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Fabrication and Properties of 3D Mullite Fiber-Reinforced Al₂O₃ Matrix Composites Prepared by Sol-Gel Process

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Abstract. Fiber toughening is an effective method to improve the brittleness of ceramic materials. In this paper, three-dimensional mullite fiber reinforced alumina ceramic matrix (3D mullite_f/Al₂O₃) composites were prepared by sol-gel process. Alumina sol was prepared by two ways in the inorganic aluminium salt method, and the alumina sol with good fluidity and high solid content was used as a precursor. The preparation process of alumina sol was studied by XRD and TGA-DSC. The results show that the sol is transformed into Al₂O₃ at about 1100°C, and the crystal phase is α-Al₂O₃ phase. The mechanical properties of the sample were analyzed by three-point bending test. The microstructure of the fractures was observed by scanning electron microscopy. The results show that with the increase of the immersion cycles, the density of composites increases continuously, and the toughening mechanism of continuous fiber extraction, interfacial debonding and crack deflection is fully utilized during fracture, which is characterized by ductile fracture behavior and achieved the purpose of toughening.

1. Introduction

With the development of high-performance aviation turbine engines, turbine inlet temperatures continue to increase, the temperature of the hot-end parts can reach above 1600°C, and the working temperature has far exceeded the working limit of superalloys [1,2]. Continuous non-oxide fiber reinforced non-oxide ceramic matrix composites are prone to oxidative failure and even catastrophic failure in service environments with high temperatures, oxygen and moisture [3,4]. Oxide ceramic matrix composites are resistant to high temperatures and oxidation, and they don't form catastrophic fractures due to oxidative failure. This type of composite is relatively low cost and is one of the most promising candidates for aero-engine hot end components. Countries such as the United States and Japan began to focus on the field of oxide/oxide ceramic matrix composites at the end of the last century, and gradually realized their application in the field of hot end components such as aeroengines [5,6].

Oxide reinforcing fibers generally used are continuous mullite fibers or alumina fibers, but the surface activity of the oxide fiber is high, and it is easy to react with the matrix to form a strong interface during the preparation of the composite, or the fiber is eroded during the preparation process, resulting in a decrease in performance. There are usually two ways to avoid the strong interface

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between the fiber and the matrix. (1) Preparation of interface layers on the fiber surface, for example, BN, SiC and other oxide ceramic interfaces can be prepared on the fiber surface; For example, Chen Zhaofeng et al [7] used the chemical vapor infiltration method (CVI) to deposit PyC and PyC/SiC interfaces on Nextel 720 fibers, and the flexural strength of the composites was measured to be 56 MPa and 267 MPa, respectively. (2) Preparation of porous matrix: cracks can undergo continuous non-linear deflection in the matrix during the fracture process, but the substrate has poor thermal creep properties, the material is prone to creep damage in high temperature environment [8], and the porous matrix has lower thermal conductivity, so commonly used in the field of non-structural materials such as heat insulation [9]. Therefore, it has become a top priority to study the preparation of an interface layer of a suitable oxide fiber/oxide ceramic matrix composite.

The preparation methods of oxide ceramic matrix composites mainly include hot pressing sintering method, precursor impregnation cracking method, sol-gel method and electrophoretic deposition method[10-13]. Among them, the sol-gel method is especially suitable for the preparation and molding of continuous fiber toughened ceramic matrix composite due to its low densification temperature, convenient process and the advantages of near-net size processing [14]. In this paper, the alumina matrix was prepared by sol-gel method, and the pyrolysis carbon (PyC) interfacial layer was prepared by chemical vapor infiltration process. And the effect of interface layer on the mechanical properties and microstructure of the composite was studied.

2. Experiment

2.1. Raw material

Mullite fiber blanket, fiber diameter $5\sim10 \ \mu\text{m}$; Aluminum trichloride hexahydrate(AlCl₃ • 6H₂O, analytical grade), Sinopharm Chemical Reagent Co., Ltd.; Anhydrous ethanol, analytical grade, Beijing Chemical Plant; Deionized water, self -made.

2.2. Sample Preparation

Formulation of alumina sol: using $AlCl_3 \cdot 6H_2O$ as precursor, preparing one solution with deionized water and absolute ethanol in a certain ratio, and stirring well to dissolve the aluminum salt. After forming the colorless transparent solution and standing for more than 2 hours, a pure, uniform and stable alumina sol is obtained.

Preparation of PyC interface phase: the mullite fiber preform was placed in a chemical vapor deposition furnace with argon gas as a kind of shielding gas at a flow rate of 1.0 L/min, butane as a kind of PyC precursor gas at a flow rate of 4.0 L/min, deposition temperature was 1000°C and deposited for 3 h to deposit the surface of the mullite fiber preform to obtain the PyC interface phase. After the deposition was completed, it was taken out and cooled by the furnace.

The cycle impregnation densification step: the sample by preparing the pyrolytic carbon interface was impregnated with the aluminum sol prepared by a vacuum impregnation process, the immersion time was 0.5 h, the gel treatment temperature was 120°C, and the time was 5 h. Then the sample was vacuum pyrolyzed at the temperature of 1100° C, heating rate of 5°C/min, constant temperature of 1 h. The above procedure was repeated 16 times to obtain a kind of densified composite material called L1. The following preparation processes were the same as the above, but the deposition time of the pyrolytic carbon interface on the L2 sample was 12 h, the deposition of the pyrolytic carbon interface time on the L3 sample was 18 h, and the deposition of the pyrolytic carbon interface on the L4 sample was 24 h. The rest of the densification process parameters were the same.

2.3. Testing and characterization

Phase analysis of the material was carried out using D8 ADVANCE X-ray diffractometer (XRD) from Bruker, Germany. The change of mullite xerogel during heat treatment was analyzed by STA 449C synchronous thermal analyzer (TGA-DSC) from Netzsch, Germany. Sample density was tested using the Archimedes drainage method. The micro-morphology of the carbon fiber-reinforced mullite-

based composites was observed by Ferri 200 field emission scanning electron microscope (SEM) from FEI.

The bending strength and flexural modulus of the composite were tested by three-point bending method. The equipment used was the Landmark dynamic and static fatigue testing system of MTS Company of USA. The sample size was $3 \text{ mm} \times 4 \text{ mm} \times 40 \text{ mm}$, the span was 30 mm, and the loading was performed. The rate was 0.5 mm/min. The fracture toughness of the composite was tested by the single-edge slit beam method. The equipment used was the AG-IC100KN electronic universal testing machine of Shimadzu Corporation of Japan. The sample size was $3 \text{ mm} \times 4 \text{ mm} \times 40 \text{ mm}$ and the span was 30 mm. The side slot had a width of 0.2 mm, a groove depth of 1.5 mm and a loading rate of 0.05 mm/min.

Table 1. Alumina sol physical parameters.

PH	Viscosity (mPa·s)	Ceramic yield (%)	Solid content(%)
2.8	8.5	20.4	29.6

3. Experimental results and analysis

3.1. Alumina sol performance analysis

The Al_2O_3 sol in this paper is close to a completely transparent liquid, and there is a kind of distinct Tyndall phenomenon when irradiated with a laser beam. After being left at room temperature for one month, the sol didn't change significantly. The physical properties of the sol are shown in Table 1. The viscosity of the sol is 8.5 mPa·s, the solid content after drying at 120°C is 29.6%, and the yield of the ceramic after heat treatment at 1100°C is 20.4%. It can be seen that the sol has the characteristics of high solid content, low viscosity and high ceramic yield. The high solid content and ceramic yield are beneficial to improve the densification efficiency of the composite material, and the low viscosity facilitates the impregnation of the sol into the interior of the mullite fiber preform.



The gel powder obtained by drying the sol at 120°C is subjected to TGA-DSC analysis, and the results are shown in Figure 1. It can be seen from the TGA curve that it is divided into three stages. The first stage: from room temperature to 150°C, the weight loss is relatively gentle, the weight loss is about 5%, and the DSC curve has an endothermic peak at 140°C at this stage. It is judged that this is mainly caused by the residual free water and crystallized in the matrix after drying. The second stage: from 150°C, the weight loss in this stage shows a linear downward trend, about 60%. This

means that the system undergoes a relatively severe chemical reaction during this phase, which can be confirmed by the obvious endothermic peak on the DSC curve. There is an obvious endothermic peak at 200°C on the DSC curve, which should be caused by decomposition of the base hydroxyl group and Cl⁻decomposition. The third stage: from 350°C to1300°C, the weight loss is very small at this stage, and there are two corresponding pairs on the DSC curve. The thermal peak is considered to be mainly caused by the formation of Al₂O₃ crystal phase, and the matrix changes from amorphous to crystalline, AlOOH $\rightarrow \alpha$ -Al₂O₃.

The XRD analysis of the gel powder after heat treatment at different temperatures is carried out, and the results are shown in Figure 2. It can be seen from Figure 2 that the XRD patterns of the samples respectively prepared at 1100°C, 1200°C, 1300°C and 1400°C have Al₂O₃ crystal plane diffraction peaks. Its crystal phase is α -Al₂O₃, which has a hexagonal crystal structure that makes the crystal structure of the sample denser, so it will cause the sample to shrink to a certain volume. However, obvious α -Al₂O₃ diffraction peaks are not showed at 900°C and 1000°C, which indicates that α -Al₂O₃ phase is not formed at this temperature. In addition, the higher the sintering temperature is, the sharper the diffraction peak becomes, and the amorphous structure gradually becomes crystalline, which indicates that the degree of crystallization of Al₂O₃ is better. It can be seen from Figure 2 that the diffraction peak of the sample sintered at 1100°C to 1400°C doesn't change much, so the sintering temperature is set to 1100°C, which can ensure that the amorphous form in the matrix is completely converted into the crystalline α -Al₂O₃ that can reduce the sintering cost and speed up the experiment.



Figure 2. XRD pattern of aluminum gel powder under heat treatment at different temperatures.

3.2. Effect of pyrolytic carbon interface on mechanical properties of materials

The properties of the four composite materials prepared are shown in Table 2. It can be seen that the PyC (pyrolysis carbon) interface attached to the fiber significantly improved the flexural strength of the material. The room temperature flexural strength of L2 composites reached 140.9 MPa, and the room temperature flexural strength of L3 composites is 167.8 MPa, while the room temperature flexural strength of L4 composites is 146.3 MPa. At the same time, it can be seen from Table 2 that the composite material deposited with PyC interface exhibits obvious ductile fracture behavior, mullite fiber effectively toughens and strengthens the alumina matrix, and the room temperature of the Mullite_f/Al₂O₃ composite without PyC interface is deposited. The bending strength is only 110.6 MPa, and the strength is low, which shows obvious brittle fracture behavior. However, the porosity and density of the three are not much different, which indicates that the deposition of PyC interface has little effect on the same aluminum sol and impregnation process.

Tuble 2. Tropentes of composites with various interfaces.					
Material	Density (g/cm ³)	Porosity (%)	Flexural strength (MPa)	Fracture toughness $(MPa \cdot m^{1/2})$	
L1	2.23	18	110.6	2.8	
L2	2.29	19	140.9	7.4	
L3	2.34	18	167.8	8.6	
L4	2.40	17	146.3	8.3	

Table 2. Properties of composites with various interfaces

In addition, the pyrolytic carbon interface layer greatly improves the fracture toughness of the material. Since the pyrolytic carbon is has loose layered structure and low density, its presence can prevent the diffusion reaction of three-dimensional mullite fiber preforms and alumina matrix at high temperatures, and the three-dimensional mullite fiber preform caused by the direct precipitation of the alumina matrix on the mullite fiber cannot function as a reinforcement. Therefore, the presence of the PyC interface phase ensures that the material has suitable interfacial strength after the high temperature preparation process and enhances the fracture toughness of the material. At the same time, the PyC interface phase has mechanical compatibility, which causes the micro-cracks of the matrix to deflect and maintain good load transfer between the fiber preform and the matrix. In the composite material containing the PyC interface, due to the barrier effect of the PyC interface, so that the fiber strength is largely retained. Due to the existence of the loose layered interface of PyC, the diffusion of the fiber and the matrix is hindered, and the fiber/matrix achieves weak interfacial bonding, which greatly improves the toughness and strength of the composite.

3.3. Effect of pyrolytic carbon interface on microstructure of materials

Figure 3 is a microscopic scan of the PyC/Mullite_f fracture at different times of deposition. The graph shows that the thickness of the interface layer is about 0.3 μ m (L2), the thickness of the interface layer of b is about 0.5 μ m (L3), and the thickness of the interfacial layer of c is about 0.7 μ m (L4). The microstructure exhibits a distinct loose layered structure. There is a significant interfacial debonding between the pyrolytic carbon interface prepared in the bending fracture test and the fiber. Figure 5 is the Mullite_f/Al₂O₃ composite containing a PyC interface phase. It can be seen that a large amount of fiber is withdrawn during the fracture process, absorbing most of the energy during the fracture process, and the crack propagation of the fiber is prevented to cause brittle fracture of the material.

Figure 4 is a microstructural view of the fracture of the Mullite_f/Al₂O₃ composite. It can be clearly seen from the figure that the fracture is flat and there is no fiber-out phenomenon. During the fracture process, the crack directly passes through the mullite fiber due to the stress concentration effect, and the toughening mechanism of the fiber is not exerted. Simultaneously, the matrix and the fiber have already exhibited a very strong bonding state during the pyrolysis process. It can be seen from the figure that there are pores which aren't densified. This is the material in the late stage of impregnation-pyrolysis. As the number of impregnation-pyrolysis increases, the pores in the fiber bundle gradually close and block, which causes the sol not to infiltrate into the pores left in the fiber bundle.



Figure 3. PyC/Mullite_f SEM images deposited at different times.



Figure 4. Microstructure images of Mullite_f/Al₂O₃ composite.



Figure 5. Microstructure images of Mullite_f (PyC)/Al₂O₃ composite.

4. Conclusions

The mullite fiber composite alumina ceramic matrix composites with different thicknesses of pyrolytic carbon interfacial layer are prepared by sol-gel method and CVI method. Studies have shown that the alumina sol prepared by the inorganic aluminum salt method is completely converted to α -Al₂O₃ at about 1100°C, after repeated cycles of impregnation and cleavage, the material of the composite pyrolytic carbon interface layer is greatly improved than that of the uncomposited material, which is characterized by typical ductile fracture behavior and the fracture toughness reached 8.6 Mpa·m^{1/2}, the bending strength reached 167.8Mpa, and the mechanical properties of the sample are the best when the thickness of the pyrolytic carbon interface layer is 0.5 μ m.

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