Processing and Properties of Oxide Fiber Reinforced Alumina Composites

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Abstract. A simple, low-cost processing method involving slurry infiltration, hot pressing and subsequent densification was developed to manufacture NextelTM 440 fiber reinforced alumina (N440/A) composites. The influence of alumina sol on the densification of alumina matrix was investigated through XRD and SEM. Results showed that the introduction of alumina sol into slurry promoted the densification of alumina matrix. Then the effect of sintering temperature from 1100°C to 1300°C on mechanical properties of N440/A composites was investigated. The optimized composite material exhibited a tensile strength > 140MPa and flexural strength > 170MPa. The analysis of the fracture surface suggested that the porous matrix played a vital role in the toughening mechanism of N440/A composites. Numerous matrices attach to pullout fibers of N440/A composites, indicating that matrix cracks propagate through micro-pores in the matrix and deflect at the fiber/matrix interface effectively.

1. Introduction

Research on oxide/oxide ceramic matrix composites (Ox/Ox CMC) has seen significant advancement over the past few decades, due to their low density, high temperature resistance and oxidation resistance[1-3]. Ox/Ox CMC is fabricated by using oxides for all constituents, including fibers, matrices and interface-control coatings[4-6].

Alumina is one of the most popular materials used for Ox/Ox CMC matrices, owing to its high strength and stiffness compared to other oxide matrix materials[7]. α-Al2O3 is the most thermodynamically stable phase of this compound and sub-micron grain sized particles possess good sintering activity[8]. Thus, sub-micron grain sized α-alumina powder has been widely used for the preparation of alumina matrix composites. This powder can be fully densified by pressureless sintering in air at a minimum temperature around 1300°C [9]. Among the commercially available oxide fibers, the most heat-resistant oxide fiber up to now can be used at about 1200°C [10]. Therefore, measures must be taken to reduce the sintering temperature of the matrix to avoid damage to the oxide fiber. Sintering aids such as SiO2, MgO, TiO2, and Y2O3 are usually added to achieve this goal[11-14]. However, the mixing of these aids may also reduce the mechanical properties of alumina ceramics due to the introduction of new phases[14].

Alumina sol is aqueous dispersion of nano-sized alumina particles. The sol-derived alumina can be totally sintered and transformed into α-alumina when heated up to 900-1200°C [15-17], which is much
lower than the sintering temperature of sub-micron grain sized alumina powder. Thus, it is possible to reduce the sintering temperature of alumina matrix composites by introducing alumina sol into sub-micron grain sized α-alumina without reducing their mechanical properties.

In the present work, alumina ceramic compacts and Nextel™ 440 fiber reinforced alumina composites (N440/A) were prepared by introducing alumina sol into slurry containing sub-micron grain sized alumina, and the properties of N440/A composites were investigated.

2. Materials and methods

2.1. Materials

Satin weave Nextel™ 440 fiber fabric (3M Co., USA) was used as reinforcement. Al₂O₃ sol (XZ-1128, Hefei Xiangzheng Chemistry Technology Co., Ltd., China) was used to prepare alumina slurry, the weight ratio of Al₂O₃ in the sol was 22.5%, and the particle size of Al₂O₃ was 10-20nm. The alumina powder used was TM-DAR (Taimei Chemicals Co. Ltd., Japan), the chemistry of which was essentially pure (99.99%) α-Al₂O₃, with a mean particle size of 0.15μm and BET surface area of 13.1m²/g.

2.2. Manufacturing Process

As shown in Figure 1, the fabrication of N440/A composites was implemented using an established slurry infiltration-sintering method. Firstly, the alumina powder was dispersed in the alumina sol (or water) to prepare alumina slurry through ball milling. Then the woven fabric was infiltrated by submersing the fabric in the slurry to prepare preregs. These preregs were then cut into the desired size and then stacked within a mold and consolidated using vacuum bagging and autoclaving at warm temperature (100-300°C), followed by pressureless sintering at high temperature (1100-1300°C). The alumina ceramic compacts were prepared by a similar process.

![Figure 1. Slurry infiltration-sintering process used for the fabrication of N440/A composites.](image)

2.3. Characterization methods

The α-Al₂O₃ formation temperature of alumina sol-derived gel was investigated by X-ray diffraction (XRD). Powder XRD was performed on a Shimadzu LabX XRD-6000 powder X-ray diffractometer equipped with a copper target. 2θ was 10-80 deg, while the scan speed was 5 deg/min and the sampling pitch was 0.04 deg. Microstructures of sintered compacts and composites were obtained by scanning electron microscopy (SEM, FEI NANO SEM 450).

Bulk density and open porosity of sintered compacts were measured according to Archimedes’ principles, with distilled water as immersion liquid. Relative density was calculated using theoretical density of alumina (3.96g/cm³).

Tensile tests were carried out at room temperature using a universal machine (Instron 5982). Specimens were in the form of dog bone specimens with an inner width of 6mm and an outer width of 12mm, and a radius of curvature of 100mm. The gage section had a length of 20mm, with an overall
length of 190mm. Tensile tests were performed in position control at a constant displacement rate of 0.5mm/min (ASTM C1295). Flexural strength tests were carried out at room temperature using a universal machine (CMT6104, MTS). Sample geometry was 60 mm×5 mm×4 mm, while the span and velocity of the crosshead were 50 mm and 0.5 mm/min, respectively (ASTM C1341-06).

3. Results and discussion

3.1. Phase development of alumina gel

XRD patterns of dried and sintered alumina gel are shown in Figure 2. It is shown that alumina gel is mainly composed of $\beta$-$\text{Al}_2\text{O}_3$. $\beta$-$\text{Al}_2\text{O}_3$ is not an isomer of alumina, but an aluminate. A meta-stable alumina ($\gamma$-$\text{Al}_2\text{O}_3$) exists in the sample sintered at 700°C, and then $\gamma$-$\text{Al}_2\text{O}_3$ transforms into ($\delta, \theta$)-$\text{Al}_2\text{O}_3$ at 900°C, and the latter is more stable. Trace of $\alpha$-$\text{Al}_2\text{O}_3$ is observed in the samples sintered at 950°C and 1000°C.

It can be seen from the results of XRD that during the calcination process, the possible reactions are as follows:

$$\beta \rightarrow \gamma \rightarrow (\delta, \theta) \rightarrow \alpha$$

The sol-derived alumina gel transforms into $\alpha$-alumina when heated to about 950°C. This temperature is much lower than the sintering temperature of sub-micron grain sized alumina powder.

![Figure 2. XRD patterns of dried gel sintered at different temperatures.](image)

3.2. Densification behavior of alumina compacts

Then alumina ceramic compacts were prepared by alumina slurry with or without alumina sol. The physical properties of sintered alumina compacts are summarized in Figure 3. The relative density (Figure 3a) increase and the open porosity (Figure 3b) decrease as sintering temperature increases from 1100°C to 1300°C. The highest relative density (97.2%) and lowest open porosity (0.5%) are obtained for the compact with alumina sol sintered at 1300°C, while the lowest relative density (65.8%) and highest open porosity (33.3%) are obtained for the compact without alumina sol.
The SEM images of microstructures of sintered compacts from the fractured surfaces are shown in Figure 4. All compacts become denser as sintering temperature increases. The compacts with alumina sol display better densification behavior against the compact without alumina sol, indicating that the mixing of alumina sol has profound effect on the densification behavior of alumina compacts. These results are in good agreement with the above physical property studies.

Although the compact with alumina sol sintered at 1300°C displays best densification behavior, an obvious grain growth is observed, this is harmful to the mechanical properties of alumina ceramic compacts. A homogeneous porous structure can be seen in the compacts with alumina sol sintered at 1100°C and 1200°C, and the compact sintered at 1200°C shows a relatively denser structure without obvious grain growth.

3.3. Mechanical properties of the composites
To better understand the effect of structure of alumina matrix on the properties of the composites, N440/A composites sintered at different temperatures were prepared, and their mechanical properties were tested. The typical tensile and flexural strength-displacement curves of N440/A composites are
shown in Figure 5. With the increase of sintering temperature from 1100°C to 1300°C, the tensile and flexural strength of the material increase first and then decrease. The composite material sintered at 1200°C shows the best performance with a tensile strength > 140MPa and flexural strength > 170MPa.

Fracture surfaces of N440/A composites after mechanical tests are shown in Figure 6. For the composites sintered at 1100°C and 1200°C, the fiber pullout behavior is distinct. However, concerning the composites sintered at 1300°C, the fracture surface is very even, and nearly no pullout fibers can be observed, indicating strong interfacial bonding.

Figure 5. Tensile strength-displacement curves (a) and flexural strength-displacement curves (b) of N440/A composites.

Figure 6. Photographs of specimens sintered at different temperatures after tensile test.

Figure 7. SEM micrograph of the fracture surface of N440/A composite sintered at 1200°C.
Figure 7 shows the SEM micrographs of the fracture surface of the specimen sintered at 1200°C, obvious porous matrix structure is confirmed, and numerous matrices are attached to pullout fibers, indicating that matrix cracks propagate through matrix micro-pores and deflect at the fiber/matrix interface effectively.

The crack propagation in N440/A composites is illustrated in Figure 8. The porous matrix is composed of alumina particles and sol-derived alumina (Figure 8a). Once the matrix crack appears, it will inevitably deflect around particle junctions and propagate in micro-pores (Figure 8b). The fiber is isolated from the matrix crack because the matrix is not sufficiently tough to support a crack. Consequently, the matrix breaks and subsequent fiber pullout behavior occurs, which consume a large amount of fracture energy. Moreover, owing to low toughness of porous matrix, a large number of matrices will attach to pullout fibers (Figure 8c), as confirmed in N440/A composites after mechanical test (Figure 7).

![Diagram](image)

**Figure 8.** Schematic illustrations of crack propagation in N440/A composite

4. Conclusions
Alumina ceramic compacts and N440/A composites were prepared by introducing alumina sol into alumina slurry through slurry infiltration-sintering process, and the properties of N440/A composites were investigated. The following conclusions can be reached:

The mixing of alumina sol into the alumina slurry has profound effect on the densification behavior of alumina compacts. The compacts with alumina sol sintered at 1100°C and 1200°C show a homogeneous porous structure, and the compact sintered at 1200°C shows a relatively denser structure without obvious grain growth.

With the increase of sintering temperature from 1100°C to 1300°C, the tensile and flexural strength of N440/A composites increase first and then decrease. The composite sintered at 1200°C shows the best performance with a tensile strength >140MPa and flexural strength >170MPa.

Owing to low toughness of porous matrix, a large number of matrices are attached to pullout fibers in N440/A composites. The inference is that matrix cracks can propagate through matrix micro-pores and deflect at the fiber/matrix interface effectively.

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