermic peak is observed at about 930° C, irregularity is observed in the DTA curve. This phenomenon around 900° C is due to the melting of the gel. The endothermic peak at about 930° C is tentatively defined as the melting temperature of the gel (T_m) as shown in Fig. 5. T_m is dependent on the composition of the glass.

3.2.2. Formation process of gel to HGS

From the change in the powders dropped through the furnace and the results of TGA–DTA–EGA,

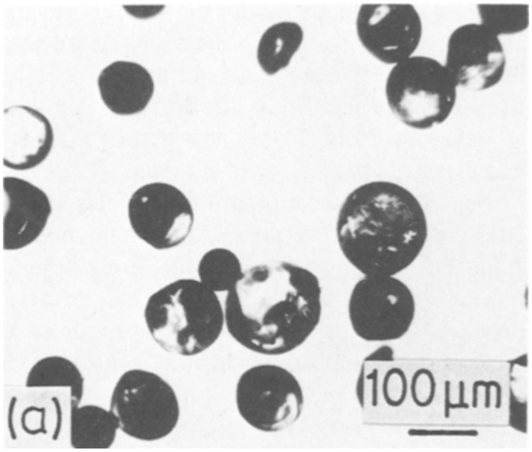
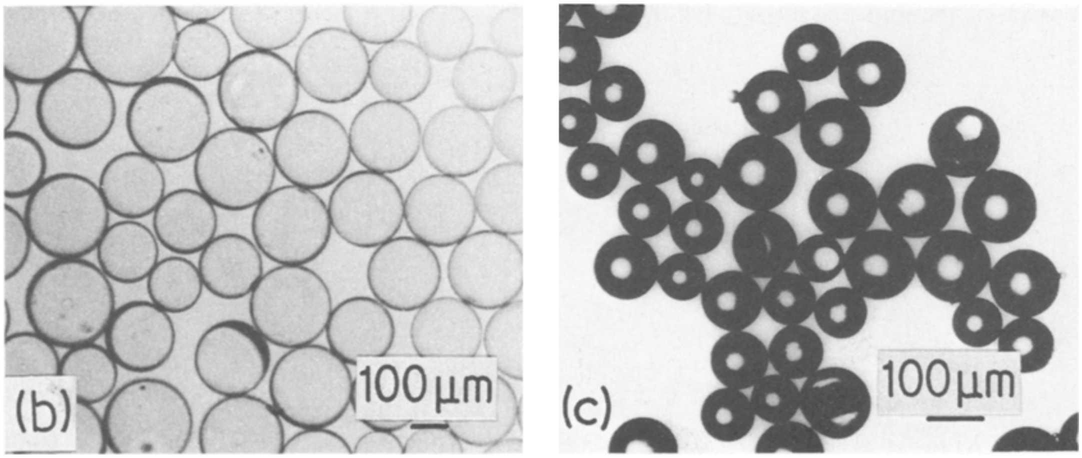


Figure 3 Optical photographs of products at 1300° C in the Na_2O–B_2O_3–SiO_2 system. (a) Sample 1, (b) sample 5, (c) sample 15.



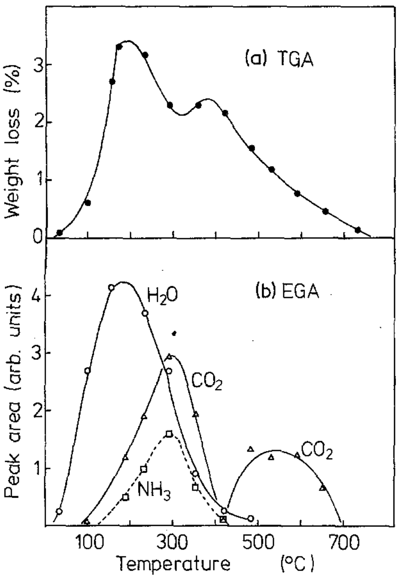


Figure 4 (a) TGA and (b) EGA curves of sample 5.

the forming process of HGS is schematically illustrated in Fig. 6.

When the powders are suddenly heated by dropping them through the heated furnace, a temperature distribution takes place in the powders. Before the gases are completely evaporated from the powder, the surface of the powder vitrifies to result in the formation of a glass layer (stage 1). At this stage, the gas components which are contained inside the powder are still not evaporated. With increasing powder temperature, the gel transfers to the glass together with the evaporation of the gas components. The precursor of HGS is formed (stage 2). The HGS precursor is expanded to its equilibrium size (stage 3). The expansion rate of HGS is controlled by the difference in gas pressure between the outside and the inside of the HGS, the viscosity and the surface energy of the glass shell. The kinetics of expansion of the HGS was previously reported in detail [4].

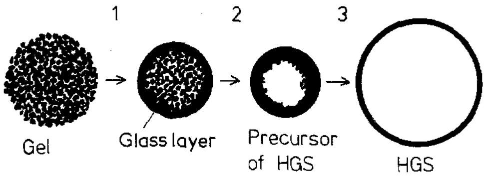


Figure 6 Schematic illustration of the formation of HGS.

Stage 1 is essential for the formation of HGS. A large amount of gas must be encapsulated in the formed glass shell. In order for this condition to occur, first it is necessary for the gel to vitrify at a lower temperature and for the formed glass to encapsulate the inner gel before the gases completely evaporate. Therefore, it is desired that the melting temperature (T_m) and the viscosity at T_m are as low as possible. Fig. 7 shows the relationships between T_m and the viscosity at T_m. The viscosity at T_m is calculated by applying the Fulcher equation for the viscosity–temperature curve [5]. In Fig. 7, open and closed marks indicate that HGS are or are not produced, respectively. The composition of the HGS produced is determined by T_m is lower than ~ 1000° C *and* the viscosity at T_m is lower than ~ 10^5 P.

Next, the texture of gel powders affects whether HGS are produced or not. HGS are only obtained from porous powders, but not from pore-free powders such as sample 3. In the case of porous powders, their low heat transfer slows down the increase in temperature in the centre of the powder. Therefore, it results in more gases being encapsulated by the HGS precursor.

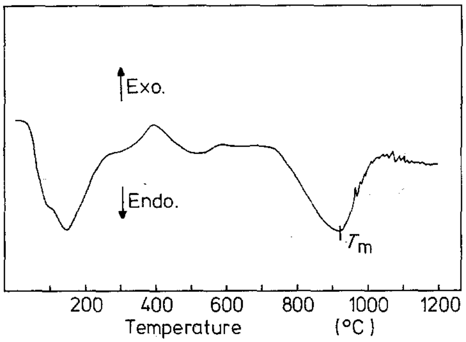


Figure 5 DTA curve of sample 5.

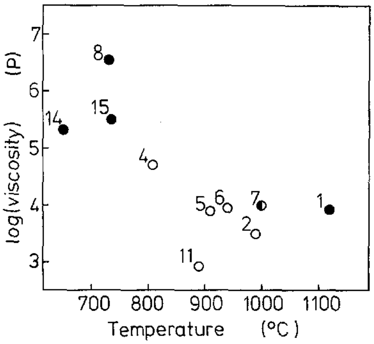


Figure 7 Relationships between melting temperature and viscosity at T_m.

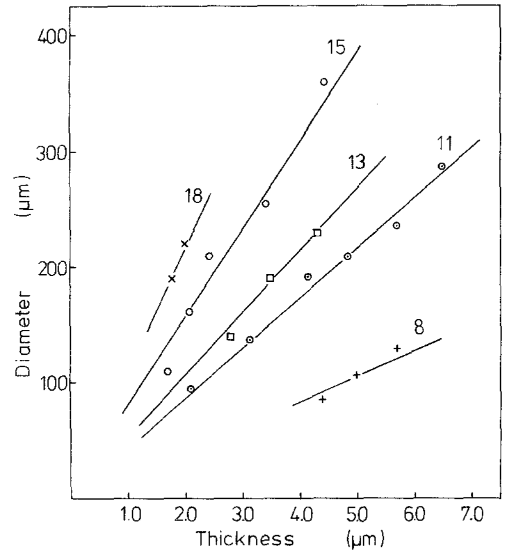


Figure 8 Diameter and wall thickness of HGS.

3.3. Effect of the amount of gas components on the size of HGS

The fabrication of HGS for use in laser fusion targets requires certain diameter and wall thickness requirements to be met. The size of HGS is considered to be dependent on the amount of gases, the viscosity and the surface energy of the glass shell.

Gels were prepared to contain 0–40% urea which was analysed to contain about several tens of per cent added urea. The ranges of powder size are six sieved groups from 63–210 μm. The furnace temperature used for production was 1300° C. The relationships between diameter and wall thickness are shown in Fig. 8 for sample 5. The numbers shown in Fig. 8 indicate the amount of both urea and water (wt%) contained in the powders. In the size range shown in Fig. 8, a linearity is observed between the diameter and the wall thickness. The aspect ratio which is defined as diameter/wall thickness, i.e. the slope of straight line, increases with increase in the amounts of gases.

It is observed that the aspect ratio of HGS increases with decrease in the viscosity of the glass shell. HGS having a low viscosity also expand to their equilibrium size within a shorter time. The low viscosity is desirable to improve the sphericity and wall uniformity of HGS. The viscosity of glass is dependent on the composition of the glass, which generally increases with increase in SiO_2 content in the $Na_2O–B_2O_3–SiO_2$ system. For HGS to be useful in laser targets, the glass composition of HGS must be selected considering such properties as chemical durability, strength or gas permeability, in addition to the size requirement.

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Received 25 January
and accepted 22 February 1982