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Preparation and characteristic of a temperature resistance buoyancy material through a gelcasting process

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HIGHLIGHTS

- A temperature resistance composite with borosilicate glass as matrix was prepared.
- The composite exhibited excellent mechanical and thermal properties.
- The exponent *m* value was lower than that of open- or closed-cell foams.
- Thermal conductivity value was close to that of Landauer's relation prediction.
- Young's modulus agreed with Ashby–Gibson model for a porosity from 65% to 89%.

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ABSTRACT

A novel temperature resistance buoyancy material with hollow glass microspheres (HGMs) as the filler and borosilicate glass (BG, similar chemical composition to the HGMs) as the high temperature matrix was prepared by a tert-butyl alcohol based on gelcasting process. The effect of solid loading and sintering temperature on microstructure and mechanical properties were investigated. The results showed that HGMs were bonded together by borosilicate glass and 45 wt.% solid loading and 700 °C were the optimal processing parameters to fabricate the samples with the best mechanical and thermal properties, and the corresponding bulk density, compressive strength, thermal conductivity and Young's modulus were 0.92 g/cm^3, 14.46 MPa, 0.15 W/m K and 1.24 GPa, respectively. The exponent *m* value for the samples fabricated in this work was 1.18, lower than that of open- or closed-cell foams, because the sample possess both the closed and open pores. The experimental values of thermal conductivity from 0.07 to 0.16 W/m K were lower than the prediction with the Hashin–Shtrikman upper bound and almost close to that predicted by the Landauer's relation. Only modulus value of SSL45 sample which possessed the maximum value was closer to Hashin–Shtrikman upper bound, while the modulus value of other samples agreed well with Ashby–Gibson model applied for a porosity ranging from 65% to 89%. The HGMs/BG composite exhibited a low density, low thermal conductivity and excellent temperature resistance, and can be used as the thermal insulation for undersea pipeline or submarine.

1. Introduction

Syntactic foams (SFs) are lightweight porous composites prepared by mechanical mixing of hollow glass microspheres (the filler) in polymeric resin (the matrix), exhibiting low density (buoyant behavior), high specific strength, high stiffness, closed porous structure, and low moisture absorption. These characteristics enable them to be used from the deepest parts of the ocean to other planets, e.g. the rudders and flaps of submarines, the deckhouse of USS Zumwalt (DDG 1000) guided missile destroyer, USS Memphis. Besides, Cuming Corporation reports that the SFs can also be used as thermal insulation for undersea pipeline [1]. However, they would be subjected to mechanical and high temperature impact when exposed to above conditions and the maximum operating temperature for the SFs were no more than 300 °C [2]. Although there have been many studies addressing the mechanical properties of SFs during the past decades, improving the temperature resistance of SFs was still a problem and literatures in this aspect were rare; thus we should highlight the importance of temperature resistance of syntactic foam, especially when they were used in harsh environment. Currently, some researchers tried to improve the temperature resistance of the SFs through the incorporation of inorganic microballoons [3–5], such as cenospheres,

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hollow silica microsphere, or silas balloons. Okuno [5] successfully prepared phenolic resin syntactic foams by injecting hollow microspheres into the phenolic resin and temperature resistance of the syntactic foams was only up to 300 °C. The results indicate that temperature resistance was effectively improved since the main factor determining the temperature resistance of SFs was not identified. In typical two-phase SFs, the temperature resistance depends on two components: the matrix (usually referring to epoxy resin) and the filler (using referring to hollow glass microspheres). Hollow glass microspheres (HGMs), made of a soda-lime-borosilicate glass, possess superior temperature resistance and the matrix, composed of organic compounds, has poor temperature resistance. It is not difficult to find that the temperature resistance of the matrix was the main factor determining the temperature resistance of SFs and it is essential to improve the temperature resistance of the matrix to further enhance the temperature resistance of SFs.

Ceramics as a traditional material possess unique chemical (high temperature stability), mechanical (high specific strength and low thermal conductivity), and thermal properties (temperature resistance), which make them good candidates for both functional (filtration and thermal insulation) and structural applications (lightweight structures) [6]. Compared with polymer-matrix or metallic-matrix composites, ceramic-matrix composites display excellent temperature resistance that is obtained through a high-temperature sintering process. Therefore, if the matrix is replaced by ceramic materials, the temperature resistance of the buoyancy materials would be improved largely. To obtain the composite with temperature resistance as well as high compressive strength, the chemical composition of the matrix should be similar to that of HGMs. The HGMs were made of soda-lime-borosilicate glass and thus, borosilicate glass (BG) with similar chemical composition to the HGMs was chosen as the matrix in this study.

Ceramic-matrix composite was usually prepared by dry pressing, hot isostatic pressing, and extrusion and these methods may damage the HGMs. Gelcasting as a near-net shape forming process is similar to slip casting and injection moulding, but with several advantages: (1) high green strength, (2) a short processing time, (3) high-quality homogeneous bodies with complex shapes, (4) machinability, etc. [7–12] and many porous ceramics (e.g. Al_2O_3, Si_3N_4, SiC, and ZrO_2) have been prepared by this process. To maintain the integrity of HGMs, a tert-butyl alcohol (TBA)-based gelcasting process was selected to prepare the hollow glass microspheres/borosilicate glass (HGMs/BG) composite. The aim of this research work was the development of a novel buoyancy material with temperature resistance and high compressive strength. The effect of solid loading and sintering temperature on mechanical performances of the composite were also discussed.

2. Experimental procedure

2.1. Raw materials and preparation procedure

Hollow glass microspheres (S38HS, softening temperature 600 °C) as raw material were purchased from 3 M Co., USA, and the properties were shown in Table 1. Borosilicate glass (BG (XY-610F, sieved with 200-mesh screen), was supplied by Xuanyang, Zhuhai, Co., China and the softening temperature was 650 °C. Tert-butyl alcohol (TBA, $(CH_3)_3COH$), Acrylamide (AM, $C_2H_3CONH_2$), and N, N′-methylenebisacrylamide (MBAM, $(C_2H_3CONH_2)_2CH_2$) were used as the solvent, monomer, and cross-linker, respectively. The details of preparing premixed solution were according to the reference [11] and ammonium persulfate (APS, $(NH_4)_2S_2O_8$) was used as the initiator of polymerization reaction. To produce stable suspension, citric acid (CA) as dispersant (2 g per 100 g slurry) was used in the premixed solution. All the chemicals in the study were analytical regent.

Fig. 1 was a flowchart for the preparation of HGMs/BG composite and the green bodies were shown in Fig. 2. To make a homogenous suspension, a slurry containing BG, TBA, AM, MBAM and CA was prepared through a high-energy ball milling at 600 rpm for 4 h. Sample with solid loading of 25, 30, 35, 40, and 45 wt.% (denoted by SSL25, SSL30, SSL35, SSL40, SSL45) were prepared by a TBA-based gelcasting process, respectively, and the mass ratio of HGMs to BG was 1:1. Suspension was de-aired under vacuum to remove air bubbles introduced during ball milling. After addition of the initiator solution (10 wt.%, 2 ml), the suspension containing HGMs were poured into moulds with a nominal size of 20 × 20 × 20 mm. Then the mold was heated at 40 °C for 0.5 h and the dried samples were sintered at temperatures from 650 to 750 °C at heating rate of 1 °C/min, holding for 3 h. Fig. 3 shows the sample of SSL45 sintered at 650, 700 and 750 °C, respectively.

2.2. Characterization

The elemental composition of HGMs and BG was measured by Energy Dispersive X-ray Spectroscopy (EDXS) and the microstructure of the fracture surface was observed by scanning electron microscopy (SEM, SU1510, Hitachi, Japan). The radius ratio (η) and wall thickness (δ) of the HGMs were calculated using Eqs. (1) and (2).

$$\eta = \frac{r_i}{r_0} \tag{1}$$

$$\delta = r_0(1-\eta) \tag{2}$$

where, r_i and r_0 is the inner and outer radius of the HGMs, respectively. The linear shrinkage of samples sintered at different temperature was determined by

$$l_{\text{shrinkage}} = \left(\frac{l_a - l_b}{l_a}\right) \times 100\% \tag{3}$$

where, l_a and l_b are the diameter (mm) of the dried samples and sintered ones, respectively. The total porosity v_p (%) (open pore and closed pore) is calculated using

$$v_p = \left(1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{true}}}\right) \times 100\% \tag{4}$$

where, v_p is the porosity (%) of HGMs/BG composite and ρ_{true} is the true density (g/cm^3) of the composite measured on a pycnometer, respectively. ρ_{bulk} is the bulk density (g/cm^3) of the composite evaluated from the dry weight-to-volume ratio of the specimens. In order to damage the hollow structure of HGMs, the composite was ground into powder and sieved with 300-mesh screen. The resultant powder was used as the testing sample for the measure-

Table 1
Properties of the hollow glass microspheres.

	Isostatic crush strength (MPa)	Typical density (g/cm^3)	Radius ratio η	Particle size distribution (μm)		
				10% th	50% th	90% th
Hollow glass microspheres	37.9	0.38	0.949	15	40	75