Fabrication of Al$_2$O$_3$-Bonded Fibrous Ceramics by An Aqueous Gel-Casting Process

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Abstract. The traditional gel-casting method mostly uses organic compounds, which are complex process, expensive and pollute the environment. In order to overcome the disadvantage of the traditional gel-casting method, an environment friendly aqueous gel-casting process is introduced in this paper. Al$_2$O$_3$-bonded fibrous ceramics with high porosity and low thermal conductivity have been prepared by a novel hydrated alumina gel-casting process using the p-Al$_2$O$_3$ and mullite fibers or YSZ fibers as raw materials and the deionized water as hydration agent. A bird-nest-patterned three-dimensional reticular skeleton structure was established by the fibers to ensure a certain mechanical strength. The effects of the amount of mullite fibers and YSZ fibers on the properties of porous ceramic, such as phase composition, microstructure, sintering behavior and relative properties were investigated. Results showed that the as-prepared Al$_2$O$_3$-bonded fibrous mullite ceramics have high porosity of 66.9%~78.6%, low thermal conductivity of 0.236~0.479 W/m·K, and relatively high compressive strength of 0.80~2.78 MPa. The as-fabricated fibrous YSZ ceramics had a high porosity (71.1%~72.7%), a low thermal conductivity (0.209~0.503 W/m·K) and a relatively high compressive strength (3.45~4.24 MPa). Comparing to the as-fabricated fibrous mullite ceramics, the compressive strength of as-fabricated fibrous YSZ ceramics is promoted obviously.

1. Introduction

The development of ceramics has a history of several thousand years, and the emergence of ceramics has greatly promoted the progress of society. With the advancement of society, the variety of ceramics has gradually increased, and ceramics of various properties have appeared. For many different types of ceramics, there are different requirements for their performance depending on the application conditions. Among all the ceramics, the porous ceramics has been received widespread attention due to its excellent performance such as high chemical and thermal stability, higher porosity, low thermal conductivity, and high mechanical strength. Widely used in microfiltration membrane applications [1], humidity self-regulating [2], wastewater treatment [3], high-temperature catalyst supports [4], filtration and adsorption [5]. With the development of porous ceramics, its preparation methods are diverse, such as the addition of pore-forming agent [6,7], impregnation method [8], in-situ synthesis [9,10], foam-gelcasting technique [11], tert-butyl alcohol-based gel-casting [12-14], an epoxy resin gel-casting process [15], the pyrolysis route [16], binder bonding method [17], the self-organization method [18], gel freeze drying [19,20], and slip casting [21].

In the last decade, fibers have been used as reinforcement phase to enhance the strength of ceramics. Fiber ceramics is an emerging composite material for social development. Fiber ceramics is a material of particular interest because of its unique set of properties, such as high porosity, low...
thermal conductivity, and high mechanical strength, which makes it a promising candidate for use in structural ceramics (such as filters [22], sensors, thermal insulators [23], catalyst supports [24], separation membranes [25]). Nowadays, with the boosting development of innovation technology, various emerging methods have been used in fibrous ceramics fabricate, such as sol-gel vacuum impregnation [26], direct coagulation casting (DCC) combined with 3D printing [27], vacuum squeeze moulding technique [28], pressure and freeze-casting method [29], silica sol method [30], and gel casting process [31,32].

An aqueous gel-casting process has emerged as a promising candidate because of its numerous advantages over the traditional gel-casting method. First, an aqueous gel-casting process could fabricate ceramics with simple process. Second, it could be used to produce ceramics with low cost. Besides, the process does not pollute the environment because it does not use any organic compounds. However, so far, little research has been done on aqueous gel-casting process.

In this work, a novel fibrous ceramic with three-dimensional skeleton structures is prepared by an aqueous gel-casting process using the polycrystalline mullite fibers or YSZ fibers as skeleton and ρ-Al₂O₃ powder as inorganic binder.

In this paper, as a skeleton structure, the fiber effectively enhances the strength of the fiber ceramic. The hydratable alumina (ρ-Al₂O₃)is used as the gelling source because of its special hydration properties. The hydratable alumina reacts with water to rapidly form a hardened Al₂O₃-bonded fibrous green body. The equation for the hydration reaction of hydratable alumina with water can be described as follows:

\[
ρ-Al₂O₃ (s) + 2H₂O (l) = Al(OH)₃ (gel) + AlOOH (gel)
\]  

(1)

The aqueous gel-casting process using ρ-Al₂O₃ as the gelling source is a new environmentally friendly process for preparing ceramics, and mullite fibers and YSZ fibers are added to prepare different alumina-based fiber ceramics. The effects of different fibers and fiber addition on the mechanical and thermal properties of the sintered samples are investigated. In this paper, the performance test results of the prepared alumina-based mullite fiber ceramics and YSZ fiber ceramics are compared.

2. Experimental procedures

2.1. Raw material

Polycrystalline mullite fibers (Purity≥99.5%) and YSZ fibers (ZrO₂–15 wt% Y₂O₃) as the skeleton structure of the ceramic were purchased from Zhejiang Weiyi Crystal Fiber Co., Ltd., China and Zhejiang Thermal-Tec Insulation Co., Ltd., China, respectively. The diameter and length of the YSZ fibers ranged from 5-10 μm and 7-10 mm, respectively. The commercial ρ-Al₂O₃ (Purity≥90%, LOI (Loss on ignition) ≤ 10%, D₅₀ ≤ 1 μm, Zhengzhou Non-ferrous Metals Research Institute Co., Ltd., Henan, China) was utilized as the high temperature binder. Deionized water was used in all experiments as solvent and freezing medium.

![Fabrication flow chart of fibrous ceramics.](image)

**Figure 1.** Fabrication flow chart of fibrous ceramics.
2.2. Preparation
The Al$_2$O$_3$-bonded fibrous ceramics were fabricated through an aqueous gel-casting process. In this work, it include two part experiments. One was Al$_2$O$_3$ bonded with mullite fibers, the other was Al$_2$O$_3$ bonded with YSZ fibers. The processing route schematic of porous fibrous ceramics materials is shown in Figure 1.

First, introduce the preparation process of Al$_2$O$_3$ bonded with mullite fibers ceramics. Due to the difference between the mullite fiber and the YSZ fiber, it was necessary to calcine the mullite fiber at 600 °C for 2 hours. The fibers were vigorously stirred and ultrasonically shaken in an ethanol solution, and then uniformly dispersed to remove impurities. Second, it was dried in a dry box for 48 hours for subsequent experimental procedures.

Inorganic binder alumina slurries were prepared by mixing an appropriate amount of ρ-Al$_2$O$_3$ powder with deionized water. Then fibers were gradually dispersed into the premix slurry by ultrasonic oscillation with vigorous stirring until the fibers were uniformly dispersed. After well stirring, the stable suspension slurry was poured into the mold immediately. At room temperature, the slurry solidified to form a uniform body. After removed from molds, the green bodies were dried in a dry box. Finally, the dried samples were sintered at 1600 °C.

The processing route of YSZ fibers ceramics was as follows: the YSZ fibers were pretreated by wash and dry. The powders of ρ-Al$_2$O$_3$ were dispersed in the deionized water to form the stable and uniform ceramic slurry after stirring and oscillating. Then the as-treated YSZ fibers were added and fully mixed to form fiber-ceramic slurry. The slurry was poured into the mold, and then froze and vacuum dried in the freeze dryer. Finally, the samples after the demolding treatment were sintered at 1600°C.

In order to investigate the effects of fiber content and the fiber species on the properties and structure of porous ceramics, different of the raw materials ratio was adopted, as shown in Table 1.

2.3. Characterization
The crystalline compositions of samples were investigated using X-ray diffraction technique (XRD, Model D500, Siemens) with Cu Kα radiation. The microstructure of the samples was observed by field emission scanning electron microscope (FE-SEM, Model Ultra Plus, ZEISSL, Germany) with an X-ray energy dispersive spectroscopy (EDS, Oxford, UK) unit. Apparent porosity of the sintered samples was determined by the Archimedes method using water as the medium. Room temperature thermal conductivity of the samples was measured by the thermal conductivity instrument (LFA 457, NETZSCH/Micro Flash, Germany). The compressive strength of sintered samples was measured according to GB/T 5072-2008 by using hydraulic press machine (5015 type, China) with a crosshead loading speed of 0.05 mm/min.

3. Results and discussion
3.1. Phase composition
Figure 2 and Figure 3 represent XRD patterns of Al$_2$O$_3$-bonded mullite fibrous ceramics and Al$_2$O$_3$-bonded YSZ fibrous ceramics by an aqueous gel-casting process with different amount of fibers added.
Figure 2 shows the XRD patterns of ceramic samples of M1–M4 after sintered at 1600°C. The ratios of powder to mullite fiber of samples of M1-M4 are 1:0.5, 1:1, 1:2 and 1:3, respectively. It can be seen that no other phase is observed except the mullite and Al2O3 phase. From the pattern, it can be inferred that no solid solution reaction occurred. As the amount of fiber added increases, the peak intensity of mullite increases significantly. In particular, as shown in Figure 2, the peak intensity of mullite of M4 is the strongest, while the mass ratio of powder to fiber is 1:3.

Figure 3 shows the XRD patterns of samples of Z1, Z2, Z3 and Z4 prepared by the aqueous gel-casting process using YSZ fiber and ρ-Al2O3 powder. The ratios of powder to YSZ fiber of samples of Z1-Z4 are 1:0.5, 1:1, 1:2 and 1:3, respectively. It can be observed that only YSZ phase and Al2O3 phase were detected in all the samples. As the mass ratio of powder to fiber decreases, the peak intensity of alumina decreases significantly, and the peak intensity of YSZ phase increases significantly.

Comparing Figure 2 and Figure 3, it can be seen that the phase composition is relatively pure, one group is alumina phase and mullite phase, and the other group is alumina phase and YSZ phase. Furthermore, the peak intensity of the alumina in the product decreases as the powder content
decreases. This means that the higher the content of each component in the samples, the stronger the intensity of the corresponding peak.

3.2. Micromorphology and microstructure
Figure 4 and Figure 5 show the fracture surface micrographs of Al₂O₃-bonded mullite fibrous ceramics and Al₂O₃-bonded YSZ fibrous ceramics, respectively.

![Figure 4. SEM micrographs of the samples fabricated with different content of mullite fibers. (a) 33wt%mullite fibers, (b) 50wt%mullite fibers, (c) 67wt%mullite fibers, (d) 75wt%mullite fibers.](image)

The SEM micrographs of the samples fabricated with different content of mullite fibers are shown in Figure 4. Figure 4 shows various forms in which the fibers are randomly arranged and bonded by solid particles. The fibers are interlaced with each other to form a network structure, and the interlaced fiber joints or the fibers arranged in parallel are covered by solid particles. There are various crystal grains with different sizes and shapes on the surface of the fiber. The shapes of the crystal grains are various: long strip, small spheres, and large irregular. As the powder content is high, the solid particle aggregation phenomenon is remarkable, as shown in Figure 4(a). In addition, high inorganic particles content would lead to the reduction of porous. With the powder content decreasing, the inorganic particles are more dispersed and adhered to the surface of the fiber.

The fracture surface micrographs of samples fabricated with different content of YSZ fibers are shown in Figure 5. For the aqueous gel-casting method, the content of fiber is the most important parameter which has influence on sample's microstructure and properties. Because of the random arrangement fibers, a fibrous skeleton ceramic structure and a stable morphology of porous ceramic are formed during the sintering process. Figure 5(e) illustrates the morphology of the fibrous ceramics prepared by adding a maximum 0.6p-Al₂O₃ powder and less YSZ fibers. Alumina bindings enwrap the crossing points of the fibers and coated fiber aggregate. As the addition of fiber added increases, the accumulation of fiber became compact.

Comparing Figure 4 and Figure 5, the grain size of fiber surface of the mullite fiber ceramic has a large difference and a variety of shapes; the grain size of the surface of the YSZ fiber is similar. It can be found that the fiber undergoes secondary crystallization during the sintering process. As shown in Figure 4 and Figure 5, the average diameters of the mullite fibers and the YSZ fibers were 10μm and
5\mu m, respectively. It can be found that the spatial structure of the alumina-bonded mullite fibrous ceramics is larger than that of the alumina-bonded YSZ fibrous ceramics, and the pores formed are larger. The larger the size of the fibers, the larger the skeleton space structure is constructed and the larger the pores are formed. The size of the fibers is smaller, the fibers are more densely packed, and the pores formed by the space skeleton are smaller. It indicates that the diameter and length of the fiber directly affect the pore size and pore distribution of the fiber skeleton structure. It means that the size of the fibers directly affects the spatial structure of the fiber skeleton.

Figure 5. SEM micrographs of the samples fabricated with different concern of YSZ fibers. (e) 33wt% YSZ fibers, (f) 50wt% YSZ fibers, (g) 67wt% YSZ fibers, (h) 75wt% YSZ fibers.

Figure 6. The effect of different fibers and different content on the apparent porosity of fiber ceramics.
3.3. Behaviors and properties

Figure 6 displays the changes in apparent porosity of samples of Al$_2$O$_3$-bonded mullite fibrous ceramics and Al$_2$O$_3$-bonded YSZ fibrous ceramics prepared by the novel aqueous gel-casting method. It could be seen that the apparent porosity of the prepared porous ceramic increased with increasing the amounts of fibers, which was consistent with the investigation of the SEM images (Figure 4 and Figure 5). As shown in Figure 6, the apparent porosity of mullite fibrous ceramics increased from 66.9% to 78.6%, and the apparent porosity of YSZ fibrous ceramics ranged from 71.1% to 72.7%.

The three-dimensional network structure was constructed by intertwined fibers. This structure serves as a skeleton support. The increase of the fibers was the main reason for the increase of apparent porosity. There were more pores formed in the structure with the fiber content increases, resulting in the apparent porosity increases. However, the apparent pore porosity is lower when the content of the fiber increases to a certain value. This is because accumulated fibers fill some pores. Therefore, as shown by the two curves in Figure 6, the trend is an overall increase, and finally a slight decrease.

It can be seen from Figure 6, the apparent porosity of the ceramics prepared in the same proportion of different fibers is different. Al$_2$O$_3$-bonded mullite fibrous ceramics have higher apparent porosity than Al$_2$O$_3$-bonded YSZ fibrous ceramics. This is closely related to the size of mullite fibers and YSZ fibers. The mullite fiber with larger diameter and longer length has larger spatial structure and larger pore diameter. In the preparation of YSZ fiber ceramics, since the YSZ fiber has a small diameter and a short length, it is densely packed during the preparation process, and the three-dimensional skeleton structure has a small number of pores and a small size. The result is consistent with the investigation of the SEM images (Figure 4 and Figure 5).

In addition, it can be seen from Figure 6 that the ceramic porosity prepared by the mullite fiber has a wide range, and the ceramic porosity ratio prepared by the YSZ fiber is close. The YSZ fiber can be explained by its small size and easy compressed accumulation, and it also shows that the mullite fiber has a great influence on the pore formation.

As shown in Figure 7, the thermal conductivity of Al$_2$O$_3$-bonded mullite fibrous ceramics and Al$_2$O$_3$-bonded YSZ fibrous ceramics using $\rho$-Al$_2$O$_3$ gels with different fiber contents from 33wt% to 75wt%. It also can be seen that, the thermal conductivity ranges of the prepared mullite fiber ceramics and YSZ fiber ceramics were from 0.236 W/(m·K) to 0.479 W/(m·K) and from 0.209 W/(m·K) to 0.503 W/(m·K), respectively. With the increase of fiber addition, the overall thermal conductivity of the ceramics tends to decrease, and the overall thermal conductivity of mullite fiber ceramics lower than YSZ fiber ceramics.

![Figure 7](image_url)
As the mullite fiber content increases, the thermal conductivity shows a significant decrease. When the mullite fiber content reaches 75%, some of the pores were reduced by excessive fiber accumulation, thereby solid heat conduction increased and the thermal conductivity of the mullite fiber ceramic slightly increased. This is consistent with the porosity results of mullite fiber ceramics.

With the increases of YSZ fiber content, the thermal conductivity of YSZ fiber ceramics decreases significantly. This is related to the pores formed between the fibers and the binder, and to the hollow structure of the sintered YSZ fibers. After sintered, a large amount of YSZ fibers become hollow structures, which effectively reduces solid heat transfer, increases gas heat transfer, and result in a decrease in thermal conductivity of the prepared ceramics.

Figure 8. The effect of different fibers and different content on the compressive strength of fiber ceramics.

Figure 8 shows the effect of different fibers and different content on the compressive strength of fiber ceramics. It is demonstrated that the compressive strength decreases from 2.78 to 0.8 MPa and decreases from 4.24 to 3.45 MPa with the mullite fiber content and the YSZ fiber content increasing from 33% to 75%, respectively. As the fiber content increases, the fibers alternately overlap, forming more pores in the fiber ceramic. The existence of a large number of pores is equivalent to cracks, resulting in a decrease in the compressive strength of the material. The reason is that the content of binder reduced and the sample become more looser with the content of fibers increasing. Meanwhile, the cohesive force bonding point between Al₂O₃ and fibers become weaken, and the Al₂O₃ particle attached to the neighboring fibers become less. Therefore, the compressive strength of the sample of mullite fiber ceramics and YSZ fiber ceramics with the fiber content of 75% was 0.8 MPa and 3.45 MPa, respectively. Although the overall strength is a decreasing trend, its minimum strength value can still meet the material strength requirements.

Figure 9 shows the compressive strength corresponding to the different apparent porosity of the samples. It is well known that the higher the apparent porosity, the lower the compressive strength. It can be found that with the increase of the apparent porosity of M1-M3 and Z1-Z3, the compressive strength decreases significantly. The results are consistent with the general rule of porosity and compressive strength.

When the fiber content reaches a certain value, both the porosity and the compressive strength are significantly decreased, as shown by M4 and Z4. The dense accumulation of fibers occupies the space of the pores, resulting in a decrease in apparent porosity. The reduction in binder results in a weakening of the bond between the fibers.

In the fiber ceramic, the fiber as a reinforcing body has a space supporting effect and has a strong compressive strength. The function of binder is to enhance the overall bonding strength. In addition,
the compressive strength of all samples of the Al$_2$O$_3$-bonded YSZ fiber ceramics is higher than the maximum value of the Al$_2$O$_3$-bonded mullite fiber ceramics. The reasons mainly include two points as the following: First, YSZ fiber is stronger than mullite fiber. Second, the bonding effect between the YSZ fiber and the binder is better than that between the mullite fiber and the binder. It is also shown that the compressive strength of materials prepared with YSZ fibers is higher than the compressive strength of materials prepared from mullite fibers.

**Figure 9.** The compressive strength corresponding to the different apparent porosity of the samples.

4. Conclusions
(1) ρ-Al$_2$O$_3$, mullite fiber and YSZ fiber have been used as the raw materials to fabricate the Al$_2$O$_3$-bonded fibrous ceramics by an aqueous gel-casting process. Using hydraulic alumina as the gel original, the randomly interlaced fibers are bonded to form a nest-like three-dimensional skeleton network structure.

(2) With increasing the amounts of fibers, the porosity of the prepared fiber ceramics increases, the binder attached to the fiber decreases, the corresponding thermal conductivity decreases, and the compressive strength decreases. However, when the fiber content is increased to a certain value, the influence on the porosity and the thermal conductivity is reduced.

(3) This paper explores the effects of added mullite fibers and YSZ fibers on the properties of fiber ceramics. The same content of fiber, mullite fiber ceramic has a higher porosity, lower thermal conductivity and compressive strength. The fiber content ranges from 33% to 75%, and the mullite fiber ceramics have a wide range of porosity ranging from 66.9% to 78.6%. However, the porosity of YSZ fiber ceramics is narrow, ranging from 71.1% to 72.7%. The compressive strength of all samples of YSZ fiber ceramics is higher than the maximum value of mullite fiber ceramics. It indicated that YSZ fiber is stronger than mullite fiber.

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