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Mechanical properties and thermal conductivity of a temperature resistance hollow glass microspheres/borosilicate glass buoyance material

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ABSTRACT

A temperature resistance buoyancy material was fabricated through a tert-butyl alcohol gelcasting process with borosilicate glass (BG) and hollow glass microspheres (HGMs) as the matrix and filler, respectively. The effects of the mass ratio of HGMs to BG and sintering temperature on the microstructure, thermal conductivity, and mechanical properties of the composite were studied. The results show that HGMs were bonded together by the BG, and the sample sintered at 750 °C exhibited a broad pore size distribution, from several microns to more than one hundred microns. The thermal conductivity experimental values of all the samples were less than that of Hashin-Shtrikman upper bound (HS^+) prediction but agreed well with that predicted from effective medium percolation theory. The relationship between compressive strength and relative density was predicted by the Gibson-Ashby model, with the calibration factor phi below 0.7. Young's modulus values obtained from the experiment were below that of HS^+ prediction. The modulus values of the four types of samples sintered at 650 °C agreed well with the Pabst model prediction, while the values of the samples sintered at 700 °C and 750 °C were distributed in a zone between Ashby-Gibson model and HS^+ prediction.

1. Introduction

Epoxy resin syntactic foams (SFs) with closed cell structure prepared by dispersing hollow microspheres in a resin exhibit excellent properties containing low density, high compressive strength, low moisture absorption, and low shrinkage. The SFs, as a core material for sandwich structures, are commonly used in the field of aerospace and deep sea [1–6]. In case of carrying out anti-ship missile experiment under the deep-sea environment, SFs as one of the important parts of the submarine would be subjected to high temperature (from several hundred degrees Celsius to thousands of degree Celsius) erosion generated during the launching process. Meanwhile, the mechanical performance of the SFs may be also affected under these conditions. Thus, the fabricated SFs foams should possess excellent temperature resistance behavior in order to be used in the high temperature environment.

At present, literatures on improving the temperature resistance of foams materials were quite limited, and injecting some temperature resistance filler into the matrix may be a possible way of improving the temperature resistance. The fillers can be fly ash cenospheres, hollow silica microspheres, and hollow carbon microspheres [7,8]. However, the temperature resistance of the foams prepared with the above fillers was not largely improved. The main reason is that the researchers may not identify the factor influencing the temperature resistance of the SFs. The temperature resistance of the epoxy syntactic foams was dependent on the epoxy resin (the matrix) and hollow glass microspheres (the filler). Epoxy resin, a type of organic compound, composed of a series of epoxy groups with low molecular weight, exhibited poor temperature resistance. On contrary, the filler of HGMs possessed excellent temperature resistance because of the chemical composition of soda-lime-borosilicate glass [9]. In view of the above factor influencing the temperature resistance of buoyance material, it is not hard to see that the matrix plays a rather importance role in determining the temperature resistance of the SFs. Therefore, we should seek for a new matrix in order to obtain the foams with excellent temperature resistance.

Compared to metal or polymer matrix composite, the ceramic matrix composite possessed outstanding temperature resistance [10,11], and if the matrix was replaced by the ceramics, the temperature resistance of the buoyance material would be greatly

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improved. Borosilicate glass (BG), a type of ceramic material, possessed distinguished temperature resistance and mechanical properties, and superior wettability. Besides, the chemical composition and softening temperature of the BG was similar to that of the HGMs, which may be beneficial to enhance the bonding strength among the HGMs. In previous study [12], we have successfully prepared a novel temperature resistance hollow glass microspheres/borosilicate glass (HGMs/BG) buoyance material through a tert-butyl alcohol (TBA)-based gelcasting process. During the experiment process, we found that the mass ratio of HGMs to BG played a significant role in the mechanical properties and thermal conductivity of the HGMs/BG composite. The effect of hollow particles addition on the mechanical property and microstructure of the cellular material has been reported in previous study. Kim et al. [13] found that the porosity of the cellular glasses can be adjusted from 42% to 62% with hollow glass microspheres ranging from 30% to 100%. In Su's study, the results [14] indicated that the porosity of the Al_2O_3 ceramic varied from 22.3% to 60.1% with the Al_2O_3 hollow sphere from 30% to 50%. The results of the Dr. Zhao's study [15] revealed that the amount of hollow ceramic microspheres would have an effect on the mechanical properties and porosity of Al matrix syntactic foams. However, less study has been performed on the influence of the mass ratio of HGMs to BG on mechanical property and thermal conductivity of the HGMs/BG composite. The aim of this study was to investigate the effect of mass ratio of HGMs to BG on the mechanical and thermal properties of the HGMs/BG composite. The composite with excellent temperature resistance and mechanical property would be used in marine and aerospace in the near future.

2. Experimental procedure

2.1. Raw materials

Hollow glass microspheres (softening temperature of 600 °C) as raw materials were supplied by 3 M Co., USA, and the basic parameter was list in Table 1. The particle size distribution and phase composition of the HGMs were shown in Fig. 1. Borosilicate glass (softening temperature 650 °C [16], sieved with 200-mesh screen) was purchased from Xuanyang Co., Ltd., Zhuhai, China and their properties were list in Table 2. Tert-butyl alcohol ($C(CH_3)_3OH$, TBA), acrylamide (CH_2=CH CNH_2, AM), and N, N′-methylene bisacrylamide ($(CH_2$=$CHCONH)_2CH_2$, MBAM) were used to prepared the premixed solution. The procedure was carried out as described previously [17] and ammonium persulfate (APS) and citric acid (2 g per 100 g slurry) acted as the initiator and dispersant in the gelation reaction, respectively. All the chemicals purchased from Kemiou Chemical Reagent Co., Ltd., Tianjin, China were analytical regent.

2.2. Preparation procedure

The homogeneous suspension was prepared through a high-energy ball milling of a mixture of BG, TBA, AM, MBAM and CA at 600 rpm for 4 h, and then the HGMs were added into the suspension. The samples were prepared through a TBA-based gelcasting process and the solid loading of 45 wt% remains unchanged during the experimental process. To investigate the effect of the mass ratio of HGMs to BG on the mechanical performance, microstructure, and thermal properties of the HGMs/BG composite, four types of composites were prepared with mass ratios of HGMs to BG of 3:7, 4:6, 5:5, and 6:4, denoted as HGMs/BG-37, HGMs/BG-46, HGMs/BG-55, and HGMs/BG-64, respectively. Then the suspension was de-aired under vacuum to remove air bubbles introduced during ball milling. After the addition of initiation solution (10 wt%, 2 ml), the suspension was poured into the mold with a size of 20 × 20 × 20 mm. Finally, the mold was heated at 40 °C for 0.5 h, and after drying the samples were sintered at 650, 700, and 750 °C, respectively, at heating rate of 1 °C/min, holding for 2 h. Fig. 2 showed a process scheme for the preparation of HGMs/BG composites by a TBA-based gelcasting process.

Table 1
Properties of the hollow glass microspheres.

	Isostatic crush strength (MPa)	Typical density (g/cm^3)	Weight composition (%)					
Hollow glass microspheres	37.9	0.38	B 36.57	O 28.83	Na 3.11	Al 0.21	Si 24.28	Ca 7.00

2.3. Characterization

The morphology of the HGMs and HGMs/BG composites was observed by scanning electron microscope (SEM, SU1510, Hitachi, Japan). The pores size distribution of closed cells of the composite was determined by quantitative image analysis of cross-section SEM micrographs. The linear shrinkage of the samples was calculated using Eq. (1),

$$l_{shrinkage} = \left(\frac{l_0 - l_1}{l_0}\right) \times 100\% \quad (1)$$

where, l is the length (mm) of the sample, the subscript *0* and *1* represent before and after sintering, respectively. The pore volume fraction υ_p (the sum of open porosity and closed porosity) is calculated from Eq. (2),

$$\upsilon_P = \left(1 - \frac{\rho_{bulk}}{\rho_{true}}\right) \times 100\% \quad (2)$$

where, ρ_{true} and ρ_{bulk} is the true density (g/cm^3) and bulk density (g/cm^3) of the sample measured by a pycnometer and weight-to-volume ratio of the samples, respectively. The open porosity was measured using Archimedes method, according to National Standard of the People's Republic of China (GB/T 1966-1996) and to ensure the samples completely sunk in the bottom of water, a heavy object was tied to the samples and the weight and density of the object was given in the experiment. The thermal conductivity at room temperature was carried out on a Thermal Properties Analyzer (XIATECH TC 3000), according to the National Standard of the People's Republic of China (GB/T 10297-2015).

Uniaxial compressive test was performed by using an electronic universal testing machine (CSS-44100) with a crosshead speed of 0.5 mm/min, according to National Standard of the People's Republic of China (GB/T 4740–1999) and Young's modulus can be calculated from the elastic stage of the stress-strain curves. The specific strength (σ_{sc}) was calculated using Eq. (3),

$$\sigma_{sc} = \frac{\sigma_c}{\rho_{bulk}} \quad (3)$$

where, σ_c and ρ_{bulk} is maximum compressive strength (MPa) and bulk density (g/cm^3) of the composites, respectively.

3. Results and discussion

3.1. Effect of the mass ratio of HGMs to BG on the green body

To keep the integrity of the HGMs, TBA-based gelcasting