Preparation and Characterization of An All Oxide Ceramic Matrix Composite by A Novel Method

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Abstract. Due to the characteristics of high temperature oxidation resistance and high reliability, all oxide composites are ideal materials for components in hot end of aeronautics and astronautics. In this paper, all oxide ceramic matrix composite (CMC) was prepared by a novel method which combined warm pressing of prepreg with PIP using polysilialumoxane as the precursor of mullite. The morphology, structure and mechanical properties of the all oxide CMC were characterized. The results show that polysilialumoxane with a ceramic yield of 53wt\%can be completely changed to ceramic at 1200°C and form mullite crystals. The composite with alumina and mullite matrix derived from alumina powder slurry indicated the best mechanical properties, the flexural strength and fracture toughness of the composite reach 208.3Mpa and 128.6Mpa respectively, and the pull-out effect of the fibers is obvious in the process of tensile fracture, and the composites show ductile fracture whereas the mechanical property decreases significantly after heating at 1200°C for 100 hours due to the densification of matrix and abnormal growth of alumina grains in fibers.

1. Introduction

The Continuous fiber reinforced ceramic matrix composite (CFCC) has excellent mechanical properties and temperature resistance, and has become the most promising material system in the field of aeronautics and astronautics high temperature resistance. In the past decades, continuous fiber reinforced ceramic matrix composites have been mainly concentrated in SiC\textsubscript{f}/SiC system. SiC\textsubscript{f}/SiC ceramic matrix composites have been successfully tested in aero-engines, and have been applied to aero-engine components such as nozzle regulators and combustion chamber linings[1]. However, SiC\textsubscript{f}/SiC ceramic matrix composites are facing severe challenges in the long service environment due to oxidation embrittlement in 800-1000°C. Compared with SiC ceramics, oxide ceramics have outstanding advantages in water and oxygen stability. Oxygen ceramic matrix composites have become an ideal material system for long-term service in oxidation environment ($>10^4$h)[2].

In the oxide CMC matrix system, alumina is notable to exhibit the highest strength and stiffness compared to the other oxide matrix materials. However, its thermal expansion is large and thermal shock resistance is poor, while Mullite has a relatively high strength, lower elastic modulus and, most importantly, higher temperature stability and creep resistance in comparison to alumina. Therefore, by compounding alumina and mullite in the matrix, the material has both high mechanical properties and good creep resistance, which can meet the requirements of long-term use of composite materials at
high temperature. Usually there are three approaches to obtain mullite ceramic matrix, they are sintering of mullite powder, reaction of α-Al₂O₃ or γ-Al₂O₃ with silica respectively. Among them, the temperature of sintering mullite powder and reaction of α-Al₂O₃ with silica to form mullite is higher, which has a greater thermal damage to fiber properties, while the temperature of mullite formed by reaction of γ-Al₂O₃ with silica is much lower, but the volume shrinkage is larger after reaction which is easy to cause matrix cracks[3], then the properties of composites are reduced.

In order to solve the problems of high sintering temperature and volume shrinkage of mullite ceramics, a novel method was researched in this paper, i.e., polysilialumoxane was used as mullite precursor to prepare alumina fiber reinforced oxide ceramic matrix composite by prepreg warm pressing combined with PIP process.

2. Material and methods

2.1. Design of composite structure and materials

Nexel™️ 610 aluminum oxide fiber (1500 denier, 3M Co.) weave cloths were used for reinforcement. The matrix was porous ceramic composed of alumina and mullite. No interface was needed. The composite is named N610/ A+M CMC for short. Polysilialumoxane was synthesized by Institute of Chemistry, Chinese Academy of Sciences. Taimicron TM-DAR alumina powder was purchased from Taimei Chemicals Co..

2.2. Preparation of slurry with polysilialumoxane

Polysilialumoxane is a transparent red-brown solid, soluble in toluene, n-propanol and ethylene glycol ether, etc. First, polysilialumoxane was dissolved in ethylene glycol ether to form a solution. The mass content of polysilialumoxane in the solution is 60%. Then the solution and alumina powder are mixed by ball milling in a high-energy sand mill according to the mass ratio of 1:1. After mixing, the slurry with a viscosity of about 550 mPa.s could be obtained.

![Figure 1. Technological process of all oxide CMC preparation.](image)

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\text{\begin{align*}
\alpha-\text{Al}_2\text{O}_3 \text{ powder} & \quad \text{Mullite precursor} & \quad \text{Alumina Fiber Fabric} \\
\text{Alumina slurry} & \quad \text{Impregnation} & \\
\text{Mullite precursor} & \quad \text{Prepreg} & \text{Heating} \\
\text{Solidification} & \quad \text{Pyrolysis} & \text{Green Body} \\
\text{No Impregnation} & \quad \text{Sufficiently Dense?} & \text{Yes Sinter} \\
\text{All Oxide CMC} & \\
\end{align*}}
\]
2.3. Preparation of all oxide CMC

In this paper, alumina ceramic matrix composites are prepared by warm pressing of prepreg and PIP process. The detailed process is shown in Figure 1. Firstly, the fiber fabrics were cut into shape and put into muffle oven at 600°C for 2 hours, then the surface sizing agent was removed. Then the slurry was coated on the degummed fiber fabric. After drying the fabric, the uniform impregnated prepreg could be obtained. The prepreg was placed in the mould and laminated. Then pressed slowly at room temperature for 30 minutes and heated at 200°C for 2 hours. Ensure that the solvent is completely removed. The demoulded green body was pre-sintered in a high temperature muffle furnace, and the sintered sample is repeatedly impregnated with polysilialumoxane until the density of the fiber matrix met the requirements. Finally, high temperature pressureless sintering was carried out in the muffle furnace.

![Figure 2. TG/DSC curve of alumina precursor.](image)

![Figure 3. XRD pattern pyrolysis productions under different calcinations temperatures.](image)
3. Results and discussion

3.1. Performance of polysilialumoxane

3.1.1. Ceramization of Polysilialumoxane. Figure 2 is the TG-DSC curve of polysilialumoxane. It shows that the weight of the precursor decreases sharply before 500°C, which is mainly the decomposition process of organic compound. No obvious weight change after 500°C, and the retention rate is about 53wt% until 1200°C. There is an exothermic peak at 900°C, which indicates that mullite crystals begin to form in accordance with the XRD diagram of the precursor at different heat treatment temperatures in Figure 3, there are mullite diffraction peaks at 900°C. With the increase of temperature, the diffraction peak of γ-Al₂O₃ appears at 1100°C, whereas, only mullite phase was detected at 1200°C.

3.1.2. Process adaptability of polysilialumoxane. Viscosity and solid content are two critical parameters in PIP process. Usually, viscosity increases with the increase of solid content. If solid content is too low, the pyrolysis products decreases and the impregnation efficiency would be low which would lead to long process cycle. In the other way, When the solution viscosity is too high, it is difficult to permeate into the micro-pore of matrix, especially when the thick one. Therefore, it is important to regulate and control the solution viscosity by control the solid content. In addition, viscosity also be affected by temperature, usually a simple and feasible process requires solutions which can be operate at room temperature. So, for effective impregnation of the precursor, the relationship between concentration-viscosity and temperature-viscosity of precursor solution is studied (shows in table 1 and table 2). The result shows that when the solid content is 50wt%, the viscosity is about 100mPa.s and relatively stable in the range of 20°C to 30°C.

Table 1. The relationship between concentration-viscosity of polysilialumoxane solution.

| Solid content, wt% | 40 | 45 | 50 | 55 | 60 |
|-------------------|----|----|----|----|----|
| Viscosity, mPa.s(20°C) | 45 | 78 | 106 | 270 | 4300 |

Table 2. The relationship between temperature-viscosity of polysilialumoxane solution.

| Temperature, °C | 10 | 20 | 30 | 40 | 50 | 60 |
|-----------------|----|----|----|----|----|----|
| Viscosity, mPa.s(50wt%) | 188 | 106 | 98 | 79 | 60 | 42 |

Figure 4. SEM photograph of mullite derived from polysilialumoxane (a) One impregnation-pyrolysis; (b) 12 times impregnation-pyrolysis

Figure 4 shows the micro-morphology of pyrolysis production of polysilialumoxane at 1200°C. many voids are left in the pyrolysis production without repeating impregnation (figure 4a). However, 12 times impregnation-pyrolysis process later, there is a distinct densification(figure4b). So we can conclude that it’s a feasible method to prepare mullite ceramic with polysilialumoxane infiltration and
pyrolysis. And the densification rate can be adjusted by controlling the impregnation times which is very flexible.

3.2. Study on sintering properties of alumina particles

Although there are many advantages with PIP process, but repeat infiltration and pyrolysis is needed for densification. For solving the problems of the long process cycle, alumina powder was added to polysilialumoxane solution to make slurry which could significantly improve production efficiency.

Although the addition of alumina powder can improve the densification cycle and the mechanical properties of CMC. But the alumina powder must meet the a few conditions. First, as alumina ceramic matrix is mainly formed by sintering alumina powder or alumina powder precursor which might need very high temperature, it is important to produce the matrix at low temperatures to avoid fiber degradation. Secondly, the level of porosity of the matrix is then very important since matrices that are “too dense” show a much lower fracture toughness [4-6]. In additional, the shrinkage from the dense process would lead to the formation of matrix cracks. So much attention must be concentrated on the sinter kinetics of alumina powder so as to achieve the purpose of strengthening and toughening the CMC.

Table 3. Mechanical properties of alumina particles sintered at different temperature.

| Temperature (°C) | Density (g/cm³) | Shrinkage rate (%) |
|----------------|----------------|-------------------|
| 1100           | 3.16           | 5.11              |
| 1150           | 3.28           | 7.38              |
| 1200           | 3.37           | 9.91              |
| 1250           | 3.55           | 11.88             |

Figure 5. SEM photographs of matric ceramic sintered at different temperatures.

To improve the activity of the powder and reduce the sintering temperature, alumina particles was milled in high-energy sand mill first. Then ceramics were prepared by gel-casting to study the sinter performance of the alumina particles. Table 3 shows the density and shrinkage of ceramics sintered from the treated powders. It can be seen from the table that the density and shrinkage of ceramics increase with the increase of temperature. Figure 5 is the micro-morphology of ceramics at different sintering temperatures. It can be seen from the figure that the sintering density increases with the increase of sintering temperature. When the sintering temperature is 1100 ~ 1150°C, the cervical area
between particles is less. When the sintering temperature is 1200 ~ 1250°C, the sintering phenomenon of powders is more obvious.

3.3. Mechanical and morphological analysis of N610/ A+M CMC
By comparing with sol-gel which is the most universal method for making oxide/oxide CMC, the novel process studied in this paper has advantage in short cycle of fabrication, also it is more suitable for making complex shape parts than the slurry impregnation hot pressing (SIHP). Figure 6 shows the all oxide CMC prepared by the novel method. Furthermore, the matrix here without the presence of silica glass phase which can react with the oxide fibers at elevated temperature.

![Figure 6. Morphology of all oxide CMC prepared by the novel process](image)

(a) Plate specimen (200mm*200*3), (b) Combustor lining, (c) Tensile specimens (RT); (d) Tensile specimens (HT)

Table 4. Mechanical properties of all CMC sintered at different temperature.

| Sintering temperature(°C) | Density(g/cm³) | Porosity(%) | Flexural strength(MPa) | Tensile strength(MPa) |
|---------------------------|----------------|-------------|------------------------|----------------------|
| 1150                      | 2.53           | 35.8        | 99.8                   | 92.6                 |
| 1200                      | 2.78           | 27.6        | 208.3                  | 128.6                |
| 1250                      | 2.91           | 22.1        | 167.9                  | 88.3                 |

Table 4 shows the properties of the composite after treatment at different temperatures. With the increase of temperature, the density of the composite increases and the porosity decreases gradually, but the bending strength and tensile strength both increase with the increase of temperature and then decrease after. The bending strength is 208.3MPa, and the tensile strength is 128.6MPa while the sinter temperature is 1200°C, the reason for that may be the degradation of the fiber. When the treatment temperature is 1250°C, the matrix density is higher, but because the reinforced fibers contain 99% alpha alumina crystals, when the sintering temperature is higher than 1200°C, the initial properties of the fibers begin to decline. When the treatment temperature is 1200°C, the strength of 610 fibers changes very little, and when the treatment temperature reaches 1250°C, the strength retention rate is about 80% (as shown in Figure 7). Another probable reason is that when the density of the matrix is too high, the porosity of the matrix decreases, which leads to the strong bonding force between the fiber and the matrix, and the pull-out effect of the fiber decreases, which reduces the
mechanical properties of the composites. At the same time, the matrix shrinkage is too large, resulting in more micro-cracks in the matrix.

Figure 7. 3M™ Nextel™ ceramic roving strength at temperature [7].

Figure 8 shows the tensile section and cross-section microstructure of the composites when sintering temperature is 1200°C. It can be seen from the diagram that the matrix is filled in the fiber bundles of the composites without obvious void and crack defects, but there are many small holes of about 0.2μm in size. At the same time, the composites have obvious fiber pullout during the tensile fracture process, and the properties of the composites are improved.

Figure 8.SEM photographs of all oxide CMC (a) Fracture surface; (b), (c) Cross-section

3.4. Study on long-life performance of N610/ A+M CMC
The mechanical properties and microstructures of the composites were analysed after oxidation at 1100°C and 1200°C respectively for 100h. The results show that the quality, density and strength of the composites have not changed much after treatment at 1100°C. The quality of the composites remains unchanged after treatment at 1200°C for 100 hours, but the density increases and the strength decreases greatly(shown in table 5). In oxide composites, the change of mass mainly occurs during oxidation or volatilization. The fibers we mention in this paper composes 99% α-Al2O3 and the matrix compose of alumina and mullite only, which are pure polycrystalline. There is no oxidation problem happen at this temperature, so the quality is basically unchanged. The graph shows the fracture mode of the composites after oxidation at 1100 °C for a long time. There are still tough fracture modes of debonding and pulling out of the fibers during the fracture process. However, after oxidation at 1200 °C for 100h, the density of the composites increases by 5%, the bending strength and the tensile strength decrease by 46.3% and 35.8%, respectively. The fracture surface is smooth and the fracture mode is typical brittle fracture (shown in figure 9). The main reason for the change of density and
strength is that the matrix begins to sinter at 1200°C and the matrix becomes denser after 100h. The denser matrix results in stronger bonding force between the fibers and the matrix. When the crack in the matrix extends to the interface, no deflect can happen. In addition, the abnormal grain growth of 610 fibers after long sintering at 1200°C (as shown in figure 10) results in a significant decrease in the strength of the fibers.

**Table 5.** Long-life performance data of composite materials /

| Quality Retention | Density (g/cm³) | Flexural strength (MPa) | Tensile strength (MPa) |
|-------------------|----------------|------------------------|-----------------------|
| Original          | 100%           | 2.78                   | 208.3                 | 128.6                 |
| 1100°C, 100h      | 100.01%        | 2.78                   | 213.2                 | 127.8                 |
| 1200°C, 100h      | 100.01%        | 2.92                   | 111.8                 | 82.5                  |

![Figure 9. Fracture surface SEM photographs of all oxide CMC after 100h treatment](image)

**Figure 10.** SEM photograph of precursor after calculated under 1200°C

4. Conclusions

With the novel method that the slurry was prepared by mixing polysilialumoxane with ceramic powder and the prepeg was obtained by brushing the slurry onto alumina fibers. then, the composite material was obtained by moulding the prepeg. the problems of high sintering temperature and volume shrinkage of mullite ceramics have been solve effectively, and also has the advantage of short preparation period and being suitable for making complex CMC parts. The results are as follows:

1. Polysilialumoxane can be completely changed into ceramic at 1200°C to form mullite crystals with a ceramic yield of about 53%;
2. In the process of pyrolysis, polysililumoxane first changed from γ-Al₂O₃ amorphous form to α-Al₂O₃ amorphous form. With the increase of temperature, it all changed to α-Al₂O₃ at 1200°C;
3. Porous matrix was obtained when the sintering temperature was 1200°C. The flexural strength and fracture toughness were 208.3MPa and 128.6MPa, respectively;
4. The properties of the composites remain unchanged after treatment at 1100°C for 100h. Whereas, when the temperature rises to 1200°C, the interfacial bonding of the composites is strong.
due to the compactness of the matrix and the abnormal growth of the grains in the alumina fibers, which resulting in a significant decrease in the mechanical strength of CMC.

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