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Preparation and characterization of highly porous Yb_2SiO_5 ceramics using water-based freeze-casting

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Abstract This study introduces a new, highly porous Yb_2SiO_5 ceramic prepared using a water-based freeze-casting technique. The prepared porous Yb_2SiO_5 ceramic had ultra-high porosity (82–86 %) and tailored pore structures. The effects of sintering temperature on the pore structure, thermal conductivity, and mechanical properties of these ceramics were investigated. The sample with 15 vol% solid content prepared at 1450 °C had ultra-low linear shrinkage (4.85 %), ultra-high porosity (83.95 %), high compressive strength (2.15 MPa), and low thermal conductivity (0.121 W/m K). In addition, this sample showed a relatively high compressive strength (1.15 MPa) at 1500 °C. These results highlight the potential application of highly porous Yb_2SiO_5 ceramics as thermal insulator materials in ultra-high temperature environments.

Keywords Porous ceramics · Freeze casting · Ultra-high porosity · Mechanical properties

1 Introduction

During the past decade, thermal insulator ceramics have been widely studied because of their contribution in the rapid development of aircraft. Porous ceramics, which have many excellent properties such as low density, low thermal conductivity, and high strength, have attracted the attention of material scientists and engineers as thermal insulator materials [1, 2]. In recent years, porous Al_2O_3, SiO_2, mullite, and yttria-stabilized zirconia have been identified as the common ceramic thermal insulators [3–6]. These porous ceramics individually possess particular merits; however, optimal overall performance in ultra-high temperature environments (>1500 °C) is difficult to achieve. Therefore, the development of new porous ceramics is the future trend for application in ultra-high temperature environments.

Ytterbium monosilicate (Yb_2SiO_5) is a material of particular interest because it has a unique set of properties, such as long durability in water vapor, superior high-temperature stability, and excellent mechanical and chemical compatibility with silicon-based matrices [7, 8], thus making it a promising candidate for high-temperature structural applications. In addition, Yb_2SiO_5 has a high melting point, excellent hot-corrosion resistance, and low thermal conductivity (<1.4 W/m K) [8–10]. Single-phase Yb_2SiO_5 was prepared using a solid–liquid reaction method by Zhou et al.; they found that the intrinsic thermal conductivity of Yb_2SiO_5 approaches a minimum value (0.74 W/m K) at high temperatures [10]. Therefore, it is suitable as an ultra-high temperature thermal insulator material, and this study attempts to prepare highly porous ceramics with Yb_2SiO_5. It was expected that these ceramics would combine the merits of Yb_2SiO_5 ceramics and highly porous ceramics and exhibit extremely low thermal conductivity, high strength, and low density at ultra-high temperatures.

Freeze-casting is a new method of preparing highly porous ceramics. As a wet shaping technique, the strength of freeze-casting lies in its ability to create materials with adjustable porous microstructures [11]. Deville prepared cylindrical porous ceramics by the directional freeze-

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casting method and found that at a given material porosity, their axial compressive strength was four times higher than that of porous ceramics prepared by other methods [12]. In particular, water-based freeze-casting offers great advantages compared with TBA- or camphene-based gel casting as it is a simple, low-cost, versatile, and environmentally friendly fabrication technique for preparing ultra-high porous ceramics [13]. In addition, the ice nucleation and crystal growth processes intrinsic to this method have been extensively studied, resulting in greater understanding and control of multiple pore structures of porous ceramics [12, 14]. In our previous study, porous Y_2SiO_5 ceramics with different sintering temperatures and solid content were prepared using the freeze-casting method [15, 16].

This study explores the application of the water-based freeze-casting method for the preparation of highly porous Yb_2SiO_5 ceramics. The effects of sintering temperature on the microstructure and properties of highly porous Yb_2SiO_5 ceramics were investigated. The compressive strengths of these ceramics at ultra-high temperatures (1500 °C) were measured and analyzed. The results of this study show that the highly porous Yb_2SiO_5 ceramics prepared by the water-based freeze-casting method are promising thermal insulator materials for application in ultra-high temperature environments.

2 Experimental procedures

Yb_2SiO_5 powders were synthesized by a solid–liquid reaction method. The initial Yb_2O_3 and amorphous SiO_2 powders were ball-milled in isopropyl alcohol for 12 h and then dried at 100 °C for 1 day. The dried mixed powders were uniaxially compacted under a pressure of 10 MPa in a steel mold. The compacted powder mixture was then calcined at 1600 °C for 2 h and ball-milled again for 12 h to break up agglomerates. The Yb_2SiO_5 powders produced were subsequently dried and screened through a 150-mesh sieve. Slurries were prepared by mixing the powders (15 vol%) and distilled water with 0.3 wt% ammonium polymethacrylate anionic dispersant (Sigma-Aldrich Trading Co., Ltd., Shanghai, China), polyvinyl alcohol binder (1 wt% of the Yb_2SiO_5 powders) and glycerol cryoprotectant (10 wt% of solvent); the resulting mixtures were then ball-milled with alumina balls for 12 h. The green bodies of highly porous Yb_2SiO_5 ceramics were fabricated by freeze-casting. The detailed freeze-casting process can be found in our previous work [15, 16]. The green bodies were carefully placed into a ZrO_2 crucible and sintered in a convection furnace under air atmosphere at 1150–1550 °C for 60 min. Both the heating and cooling rates were 5 °C/min.

The water-immersion technique was conducted using the Archimedes method to determine open porosities and densities of the sintered samples. The density of dried green bodies was calculated from the mass and dimension of samples. Porosity was calculated from the ratio of apparent density of porous samples to the theoretical density of dense Yb_2SiO_5 ceramic ($qs = 6.92$ g/cm^3) [10]. Each parameter was an average of the results of at least five samples. Thermal conductivity was measured by the guarded heat flow test method (DRE-III, Xiangtan Xiangyi Instrument Co., Ltd., Xiangtan, China).

According to GB/T 8489-2006 standard [17], the compressive strength of the cylindrical samples with Φ (11–14) mm × 20 mm was measured by a testing machine (Zwick Z050, Zwick, Ulm, Germany) with a crosshead speed of 0.5 mm/min. Before high temperature compression testing, the linear shrinkage of the samples was measured after calcination at 1500 °C. The high temperature compressive testing of porous Y_2SiO_5 samples was measured at 1500 °C in air using an ultra-high temperature mechanical property testing system assembled in our laboratory [18]. The samples were machined with the compressive surface perpendicular to the freezing direction. More than six samples of each measurement were selected to obtain the average value. The microstructure of the as-prepared products coated with a thin layer of gold was observed by a scanning electron microscope (FEI Quanta 200, FEI Company, Hillsboro, USA).

3 Results and discussion

3.1 Microstructure of porous Yb_2SiO_5

All the porous Yb_2SiO_5 ceramics were prepared with the same solid content (15 vol%), and the effects of the sintering temperature (1150–1550 °C) on the porosity of the samples were observed. The resultant porosities of the prepared ceramics are listed in Table 1. As can be seen, the prepared samples had ultra-high porosities (>82 %). As the sintering temperature increased from 1150 to 1550 °C, the bulk density and linear shrinkage of the ceramics increased from 0.99 to 1.23 g/cm^3 and 1.45 to 7.60 %, respectively. Simultaneously, the porosity decreased from 85.65 to 82.15 %. The porosities were measured using the Archimedes method, which gave porosities almost similar to those calculated from the relative density. Therefore, most of the pores in the prepared porous Yb_2SiO_5 samples were open.

Figure 1a–e show the morphology of the porous Yb_2SiO_5 ceramics with 15 % solid content prepared at different sintering temperature (1150–1550 °C). Large

Table 1 Linear shrinkage, bulk density, porosity and linear shrinkage after calcination at 1500 °C of the porous Yb_2SiO_5 ceramics with 15 vol% solid content

Sintering temperature (°C)	Linear shrinkage (%)	Bulk density (g/cm^3)	Porosity (%)	Linear shrinkage after calcination at 1500 °C (%)
1150	1.45	0.99	85.65	29
1250	2.10	1.02	85.20	20.5
1350	3.65	1.06	84.65	15
1450	4.85	1.11	83.95	0.2
1550	7.60	1.23	82.15	0

directional interconnected pores of 10–50 μm in size can be observed. It is known that in water-based freeze-casting technology, the initial solid loading and freezing rates have a significant impact on the porosity, pore size, and pore network characteristics of the prepared samples [19–21]. A solid loading of 15 % solid content is relatively low so that solid particles may be rejected by the formation of ice crystals. The ice crystals grew into elongated strips along the direction of the thermal gradient. The freezing rate provided by liquid nitrogen was very fast so that the ice crystals would not grow too large; large pores in porous ceramics have a negative effect on the strength. Sublimation of the water resulted in highly interconnected and homogeneous microstructures in the samples. It was easy to see that the microstructure of these porous ceramics had obvious directionality, which is the direction of the ice crystal growth. Higher sintering temperatures led to large body shrinkage. As shown in Figs. 1a–e, the size of the pore channel obviously decreased from 50 to 30 μm when the sintering temperature increased from 1150 to 1550 °C.

Figures 1f–j show enlarged micrographs of the pore morphology of the porous Yb_2SiO_5 ceramics at different temperatures (1150–1550 °C). There are small interconnected pores of sizes 0.3–1.0 μm present in the skeleton. As the sample was sintered from 1150 to 1250 °C, it was easy to see that hexagonal grains were formed and stacked together, which means that the ceramic grains link weakly. When the sintering temperature was increased to 1450 and 1550 °C, the ceramic grains were transformed into quasi-ellipsoids and were fused together, which means that they linked strongly. Therefore, in the skeleton of the porous Yb_2SiO_5 ceramics, the ceramic grains linked more strongly and the triple junction became denser as the sintering temperature increased.

3.2 The thermal conductivity of porous Yb_2SiO_5

The thermal conductivities of the porous Yb_2SiO_5 samples sintered at different temperature are shown in Fig. 2. It can be seen that the average thermal conductivity of the samples increased from 0.117 to 0.132 W/m K as the sintering temperature increased from 1150 to 1550 °C; significantly lower than the thermal conductivity of fully dense Yb_2SiO_5 ceramics (~1.35 W/m K) [22]. The overall thermal conductivity of the ceramic is affected by many factors, such as the volume pore fractions, thermal conductivity of the solid matrix, and pore size. Han et al. [23] described the effective thermal conductivity of porous ceramics as follows:

$$K_e = (1-p)K_s + pK_p + 4d\sigma T^3 \quad (1)$$

where K_s and K_p are the thermal conductivities of the solid matrix and the pores, respectively; p is the volume fractions of the pores; d and T represent pore size and measurement temperature, respectively; σ equals the Boltzmann constant; and K_e is the effective thermal conductivity. As the thermal conductivity of air is ultra-low (0.026 W/m K), the solid matrix plays the main role in heat transfer. The thermal conductivity and porosity of the solid matrix mainly affect the effective thermal conductivity. In this study, the porous Yb_2SiO_5 samples had ultra-high porosities (>82 %), which greatly reduced their thermal conductivity. Comparing the samples sintered at 1150–1550 °C, the porosity was reduced with increasing sintering temperature and the thermal conductivity showed a similar trend. The porosity of the porous Yb_2SiO_5 sample slowly decreased as the sintering temperature increased from 1150 to 1450 °C; thus, the corresponding thermal conductivities increased slowly. When the sintering temperature reached 1550 °C, rapid reduction of the porosity caused a significant increase in the thermal conductivity. Therefore, porosity is the key factor influencing the thermal conductivity of porous Yb_2SiO_5 samples.

3.3 The room- and high-temperature compressive strength of porous Yb_2SiO_5

Figure 2 shows the compressive strengths of the porous Yb_2SiO_5 samples with 15 vol% solid content prepared at 1150–1550 °C. The compressive strength of the porous samples increased from 1.89 to 3.36 MPa when the sintering temperature increased from 1150 to 1550 °C. The

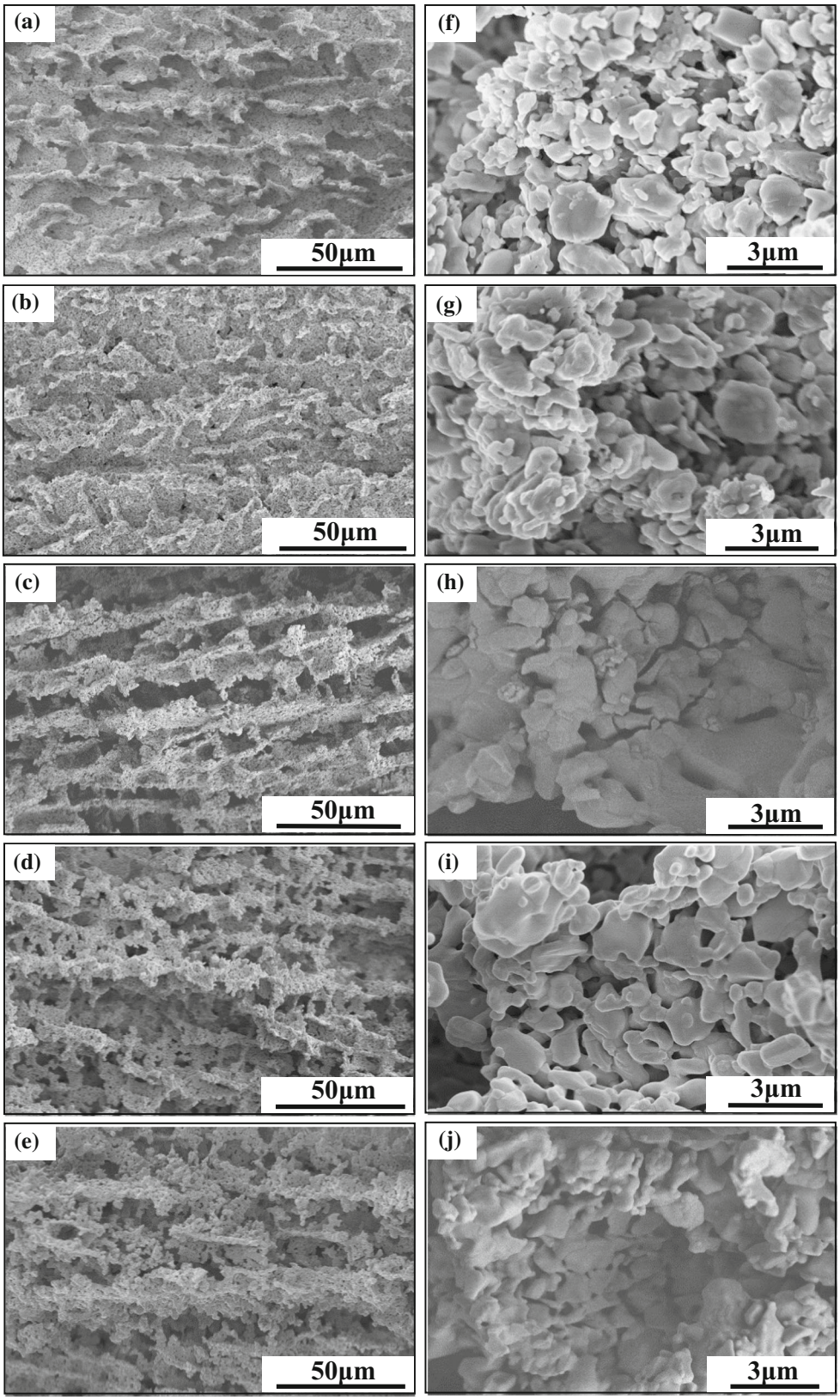

Fig. 1 SEM micrographs and corresponding enlarged micrographs of pore morphology of porous Yb_2SiO_5 ceramics with different sintering temperature: **a**, **f** 1150 °C; **b**, **g** 1250 °C; **c**, **h** 1350 °C; **d**, **i** 1450 °C; **e**, **j** 1550 °C

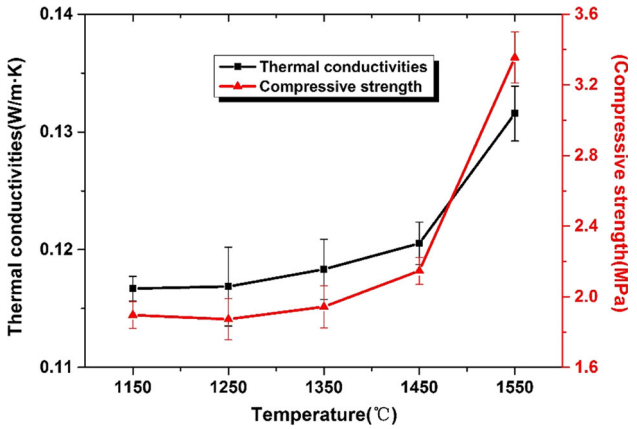

Fig. 2 The compressive strength and thermal conductivities of porous Yb_2SiO_5 ceramics with different sintering temperature

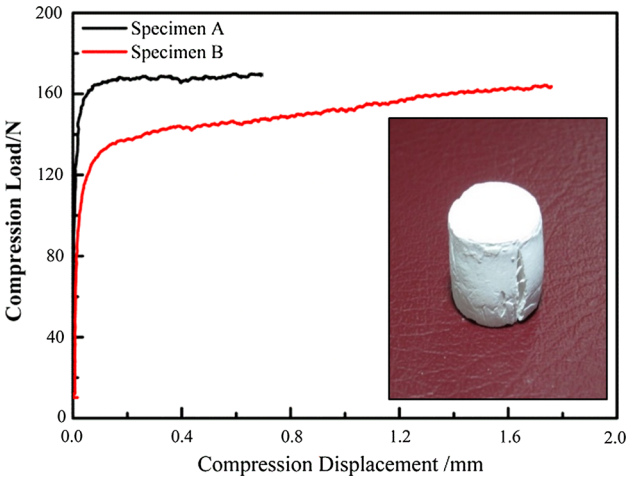

Fig. 3 The load–displacement curves of the high temperature compression testing and the sample after high temperature compression testing, the specimen sintered at 1550 °C (*A*) and 1450 °C (*B*)

mechanical properties of the ceramics were affected by the microstructure, pore structure, porosity, and morphology of the grains. As shown in Table 1, the porosity decreased slightly from 85.65 to 82.15 % when the sintering temperature increased. The compressive strength increased slowly from 1.89 to 2.15 MPa upon increasing the sintering temperature from 1150 to 1350 °C. However, the compressive strength increased relatively quickly from 2.15 to 3.36 MPa when the sintering temperature increased from 1450 to 1550 °C.

As discussed above, as the sintering temperature increased, the grain morphology changed from hexagonal to quasi-ellipsoid and a sintering neck grew between the grains. As shown in Fig. 1j, the quasi-ellipsoid grains linked together more strongly as the sintering temperature increased to 1550 °C, which is the reason for the rapid increase in the compressive strength of the sample.

To be considered as thermal insulator materials for use above 1500 °C, the high-temperature mechanical properties of porous Yb_2SiO_5 ceramics must be studied. Before high temperature compression testing, the sintered samples were calcined at 1500 °C, and the linear shrinkages of the samples were then measured, as shown in Table 1. As shown in the table, the samples sintered at 1150, 1250, and 1350 °C had large linear shrinkages after calcination at 1500 °C. However, the samples sintered at 1450 and 1550 °C showed almost no linear shrinkage after calcination at 1500 °C. Therefore, these large linear shrinkages mean that the porous Yb_2SiO_5 samples sintered at 1150, 1250, and 1350 °C were not suitable for effective application at ultra-high temperatures (1500 °C). Therefore, only the samples sintered at 1450 and 1550 °C were selected for measuring the high-temperature compressive strength.

High-temperature uniaxial compression testing of the porous Yb_2SiO_5 samples sintered at 1450 and 1550 °C was performed at 1500 °C using our self-developed high-temperature testing instrument. Figure 3 shows the load–displacement curve obtained. As can be seen, the sample sintered at 1550 °C shows a higher compressive strength (~1.27 MPa) than that sintered at 1450 °C (~1.15 MPa). The initial region of the load–displacement curve shows a linear segment indicating elasticity. After this first region, there is a plastic zone in which the compressive load increases slowly with increasing displacement. Figure 3 shows the sample after high-temperature compression testing. The middle part of the sample body exhibited weak bulging indicating plastic behavior. In addition, there were some micro-cracks which grew under compressive loading. As the load increased, the micro-cracks coalesced into a large crack, which caused a lack of load-bearing ability at the critical load. It is known that porous Yb_2SiO_5 ceramics exhibit the behavior of brittle materials at room temperature. However, under this high-temperature uniaxial compression testing, the bulging body of the porous Yb_2SiO_5 samples exhibited behavior typical of plastic materials under load, and the big cracks fracturing the samples exhibited failure behavior typical of brittle materials. The high-temperature compression testing revealed an elastic–plastic transformation of the porous Yb_2SiO_5 ceramics in an ultra-high temperature environment. Porous Yb_2SiO_5 ceramics can therefore exhibit plastic deformation.

4 Conclusions

New, highly porous Yb_2SiO_5 ceramics with porosity >82 % were prepared by a water-based freeze-casting method. The effects of sintering temperature on the microstructures and properties of these ultra-high porous

ceramics were studied. There is a clear trend: when the sintering temperatures were lower than 1450 °C, the properties of the ceramics were affected relatively slightly by the sintering temperature. As the sintering temperature increased from 1450 to 1550 °C, the properties of the ceramics changed significantly, i.e., the porosity decreased from 83.95 to 82.15 %, the compressive strength increased from 2.15 to 3.36 MPa, and the thermal conductivity increased from 0.121 to 0.132 W/m K. In addition, the ceramics sintered at 1450–1550 °C exhibited high-temperature compressive strength (1.15–1.27 MPa) and excellent plastic deformation. Therefore, the highly porous Yb_2SiO_5 ceramics studied in this paper show potential as thermal insulator materials for application in ultra-high temperature environments.

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