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Mechanical properties and high-temperature resistance of the hollow glass microspheres/borosilicate glass composite with different particle size

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A B S T R A C T

Buoyancy material with high temperature resistance was successfully prepared through a tert-butyl alcohol gelcasting process. Borosilicate glass (BG) and hollow glass microspheres (HGMs) with different average diameters were used as the matrix and the filler, respectively. Results show that the compressive strength increased with the decrease of the mean diameter of HGMs, and the sample consisting of the filler of HGMs with a small average diameter exhibited high compressive strength of 25.04 MPa. Young's modulus values of the composite sintered at 700 °C and 750 °C were distributed over in the range of the values predicted from Ashby-Gibson model to Hashin-Shtrikman model and other moduli values agreed well with that of Past model prediction. Weibull moduli (m) reflecting the variation degree of the sample compressive strength were in the range of 5–15. The compressive strength of the composites composed of the HGMs with small average particle size tested at 500 °C was as high as 7.94 MPa.

1. Introduction

Glass-microspheres/epoxy resin-matrix composites, known as syntactic foams (SFs), exhibited excellent mechanical and physical properties, such as low density, high specific strength, low moisture, and high energy absorption [1–3]. As a type of lightweight materials, they are widely used as the sophisticated structural materials of the submarine, such as the pressure shell of the bathyscaphe and the torpedo [4]. During the anti-ship missile launching process, SFs material as a significant component of the above mentioned submarine may be subjected to high temperature corrosion. To eliminate the destruction caused by the high temperature and improve the temperature resistance of the SFs material, we should seek for a new type of buoyance material with excellent temperature resistance. Investigators have attempted to embed some microspheres with high temperature resistance into the matrix, such as fly ash cenospheres, hollow silicon spheres, and hollow alumina spheres. Results reveal that the temperature resistance did not increase significantly because researchers did not identify the main factors in determining the temperature resistance of the SFs. SFs as a type of buoyance material is usually composed of the matrix of epoxy resin and the filler of hollow glass microspheres (HGMs). Considering the composition of SFs, we know that the temperature resistance is mainly dependent on the epoxy resin and HGMs. Epoxy resin as a type of organic compound possesses inferior temperature resistance; on the contrary, the HGMs, composed of soda-lime borosilicate glass [5], exhibit excellent temperature resistance. Obviously, the matrix of epoxy resin exerted a great influence on the temperature resistance of the SFs and we should select a matrix to replace the epoxy resin in order to obtain the buoyance materials with excellent temperature resistance.

In previous study, we have successfully prepared a buoyancy material with excellent temperature resistance, hollow glass microspheres/borosilicate glass (HGMs/BG), through a tert-butyl alcohol-based gelcasting process, using BG and HGMs as the matrix and the filler, respectively, and discussed the effect of solid loadings and the mass ratio of HGMs to BG on the mechanical

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properties and thermal conductivity of the HGMs/BG composite [6,7]. Besides, the particle size and the true density of HGMs may also have effect on the mechanical properties and microstructure of the HGMs/BG composite. D'Almeida et al. [8] analyzed the mechanical properties of a glass microspheres/epoxy-matrix composite as a function of the mean diameter size of the hollow microspheres. Ghosh et al. [9] and Peroni et al. [10] investigated the effects of the size distribution of hollow microspheres with the same true density on the energy absorption capacity and the mechanical behavior of the SFs under the quasi static loading conditions. The results show that the smaller glass microspheres dominate the dynamic behavior of the SFs. The studies on mechanical performance of HGMs/BG composite at high temperature were still vacant. In this study, four types of microspheres with different average size and wall thickness were used as the starting materials and the aim of this study was to discuss the effect of the particle size of HGMs on the mechanical and physical properties of the HGMs/BG composites at both room-temperature and high-temperature. The composites with the prominent temperature resistance and mechanical properties may be used in deep sea and other fields in the near further.

2. Experimental procedure

2.1. Raw materials

Four different types of HGMs, named 3M Scotchlite™ Glass Bubbles K46, S60HS, iM16K, and iM30K, respectively, were used for the fabrication of the HGMs/BG composites and Table 1 shows their physical properties. The softening temperature of the HGMs and BG (XY-610F, supplied by Xuanyang, Zhuhai, Co., China) was 600 °C [5] and 650 °C [11], respectively. Tert-butyl alcohol $(CH_3)_3COH$), Acrylamide ($C_2H_3CONH_2$), and N, N′-methylenebisacrylamide ($(C_2H_3CONH_2)_2CH_2$) were used to prepare the premixed solution. The ammonium persulfate (APS) and citric acid (2 g per 100 g slurry) are used as the initiator and dispersant, respectively. All the chemicals used in the study were analytical regent.

2.2. Preparation procedure

The green bodies were prepared through a tert-butyl alcohol (TBA) based gelcasting process and the mass ratio of HGMs to BG was 1:1. The fabrication procedures of the HGMs/BG composites were according to reference [12] and the solid loading was 45 wt% during the whole experimental process. Firstly, BG and the premixed solution were mixed through a high-energy ball milling at 600 rpm for 4 h in order to get homogeneous slurry. Then, the HGMs and the initiator (10 wt%, 2 ml) solution was added into the de-aired slurry and the slurry containing HGMs and BG were poured into a mould with nominal size of 20 × 20 × 20 mm. Finally, the mould was heated at 40 °C for 0.5 h and the dried samples were sintered at 650 °C, 700 °C, and 750 °C, respectively, with a heating rate of 1 °C/min, holding for 3 h.

2.3. 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). Phase compositions of HGMs and the composites were characterized by X-ray diffraction analysis (XRD, D/Max-2500Rigaku, Japan) with Cu Kα radiation. The radius ratio (η) and the wall thickness are defined in Eq. (1) and Eq. (2) based on the inner and outer radii of the microballoon [13,14]. The volume of the single microspheres is given by Eq. (3). Table 2 presents the average wall thickness and radius ratio of the four different types of HGMs and their schematic diagram was shown in Fig. 1.

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

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

$$V = \frac{4}{3}\pi r_0^3\left(1-\eta^3\right) \tag{3}$$

where, η and δ are the radius ratio and wall thickness (μm) of the microspheres; r_i and r_o are the inner and outer radii (μm) of the microspheres; V is the volume (m^3) of the singles microspheres, respectively. The radius ratio, η, varies between 0 and 1.

The total porosity v_p (%) is calculated by the following formula:

$$v_P = \left(1-\frac{\rho}{\rho_t}\right) \times 100\% \tag{4}$$

where, v_p and ρ are the porosity (%) and bulk density (g/cm^3) of the samples, respectively. ρ_t is the true density (g/cm^3), measured by a pycnometer method.

Quasi-static uniaxial compressive test was carried out on an electronic universal testing machine (CSS-44100, Changchun Research Institute Mechanical Science Co. Ltd., Jilin, China) with a crosshead speed of 0.5 mm/min, according to the Chinese National Standard GB/T 4740-1999. The stress-strain curves were obtained from the compression tests and Young's modulus was calculated from the linear stage of the curves. Specific strength (σ_{sc}) is the ratio of compressive strength (σ_c) to the bulk density, calculated by Eq. (5):

Table 2
The wall thickness and radius ratio of the four types of HGMs.

Hollow Glass Microspheres Type	Wall thickness (μm)	Radius ratio η
K46	1.46	0.936
S60HS	1.28	0.914
iM16K	1.34	0.933
iM30K	1.20	0.907

Table 1
Physical property of the four types of the HGMs.

Hollow Glass Microspheres Type	Typical density (g/cm^3)	Particle size distribution (μm)			Isostatic crush strength (MPa)
		10% th	50% th	90% th	
K46	0.46	15	40	70	41.38
S60HS	0.60	11	30	50	124.14
iM16K	0.46	12	20	30	113.79
iM30K	0.60	9	16	28	193.10