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Influence of titanium doping on the structure and properties of hollow glass microspheres for inertial confinement fusion

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ABSTRACT

Titanium doped hollow glass microsphere has been fabricated by dried gel method for inertial confinement fusion application. Spheres with same titanium doping level were classified into two classes based on the absorption of different visible light wavelengths. Influences of titanium doping on the structure, strength and half-life of deuterium retention of spheres, as well as differences on the structure and property between the two classes of spheres were investigated. Results showed that titanium doping of gel precursors led to formation of oxygen vacancy during shell-forming process. Besides, the uniformity of the spheres decreased with increasing titanium content. Although gas retention and mechanical strength of titanium doped spheres satisfied the requirements of fuel containers, change in the composition and deterioration in the glass structure resulted in degradation of these performances. For five batches of spheres, viz. 0%, $8\%_B$, $8\%_A$, $15\%_B$ and $15\%_A$, the average Young's moduli were 52.14, 36.68, 41.41, 33.99 and 34.72 GPa, respectively, and the average half-lives of deuterium retention were 513, 41, 470, 62, and 327 d, respectively. Class B spheres possessed thinner walls and lower titanium concentrations than class A spheres. This facilitated the formation of dense oxygen vacancies, which disrupted the continuity of glass network. Due to an inferior structure, the performance of class B spheres was not as well as that of class A spheres. Nevertheless, oxygen vacancies can be compensated via heat treatment in air.

1. Introduction

Hollow glass microspheres, due to their strength, suitable hydrogen permeability and transparency are commonly used as fuel containers in the research of inertial fusion [1–3]. Glass shells doped with titanium, a medium Z element, are useful in inertial confinement fusion (ICF) physics diagnostic experiments [4,5]. This is because on absorbing X-rays, the med- or high-Z element dopant in the ablation material helps to achieve maximum pressure and density of the fuel. In addition, it enhances the ablation stability by altering the density profile at the ablation front. Furthermore, med- or high-Z element doping facilitates diagnostic evaluation of the degree of mixing of the wall with the fuel during implosion [6,7]. In addition, hollow glass microsphere is also a promising hydrogen storage container due to the advantages of high efficiency, safety, lightness, cheapness, and simplicity. The accelerated hydrogen diffusion through titanium doped glass sphere with an intense illumination source has been found in our study, which has never been reported.

The dried gel method for making glass microspheres was pioneered by Nolen, Nowns and co-workers at KMS Fusion, Inc. in the late 1970's [8,9] and further developed in Lawrence Livermore National Laboratory [10] and Japan [11]. In the dried gel process, sol precursor is aged and dried to gel, and then ground and sieved into narrow size ranges, which is the precursor of glass sphere. The dried gel precursors transform to hollow glass microspheres in a high temperature furnace. Since this method has great flexibilities in the choice of the initial compositions of glass and in geometrical parameters, the spheres can meet the requirements of ICF targets in a wide range, such as gas retention, strength, and element doping. For the present work, we use dried gel method to prepare titanium doped glass spheres.

To find usage as fuel containers, it is essential that the titanium doped glass spheres possess certain criteria, such as sphericity, concentricity, wall uniformity, strength, and permeability to gas to be used as fuel containers. Again, some of the properties are influenced by the chemical composition of the microspheres, such as gas permeability, strength and chemical durability, and these properties are usually related with each other. Generally, titanium stays in a tetrahedral site just like silicon and acts as network former in alkali glass [12]. Titanium doping inevitably changes the composition and structure of a glass and further affects the property of glass spheres. Besides, element doping may bring in imperfections, which is also a vital consideration because that deteriorates the performance of glass spheres. Therefore, comprehending the effect of titanium on the spheres is significant for obtaining titanium doped glass microspheres with better performance in ICF programs. In this regard, the primary objective of current research involves investigation of the influence of titanium doping on the structure, strength and half-life of deuterium retention of glass spheres.

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Titanium is generally present as Ti^{4+} in silicate glass. Ti^{4+} is colorless owing to the presence of vacant 3d orbit. In transition elements, the valence electrons can move to selected energy levels causing selective absorption of different wavelengths of light. It has been reported that oxygen deficiency related Ti^{3+} can exhibit a broad absorption band of visible light [13–16]. For the present work, although majority of the titanium doped glass spheres are colorless, some spheres are found to be blue colored. The different appearances of spheres are caused by the different valence states of titanium and different structures of glass, which affects the properties of spheres. Moreover, poor transparency to visible light of glass spheres can sometimes baffle the measurements of some parameters. Thus, another focus of this work is to investigate the differences of the structures and properties between the two kinds of spheres. In addition, measure to ameliorate the structure and property of titanium doped spheres is proposed.

2. Experimental details

2.1. Preparation of titanium doped glass spheres

The composition of titanium doped glass was based on one of the optimum glass compositions reported by Qi et al. [17] with mole ratios of 69.73% SiO_2, 1.63% B_2O_3, 9.44% Li_2O, 16.43% Na_2O and 2.77% K_2O. The desired titanium content was achieved by introducing the titanium source with specific atom ratio of titanium to silicon. For convenience, letter *q* was used to denote the titanium doping level via the atom ratio of Ti to Si. The subscripts B and A after *q* denoted spheres that absorbed visible light and that did not, respectively.

Titanium doped dried gel precursors for glass spheres were synthesized via sol gel method. Details about the process can be seen elsewhere [18,19]. Hollow glass microspheres were fabricated from dried gel precursors. Titanium doped gel particles were introduced into the feeding zone at the top of a vertical high temperature furnace. While traveling vertically downward through high temperature and an inert atmosphere, formed by a mixture of helium (He) and argon (Ar) at a certain pressure ratio, the gel precursors became encapsulated by a liquid membrane on the surface of gel particles. During the foaming process, the softened gel particles swelled by decomposed gases. The molten glass spheres were refined under high temperature. Finally, the glass shells shrank during cooling process. A detailed description of the furnace and transformation processes is given in Ref. [20–22]. Unless otherwise specified, the glass spheres in this work were all prepared from the gel particles with size ranging from 200 to 250 μm, under a mixing atmosphere of 83% He and 17% Ar, at temperature of 1400 °C and pressure at 1.0 atm. To achieve the required surface smoothness and chemical stability of the spheres as fuel containers, an acid wash procedure was developed. The procedure involved washing with a special lotion (mixture of 0.1 M NH_4F and 0.5 M HNO_3), followed by rinsing in distilled water and ethanol. The spheres were finally preserved in absolute ethanol.

2.2. Characterization of the glass spheres

X-ray photoelectron spectroscopy (XPS, Thermo-VG Escalab 250) was used to analyze the composition of the glass spheres. Tests for each sample involved the surface layer and subsurface after being etched by argon ions for 30 s. Spheres of size ~550 μm were analyzed with a 250 × 250 μm tested area. UV–visible absorption spectra were recorded on a Lambda 950 UV–Vis-NIR spectrophotometer (PerkinElmer, USA). Samples were prepared by adhering spheres to a quartz substrate with ethanol. The mole ratio of titanium to silicon was tested by X-ray fluorescence (XRF, EDAX Co., Eagle III) spectrometry. Ten spheres of each batch were tested. The geometrical parameters of the spheres were characterized using optical measuring microscope (Nikon Co., MM-400) for outer diameter, D, and interferometric microscope (Veeco Co., WYKD-NT1100) for wall thickness, t_w. Micrographs of the glass spheres were obtained by VHX-600E digital microscope (KEYENCE, Japan).

2.3. Gas retention capacity of the glass spheres

The strength and permeability are important for the glass spheres in ICF experiment. Permeability of the glass spheres were characterized by the half-life for gas retention. The half-life, hereafter referred to as $t_{1/2}$, was defined by the time when the pressure within the spheres decreased to half of the initial value at constant temperature and surrounding pressure. If $t_{1/2}$ is more than 100 d, the performance could satisfy the regular process of target preparation in ICF program; In the event of 50–100 d, the interval between target preparation and target implosion should be shortened; If $t_{1/2}$ is no more than 50 d, measures to preserve the pressure within the spheres should be taken [23].

To study the capacity of gas retention, spheres were filled with deuterium gas (D_2) in an in-house designed thermal diffusion setup at elevated temperature (300 °C) and ~40 atm pressure. Owing to the transparency and high sphericity of glass sphere, interference fringe method is a good nondestructive means for pressure measurement. For the four batches, 0%, $8\%_A$, $15\%_A$, and $8\%_B$, the pressure attenuation in the spheres was tracked by interferometric microscopy. The pressure can be calculated from the tested fringes by the following equation [24]

$$P = \frac{\Delta n \lambda RT}{4fMD} \tag{1}$$

where $\triangle n$ is the variation of fringes before and after gas filling; λ is the wavelength; R is the gas constant, f is proportionality coefficient, M is the gas molar mass; and D is the diameter of microsphere. By this method, the pressure of each sphere was represented by one curve. Due to the poor transparency of $15\%_B$ samples, the pressure of this sample was measured by bubble method instead of the interference fringe method. In the bubble method, the glass sphere was crushed in glycerin and gas pressure was calculated from the bubble diameter based on the gas state equation. Three spheres were tested each time and the average pressure was recorded. An average curve was obtained from the average values. Unlike the interference fringe method, the bubble method is a destructive technique and is neither advantageous nor economical.

The $t_{1/2}$ that was too long to be tracked in experiment could be estimated from the pressure at any time according to Eq. (2) [25] and Eq. (3) [24].

$$K_p = \frac{Dt_w}{6RTt} * \ln \frac{\Delta P_0}{\Delta P_t} \tag{2}$$

$$t_{1/2} = \frac{Dt_w \ln 2}{6RTK_p} \tag{3}$$

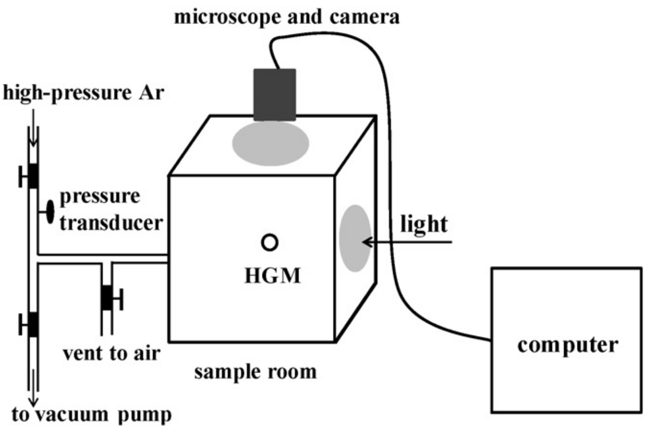

Fig. 1. Schematic diagram of in-house apparatus for pressure tests of HGMs.