Preparation and Thermal Stability of Quartz Fiber Reinforced Silicon Doped Aluminum Aerogel Composites

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Abstract. Aerogel composites have drawn great attention as innovative thermal insulation materials in the field of thermal protection. In this study, quartz fiber reinforced silicon doped aluminum aerogel composites were synthesized using aluminum chloride hexahydrate (AlCl₃·6H₂O) and tetraethoxysilane (TEOS) co-precursor by sol-gel and supercritical fluid drying. The composites were characterized by FTIR, BET, SEM and Quartz lamp simulation test. The results showed that quartz fiber reinforced aerogel composites exhibited low density, low thermal conductivity and high temperature thermal stability. The thermal conductivities of composites increased from 0.025 W·m⁻¹·K⁻¹ at 150°C to 0.121 W·m⁻¹·K⁻¹ at 1200°C. The as-prepared composites exhibited high specific surface area (515 m²/g) with low density of 0.23 g/cm³. After being heated to 1000°C and 1200°C for 2 h, the surface area of composites reached to 217 and 68 m²/g, respectively. The aerogel composites with 25mm thickness was evaluated by quartz lamp at 1200°C for 1500 seconds. The back surface temperature of 732.7°C demonstrated excellent heat insulation performance of the aerogel composites.

1. Introduction
The aerogels have broad application prospects in advanced aerospace field, insulation field and catalytic field at high temperatures due to their low density, high porosity, high specific surface area and low thermal conductivity [1,2]. At present, the synthesis routes, properties and application of silica aerogels are well studied [3]. Silica aerogels can be used for a short time under 800°C, however, pores collapse and further decrease in the specific surface area lead to failure of aerogels caused by a long time using above 800°C. In order to improve the application temperature of aerogels, numerous researchers carried on extensive studies on alumina aerogels [4-6]. Alumina aerogels exhibit excellent high temperature thermal stability and maintain large surface area above 1000°C. Hence, alumina aerogels have gradually become prominent materials used in the high temperature field. The precursors for the preparation of aluminum aerogels are mainly including organic aluminum salts and inorganic aluminum salts. Organic aluminum salts such as acetate and alkoxide [7,8], and inorganic aluminum salts such as nitrate and chloride[8,9] are usually used for preparation.

The main disadvantages of alumina aerogels are phase transition at high temperature and low mechanical strength. The addition of silica aerogels can retard the contact of aluminum aerogels particles, decrease the probability of crystal nucleation, and significantly inhibit the α-Al₂O₃ phase transition at high temperatures [4,10]. Several reinforcing fillers, such as aramid fibers, mullite fibers and glass fibers were selected to improve the mechanical properties and thermal stability [11,12].
Quartz fiber fabrics are good choice of reinforcing fillers for their good temperature resistance and low thermal conductivity under 1200°C.

The objective of this study is to fabrication quartz fiber reinforced Al₂O₃-SiO₂ aerogel composites which maintain high porosity and micro-skeleton structure at elevated temperatures. We applied the silica aerogels as filler to strengthen the network of -Al-O-Al- among the quartz fibers. Inorganic aluminum salts (AlCl₃·6H₂O) and tetraethoxysilane (TEOS) as co-precursors, and propyleneoxide (PO) as a net work forming agent were used to prepare composites. After supercritical fluid drying, the as-prepared composites were heat-treated at 600°C, 800°C, 1000°C and 1200°C and also tested by quartz lamp static simulation experiment. The obtained samples with different heat-treated temperatures were characterized using BET, FT-IR, thermal conductivity analyzer and SEM.

2. Experimental

2.1. Materials
Quartz fiber fabrics (QF, diameter of 8–15 μm) used as reinforcement were purchased from Jiangsu Tianniao High-tech Co., Ltd. (China). Silicon doped Aluminum sols were synthesized using tetraethoxysilane (TEOS) and aluminum chloride hexahydrate (AlCl₃·6H₂O) as co-precursor, H₂O and ethanol (EtOH) as solvents, and 1,2-epoxypropane (PO) as a network forming agent which were obtained from Sinopharm Chemical Reagent Co., Ltd. All agents were chemical pure grade.

2.2. Synthesis
Quartz fiber reinforced Al₂O₃-SiO₂ aerogel composites were prepared according to the following four steps. Firstly, AlCl₃·6H₂O and TEOS were added into the mixed EtOH and H₂O solution and stirring for 120 min separately, the molar ratio of AlCl₃·6H₂O: TEOS: EtOH: H₂O = 3: 1: 40: 46. After complete hydrolysis, the silica sol and alumina sol were mixed together and stirred for 30 min to form a homogeneous solution. A desired amount of PO was poured into the mixed solution with vigorous mixing for 10 min. Secondly, quartz fiber fabrics was impregnated into Al₂O₃-SiO₂ sol under vacuum and the gelation was allowed to gel at room temperature within 1 h. Thirdly, the sample was soaked in a bath of absolute ethanol for 72 h to exchange the water and reaction by products from the pores. After aging and solvent exchange, the sample was dried under supercritical fluid drying technology at last.

2.3. Characterizations
The bulk density (ρ) of the sample was calculated by measuring the volume (V) and mass (M) of the monolithic sample by the formula of ρ=M/V. Brunauer-Emmett-Teller (BET, Gemini VII 2390, USA) analysis was used to determine the surface areas, pore volumes and pore diameters of the samples. The groups of the sample were investigated by using a Fourier transform infrared spectroscope (FT-IR, Thermo Scientific Nicolet IS50, USA). The microstructure of sample was observed by Scanning electron microscope (SEM, FEIQUANTA FEG250, USA). The thermal conductivities were measured by HotDisk (DRS-III, China). The quartz lamp static simulation experiment in a condition of 1200°C (1500 seconds) was carried out in Beijing University of Aeronautics and Astronautics.

3. Results and discussion
Figure 1 shows the N₂ adsorption-desorption isotherm and SEM image (shown as inset in figure 1) of as-dried sample using supercritical fluid drying technology. The isotherm including type IV curves with type H1 hysteresis loop in the IUPAC classification indicates that the quartz fiber reinforced Al₂O₃-SiO₂ aerogel composites with mesoporous structures were prepared successfully. The desorption cycle of the isotherm shows a hysteresis loop for the sample, which is generally attributed to the capillary condensation that occurs in the mesopores.

The inset in figure 1 shows the micromorphology of the as-dried sample. The aerogel in composite exhibits nano-porous network and homogeneous structures that are composed of leaf shape nanoparticles, of which the diameters are approximately 30 nm.
Figure 1. N$_2$ adsorption-desorption isotherm and SEM image of as-dried sample.

The pore parameters of samples heat-treated at different temperatures are listed in Table 1. The specific surface areas of as-prepared samples calcined at 25°C, 600°C, 800°C, 1000°C and 1200°C are 514, 494, 391, 217 and 68 m$^2$/g, respectively. The specific surface area of the sample remains a high value as well as as-dried sample before 600°C. Due to the structural adjustment, damage to the porous network and shrinkage of the pore structure, the specific surface areas decrease rapidly after 1000°C. The pore volumes of samples show an increasing tendency before 600°C and a decreasing drift after 800°C. After calcined for 2h at 1200°C, the pore volume can still maintain 0.92cm$^3$/g, exhibiting that the as-prepared composites have excellent high temperature thermal stability and reliability.

| Heat treatment temperature (°C) | Specific surface area (m$^2$/g) | Pore diameter (nm) | Pore volume (cm$^3$/g) |
|-------------------------------|---------------------------------|-------------------|------------------------|
| 25                            | 514                             | 31.18             | 5.55                   |
| 600                           | 494                             | 34.38             | 6.73                   |
| 800                           | 391                             | 46.69             | 5.55                   |
| 1000                          | 217                             | 55.47             | 2.57                   |
| 1200                          | 68                              | 54.15             | 0.92                   |

The FT-IR spectra of samples heat-treated at different temperatures is presented in figure 2. The contribution of water is confirmed by the absorption peaks at 3441 and 1640cm$^{-1}$. The peaks at 2981 and 1340 cm$^{-1}$ are assigned to the C-H band, which indicates that carbonaceous residuals are linked to the network of the Al$_2$O$_3$-SiO$_2$ aerogel after supercritical fluid drying. The peaks at 1076, 799 and 495 cm$^{-1}$ correspond to the Al–O vibration within pseudoboehmite, which vanishing after 1000°C. The peaks at 1171, 746 and 556cm$^{-1}$ of sample heat-treated at 1200°C indicate the formation of mullite phase. The three absorption bands are evidence of Si-O-Al linkages. The FT-IR spectra demonstrates that there inforcement of quartz fibers increase thermal stability of Al$_2$O$_3$-SiO$_2$ aerogels before 1000°C.

Figure 3 shows the thermal conductivity and density of samples calcined at different temperatures. The changes of the thermal conductivity are related to the changes of the heat-treated temperatures. The as-dried sample presents an ultra-low thermal conductivity of 0.024W·m$^{-1}$·K$^{-1}$. Before 600°C, samples keep a similar thermal conductivity (0.024-0.031W·m$^{-1}$·K$^{-1}$) indicating no changes in pore structure and phase. This coincides with BET analysis and FT-IR spectra analysis. The thermal
conductivities increase obviously after 1000°C, which results from the slightly decreasing of the specific surface areas and pore volumes in the Al₂O₃-SiO₂ aerogel.

![Figure 2. FT-IR spectra of samples heat-treated at different temperatures.](image1)

**Figure 2.** FT-IR spectra of samples heat-treated at different temperatures.

![Figure 3. Thermal conductivity and density of samples heat-treated at different temperatures.](image2)

**Figure 3.** Thermal conductivity and density of samples heat-treated at different temperatures.

It is worth noting that the densities of samples change from 0.23 g/cm³ to 0.27 g/cm³ calcined from room temperature to 1200°C for 2 h. The high porosity retention caused by the reinforcement of quartz fiber. The quartz fiber maintains skeleton structure to prevent from failure and guarantee the high temperature stability and reliability of materials at high temperature.

The actual insulation effect and high temperature resistance of the quartz fiber reinforced Al₂O₃-SiO₂ aerogel composites with were 25 mm thickness tested by quartz lamp static simulation experiment. The actual control temperature and composite back surface temperature are presented in figure 4. The control temperature rises rapidly to 1200 °C within 120 seconds and keep the high temperature to test the back surface temperature of as-prepared composite. The back surface temperature curve can be divided into three stages. In the first stage he back temperature is lower than 100 °C before 340 second. In the second stage, the back temperature rises to 600°C significantly from 340 seconds to 900 seconds. After 900 seconds, the increasing back temperature slows down, and stops at 732.7°C. When heated at 1200°C for 1500 seconds, the back temperature of the composite is only 732.7°C, indicating that the
composite has good thermal insulation and high temperature thermal stability. It also can be used at high temperature for long time.

![Figure 4. Quartz lamp static simulation experiment curve of sample.](image)

Figure 4. Quartz lamp static simulation experiment curve of sample.

Figure 5 shows the microstructure of quartz fiber reinforced Al$_2$O$_3$-SiO$_2$ aerogel composites before and after quartz lamp static simulation experiment. Al$_2$O$_3$-SiO$_2$ aerogels are tightly bonded to micropores fabricated by quartz fibers. Nanopores formed by aerogels prevent contact between fibers effectively, and reduce the heat conduction and improve the thermal conductivity of the composites. Figure 5 (b) exhibits quartz fiber reinforced Al$_2$O$_3$-SiO$_2$ aerogel composite tested by quartz lamp under the condition of 1200 °C for 1500 seconds. After test, Al$_2$O$_3$-SiO$_2$ aerogels in the matrix contract obviously, forming micropores in the composites. The surface of quartz fibers remain smooth, no fracture, and maintain good skeleton structure after calcinated at 1200 °C. The good retention of density in figure 3 also proves that the quartz fibers keep a good micro-skeleton structure of the as-prepared composites.

4. Conclusions
A facile approach was developed to prepare the quartz fiber reinforced Al$_2$O$_3$-SiO$_2$ aerogel composites with ultra-low thermal conductivity and high temperature thermal stability with low density high specific surface area. The adding of silica aerogels inhibited the α-Al$_2$O$_3$ phase transition at high temperatures, and strengthened the network of -Al-O-Al- among the quartz fibers. The as-prepared
composites exhibited high specific surface area (515 m$^2$/g) with low density of 0.23 g/cm$^3$. The thermal conductivities of composites increased from 0.025 W·m$^{-1}$·K$^{-1}$ at 150°C to 0.121 W·m$^{-1}$·K$^{-1}$ at 1200°C. After being heated to 1000 °C and 1200 °C for 2 h, the surface area of composites reached to 217 and 68 m$^2$/g, respectively. After evaluated by quartz lamp at 1200°C for 1500 seconds, the back surface temperature was as low as 732.7°C which demonstrated excellent heat insulation performance of the aerogel composites.

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