Effects of Powder Additives on Thermal Shrinkage of Nanoporous Silica Insulation

JINPENG FENG¹*, YOULAN WANG² and XIA FENG²
¹College of Resource and Metallurgy & College of Chemistry and Chemical Engineering, Guangxi University, Nanning, China
²College of Resource and Metallurgy, Guangxi University, Nanning, China

ABSTRACT: In this study, four powder additives were introduced as high-temperature shrinkage inhibitors to make high performance nanoporous silica insulation. The introduction of fumed alumina could greatly improve the thermal stability of the composites at higher temperatures, and the maximum service temperature could be increased to about 1000°C. When 5% fumed alumina was added, the volume shrinkage decreased from 18.49% to 3.47%. Moreover, better results could be achieved with the increase in mass ratio. In addition, fumed titania also improved the thermal stability of the composites to some extent, while boron carbide and boron nitride led to poor performance.

1. INTRODUCTION

NANOPOROUS silica thermal insulation is a new high-efficiency material with excellent performance at intermediate temperature. It plays an important role in the fields of energy savings, aerospace, architecture, etc. [1]. The typical material is silica aerogel insulation, which has been studied for many years [2]. Several studies show that the use of silica aerogel insulation may be limited due to some disadvantages including complicated preparation method, low mechanical strength, poor thermal insulation and stability at high temperatures. Therefore, a more promising nanoporous silica thermal insulating composite has been proposed and studied, in which fumed silica is adopted as a basic material, and fiber as enforced material. Fumed silica, a high-purity non-crystalline silica, is produced by fusing naturally occurring quartz crystals of high purity at approximately 2000°C. It has many excellent properties, and especially its thermal insulating property is superior to other types of thermal insulations due to the nano-scale particle size (about 20 nm) [3–5]. Low thermal conductivity makes it a useful and basic material for thermal insulation [6]. The thermal conductivity of nanoporous silica thermal insulation is only 0.033 W/(m·K) under ambient conditions (25°C and atmospheric pressure). However, with increasing service temperature, the volume shrinkage of this material becomes critical. As a result, the value of volume shrinkage ranges from 1.18–8.49%, corresponding to the calcining temperature from 800–1000°C. The results indicate that most fumed silica particles could retain original shapes and the structure of composites has not been completely destroyed at temperatures below 1000°C. But serious sintering phenomenon is observed when the composites are treated at temperatures above 1000°C. The deformation in appearance directly affects its mechanical property and thermal insulating performance [7–9]. In order to decrease the thermal shrinkage of the composites, fumed titania, fumed alumina, boron carbide and boron nitride were selected as additives to integrate with fumed silica and fibers to study the effects on thermal shrinkage. In this way, a desirable inhibitor could be found to resolve the problem of thermal shrinkage of the composites at high temperatures.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

2.1. Materials

In this work, fumed silica, reinforced fiber, and powder additives were used as the basic components [10–12]. Fumed silica was AEROSIL 200 from Degussa with specific surface area of 200 m²/g and average primary particle size of 12 nm [13]. Reinforced fiber was alkali-free ultrafine glass fiber with average diameter of about 7 µm and length of 5 mm. The first pow-
der additive was fumed titania, which has excellent thermal stability and the weight loss percentage was below 2% when it was calcined at 1000°C for 2h [14]. Its particle size ranged between 20 and 50 nm with a weight loss percentage of 1.5%. The second powder additive was fumed alumina from Degussa with specific surface area of 130 m²/g and the weight loss percentage was below 3% when it was calcined at 1000°C for 2h and the particle size is 30 nm. Boron carbide was the third powder additive with a diameter of 1.69 µm. It is one of the hardest known materials with melting point of 2450°C. The last powder additive was boron nitride with average particle size of 1.372 μm with excellent chemical stability and its melting point was up to 3000°C in inert gas.

2.2. Preparation and Characterization Method

A range of composite samples were prepared by mechanically mixing fumed silica, reinforced fiber and additives together in different mass ratios. A high-speed multifunctional disintegrator was used as the mixing equipment and the mixing time was limited for 30 mins. Although good homogeneity of the mixture could be achieved after a long time of mixing, excessive mixing may possibly break up the fibers, resulting in a loss in mechanical strength. Then, powder samples were uniaxially compacted in a circular cross-section die at an applied pressure of 2 MPa at room temperature to make the samples of size ϕ50 mm × 15 ± 1 mm. Various samples could be prepared by adjusting the size and shape of the die. After maintaining pressures for ten minutes, fumed silica based thermal insulating composites were obtained.

In this study, different mass ratios of samples were placed into a muffle furnace to be heated to a temperature of 1000°C in order to simulate the service environment. The volume shrinkage (ϕ) was introduced to characterize the change in sample size to evaluate the thermal stability at a certain temperature, and it could be written as in Equation (1), in which V₀ and V represent the volumes of the samples before and after treatment, respectively.

\[ ϕ = \frac{V₀ - V}{V₀} \times 100\% \quad (1) \]

For ensuring the accuracy of the results, three samples were treated under the same conditions and the average volume shrinkage of three samples was the final result. In addition, the morphology of the composites was characterized by using FESEM (Field Emission Scanning Electron Microscopy).

Thermal conductivity of nanoporous silica thermal insulation was measured by a small guarded hot plate apparatus, at the National quality center for refractory material, designed for small samples of low thermal conductivity values. Thermal conductivity was measured over an area of 200 mm × 200 mm at a mean sample temperature of 25°C. The measuring zone was located on the warm upper side of the sample under measurement.

3. RESULTS AND DISCUSSION

3.1. Effects of Fumed Titania on Thermal Shrinkage of Nanoporous Silica Insulation

Effects of mass ratio of fumed titania on volume shrinkage of nanoporous silica insulation at 1000°C were investigated and the result is shown in Figure 1. It could be clearly seen that, with increasing mass ratio of fumed titania, the value of volume shrinkage was nearly constant in the range of 5–20%. When the mass ratio of fumed titania was more than 20%, the thermal shrinkage began to decrease to a certain degree. At this moment, slight sintering phenomenon was found while most particles could retain original shapes and there were many nano-scale pores in the interior of the material, as shown in Figure 2. Therefore, the addition of fumed titania was able to restrain thermal shrinkage, but the volume stability was not significantly improved. When the service temperature became higher, fumed titania was unsuitable to be adopted as an inhibitor to reduce thermal shrinkage.
3.2. Effects of Fumed Alumina on Thermal Shrinkage of Nanoporous Silica Insulation

From Figure 3, it was clear that the utilization of fumed alumina could improve the thermal stability of the composites. The volume shrinkage decreased from 18.49% to 3.47% at 1000°C with the addition of 5% fumed alumina. Moreover, there was no significant influence of mass ratio of fumed alumina on volume shrinkage. When the calcining temperature is 1000°C, the volume shrinkage ranged from 3.47% to 1.45% with the increase in mass ratio of fumed alumina. FESEM image of the composites, with 20% fumed alumina, calcined at 1000°C for 1h is presented in Figure 4. It could be seen that most particles retained their original shapes; only few particles appeared to be lightly sintered and rich nano-scale pore structures were found in the material interior. In summary, the suitable amount of fumed alumina was about 5–10% for the composites used at 1000°C. Fumed alumina, as an inhibitor, could remarkably restrain thermal shrinkage at high service temperatures. The reason for this behavior may be attributed to the following property: fumed alumina has certain inertia at high temperature, and the introduction of fumed alumina can change the diffusion mechanism and reduce thermal shrinkage of fumed silica particles at high temperatures.

3.3. Effects of Boron Carbide on Thermal Shrinkage of Nanoporous Silica Insulation

Boron carbide was selected as an additive to integrate with nanoporous silica insulation due to its excellent properties including high melting point, high temperature resistance, high hardness, high chemical stability and low density. The results in Figure 5 show
that the introduction of boron carbide has a negligible effect on the thermal stability of the composites at calcining temperature of 1000°C; even the value of volume shrinkage increased significantly. Moreover, when 20% boron carbide was added, serious sintering was found as shown in Figure 6. The experimental results show that boron carbide is not suitable to be adopted to reduce thermal shrinkage. Reasons could be explained as follows: Boron carbide, used in this study, is an ultra-fine powder with characteristics of large specific surface area, higher surface activity, more internal defects in atoms and bigger crystal lattice distortion. Therefore, the sintering process is accelerated, which causes the length of diffusion of atoms to shorten and the diffusion velocity of the particles in the solid state is improved. Additionally, because of the presence of the transition element oxides in SiO₂, the sintering temperature of boron carbide decreases and the sintering speed is accelerated, which lowers the thermal stability of the composites at higher temperatures.

3.4. Effects of Boron Nitride on Thermal Shrinkage of Nanoporous Silica Insulation

Boron nitride was selected as an additive because of its low thermal expansion coefficient. The relationship between volume shrinkage and mass ratio of boron nitride is shown in Figure 7. The volume shrinkage is proportional to mass ratio of boron nitride when a small amount of boron nitride is added. When the mass ratio of boron nitride is more than 10%, the volume shrinkage shows a negative correlation with mass ratio of boron nitride, but not significantly. Moreover, serious sintering phenomenon is observed and the porosity decreases significantly when 20% boron nitride is added, as shown in Figure 8. Boron nitride is easy to be oxidized in an oxygen atmosphere, which is the reason for the decrease in thermal stability.

3.5. Thermal Conductivity of Nanoporous Silica Composites Containing Fumed Alumina

The volume shrinkage of nanoporous silica insulation decreased gradually with increasing fumed titania, but not significantly. When 5% fumed alumina was added, the volume shrinkage decreased from 18.49% to 3.47% at 1000°C. The thermal shrinkage of nanoporous silica insulation was accelerated when boron carbide and boron nitride were introduced. Referring to the four groups of the experiments above, fumed alumina could be used as a desirable inhibitor to resolve
the problem of thermal shrinkage of the composites at high temperatures.

Therefore, the thermal conductivity of nanoporous silica insulation with 5% fumed alumina was tested to determine whether fumed alumina had a negative impact on the insulation performance of nanoporous silica. Experimentally measured values of thermal conductivity are shown in Table 1. Nanoporous silica insulation containing fumed alumina mass ratio of 5% had a low thermal conductivity of 0.022 W/(m·K) and with increasing temperature from 200–800°C, the thermal conductivity of the composites increased from 0.022 to 0.028 W/(m·K). The measurements indicated that the addition of fumed alumina led to a very small increase compared with nanoporous silica insulation without fumed alumina added. Moreover, when the testing temperature was increased to 1000°C, the nanoporous silica insulation, without fumed alumina added, did not perform well. However, the thermal conductivity of nanoporous silica insulation with 5% fumed alumina added was only 0.032 W/(m·K).

### 4. CONCLUSIONS

Higher thermal stability of nanoporous silica insulation, consisting of fumed silica, fiber and powder additives has been developed and tested for its thermal shrinkage. FESEM has been employed to characterize the microstructure. The volume shrinkage of nanoporous silica insulation could be restrained with fumed titania added, but not significantly. The utilization of fumed alumina could significantly improve the thermal stability of the composites. When 5% fumed alumina is added, the volume shrinkage decreases from 18.49% to 3.47% at 1000°C. The higher service temperature requires more addition of fumed alumina. In addition, the thermal shrinkage of nanoporous silica insulation is accelerated when boron carbide and boron nitride are introduced. Thus, fumed alumina could be adopted as an ideal powder additive to nanoporous silica insulation to decrease the thermal shrinkage.

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### 6. REFERENCES