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Influence of titanium doping on the shell-forming process and geometrical properties of hollow glass microspheres

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ABSTRACT

As hydrogen storage containers, titanium-doped hollow glass microspheres (HGMs) have been fabricated using the dried-gel method. A mathematical model was constructed to quantify the shell-forming process and make predictions on the wall thickness and aspect ratio of HGMs. Geometrical parameters of the HGMs were measured. The results showed that titanium doping would significantly change the compositions of gel precursor and glass melt. The multiple-step decomposition mode and loss of blowing agent in gels with more than 6.5 mol% titania reduced the blowing efficiency, thus producing greater wall thickness and smaller aspect ratio of HGMs. The measured aspect ratio decreased with increasing gel particle size, which was contrary to the predicted result. This was attributed to the poor blowing ability of large gel particles due to the limited residual time in the furnace. Moreover, the surface tension and viscosity of the glass melt were changed by titanium doping as well, which resulted in inadequate refining for heavily doped glass and consequently reduced the sphericity and surface finish of HGMs.

Introduction

Hollow glass microspheres (HGMs) are promising high-pressure hydrogen storage container due to the advantages of high efficiency, safety, lightness, cheapness, and simplicity [1–3]. However, the poor hydrogen release rate is a detriment to further development of this efficient hydrogen storage technology. The photo-induced outgassing in HGMs doped with metals, such as Fe, Co, Ni [4–6], provides a possible solution. It has been found that titania is also an optically active dopant in our study and titanium doped HGMs shows notable response to the illumination source, which has never been reported. HGMs also have been widely used as deuterium–tritium containers in inertial confinement fusion (ICF) experiments owing to its high strength, excellent surface finish, concentricity and sphericity [7–10]. Glass shells doped with medium or high Z element (Ge, Ti, Fe, Zn, Pd, Sn, Au, W, etc.) would be useful in ICF diagnostic experiments. Titanium doping facilitates diagnostic evaluation of the degree of mixing of the wall with the fuel during the implosion. In addition, doping with titanium not only alters the density profile at the ablation front resulting in less perturbation growth, but also helps to achieve maximum pressure and density of the fuel by absorption of X-rays that would otherwise preheat the fuel [11,12].

HGMs using alkali borosilicate glasses are often applied [13–15]. Detailed reports about the preparation of titanium-

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doped alkali borosilicate HGMs have not been found. In this study, titanium-doped alkali borosilicate HGMs are fabricated from dried gel. The dried gel method is one of the traditional techniques in the target-preparation field and has been applied with considerable success in the production of high-quality HGMs [16–18]. Flexibility of compositions is one of the outstanding advantages, which is favorable for element doping or introducing additional constituents to improve the performance of HGMs [19,20]. In addition, the diameter and wall thickness of HGMs can be strikingly increased [21,22].

As fuel containers in ICF experiments, the HGMs are required to satisfy stringent requirements on the geometrical specifications. These parameters cover sphericity, wall thickness uniformity, surface finish and sometimes diameter, wall thickness and/or aspect ratio. For example, acceptable shells always meet an out-of-round of less than 1 μm and a surface roughness lower than 50 nm. Meanwhile, manufacture needs batches in which 80% of HGMs meet the requirements [23,24]. In addition, diameter and aspect ratio are two factors to affect the strength of HGMs, which is significant for the scheme of pressurized hydrogen storage as well. Titanium doping inevitably changes the compositions of gel precursor and glass melt, not only oxide types but also the anion species, which influences the transformation process from gel to HGM. The dried gel method to fabricate HGMs is based on decomposed product to blow the glass melt, thus the wall thickness and aspect ratio of HGMs are mainly decided in the encapsulating and foaming processes. During the refining process, the surface tension and viscosity of the glass melt are two important properties to determine the sphericity and surface finish of HGMs. To obtain titanium-doped HGMs with certain geometrical specifications, it would be helpful to gain insight into the shell-forming process.

To clarify the effects of titanium doping on the shell-forming process and geometrical properties of HGMs, the focus of this work is to study the transformation process from gel precursor to glass shell and the geometrical characteristics of HGMs with different titania contents. First, the thermal behaviors of gel precursors and changes in the structures from gels to HGMs were characterized. Then, a mathematical model of the shell-forming process was constructed that could predict the changes of wall thickness and aspect ratio with two variables, gel particle size and concentration of blowing agent. Furthermore, geometrical parameters, such as diameter and wall thickness of HGMs with different doping levels were measured to verify the predicted results. Based on the predicted and experimental results, the influences of titanium doping on the compositions of gels and glass melts and the further encapsulating, foaming and refining processes were discussed. In addition, approaches to control the geometrical parameters of HGMs were proposed.

Material and methods

Gel particles synthesis

The basic compositions of titanium-containing HGMs included 69.7 SiO_2, 1.6 B_2O_3, 9.5 Li_2O, 16.4 Na_2O and 2.8 K_2O (in mol%). Gel precursors doped with titanium were synthesized using the sol–gel method. The titanium doping was implemented by dissolving tetrabutyl titanate ($Ti(OC_4H_9)_4$, TBOT) in tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS). Acetic acid (CH_3COOH, HOAc) was introduced to control the hydrolysis rate of TBOT. Three kinds of aqueous alkali acetates (lithium acetate (LiOAc), sodium acetate (NaOAc) and potassium acetate (KOAc)) supplied alkali oxides and meanwhile the acetate ions behaved as blowing agent to produce decomposing gases. The prepared xerogel grains were ground and sieved into gel particles with specific size ranges. A detailed description of the process can be found in our previous work [25].

HGMs preparation

Titanium-doped HGMs were fabricated in a vertical high-temperature tube furnace using the dried gel method. A schematic diagram of the vertical high-temperature tube furnace is shown in Fig. 1. A batch of gel particles that were roughly uniform in size were introduced into the furnace tube from the feeding zone. Gel particles went through heating, encapsulating, foaming, and refining processes and then transformed to molten glass shells when falling under gravity. After leaving the furnace tube, the molten shells quickly cooled and solidified and were collected in the collecting zone. A schematic diagram of the major stages of the dried gel method is shown in Fig. 2. More detailed descriptions about dried gel method can be seen in the literature [10,19,26]. In this work, all doping levels and compositions involved are theoretic value.

Characterization of gels and HGMs

The thermogravimetric analysis (TGA) of gel particles was performed on the Pyris 1 Termogravimeter Analyzer

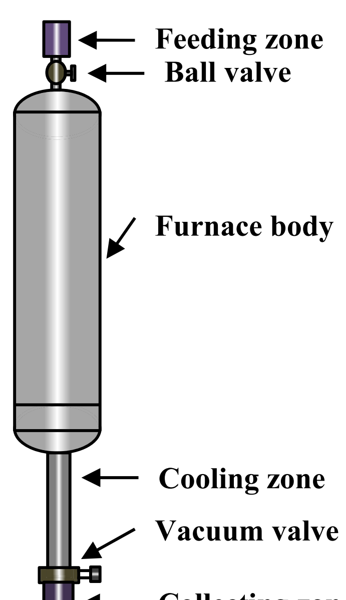

Fig. 1 – Schematic diagram of vertical high-temperature tube furnace for fabricating HGMs using the dried gel method.