PREPARATION AND PROPERTIES OF ZIRCONIA FIBRE REINFORCED BORON PHENOLIC RESIN FOR CERAMIC AND HIGH TEMPERATURE COMPOSITES

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Keywords: Zirconia Fiber, Boron Phenolic Resin, High temperature ablation, Properties

ABSTRACT

In this paper, the ablative composite materials were prepared by adding alumina, magnesia, silicon carbide, mica and other fillers, and being reinforced with zirconia fibre to test its mechanical properties and the properties of high temperature ablation. The results show that the bending strength of the material is very good, and the bending strength can reach 19.33MPa. After sintering at 1400℃, the new phase of zircon was produced, and the bending strength is also great which can reach 12.03MPa. And the corrosion resistance of the composites is excellent, and the oxygen-acetylene line ablation rate is 0.03 mm/s when the fibre content is 30wt%.

1 INTRODUCTION

The spacecraft will have severe friction with the air if it's speed is very fast when it is flying in space continuously. Then, the kinetic energy of the aircraft is converted into heat which makes the air temperature near the spacecraft rise sharply. Adding the influences of convective heat transfer and microwave radiation, the surface temperature of the aircraft will rise rapidly, which can reach several thousand degrees Celsius [1]. In order to ensure the safety of the aircraft and the normal operation of airborne equipment, the thermal protection of the aircraft must be carried out. The thermal protection of the aircraft is usually used in three ways [2-3], which contain ablation method, radiation method and heat absorption method. The heat absorption method [4] uses the materials which have large specific heat capacity, high melting point and large thermal conductivity, such as beryllium, copper, graphite and so on. It controls the surface temperature within a certain range by increasing the thickness of the material and then the purpose of thermal protection is achieved. However, because the specific heat capacity of the material is limited and the thickness can't be infinitely increased, this method has been eliminated. The radiation method [5] uses the reflective materials to radiate the absorbed heat. In this method, the structure and quality of the material will not change at all before the material reaches the damage threshold, but its anti-heat effect is not ideal. The ablation method [6] achieves a positive heat effect by sacrificing part of the materials in thermal decomposition, melting, evaporation, sublimation and other ways. The ablation method is widely used because of its reliability, safety and cost-effective. However, with the continuous improvement of aircraft technology, the flying speed is faster and faster and the requirements of high temperature ablation is getting higher and higher. So, the traditional ablative materials have been unable to meet the needs of aircraft ablation.

Ceramifiable polymer has the same properties as ordinary polymers at room temperature, and it will be converted to a ceramic protective layer with good ablation resistance at high temperatures, which protects the inside of the material from high temperature corrosion. Sheng Hu [7] and his partner prepared ceramic silicone rubber composite materials by adding ammonium polyphosphate, aluminum hydroxide, mica and the like into the silicone rubber. The results showed that the ceramic reaction takes place under the condition of 1000 ℃ or higher to produce the dense ceramic compound, which improves the bending resistance after the ablation of the material. Yan Qin [2] and his partner prepared low-density ablation insulation material by using phenolic resin as the matrix and adding functional filler beads and porcelain additives. The results showed that porcelain auxiliaries and phenolic resins begun to undergo ceramicization at 800 ℃ and above, which improved the ablation and thermal

insulation properties of phenolic composites. In this paper, the zirconia fibre reinforced phenolic resin composites were prepared with using boron phenolic resin as the matrix and adding alumina, magnesia, silicon carbide, mica and other porcelain filler, and adding zirconia fibre. And then the effect of zirconia fiber on high temperature ablative properties and mechanical properties of materials were explored.

2 EXPERIMENTAL DETAILS

2.1 Experimental materials and instruments

The raw materials used in the experimental process are: boron phenolic resin (particle size of 0.1mm, produced by Shaanxi Taihang Fire Resistant Polymer Co., Ltd), ethanol (AR, produced by Sinopharm Group Chemical Reagent Co., Ltd.), alumina (AR, produced by Sinopharm Group Chemical Reagent Co., Ltd.), magnesia (AR, produced by Shanghai Aladdin Biochemical Technology Co., Ltd), silicon carbide (AR, produced by Shanghai Aladdin Biochemical Technology Co., Ltd), zirconia fibre (produced by Nanjing Polytechnic Yulong New Materials Polytron Technologies Co., Ltd.), mica (ingredients are shown in Table 1).

The equipment used in the experimental process is: electronic balance (JA3003N, produced by Shanghai Precision Science Instrument Factory), flat vulcanizing machine (QLB-350 × 350 × 2-0.25MN, produced by Shanghai Rubber Machinery Factory), High temperature furnace (KSY-6D-16 temperature controller, produced by Wuhan Yahua Electric Co., Ltd.), oven (DZ-2BCⅡ, produced by Tianjin Tai Site Instrument Co., Ltd.).

Table 1 The table of the composition of mica

Oxide	SiO_2	Al_2O_3	K_2O	Fe_2O_3	Na_2O	MgO	Other oxides
wt%	45.20	32.50	10.08	5.10	1.45	2.24	3.43

2.2 Preparation of ablative materials

First, in order to prepare the resin solution, 100g of boron phenolic resin was weighed, and the resin was put into 100g of ethanol, then the mixed solution was stirred well. Secondly, 40g of mixed powder which contained alumina, magnesia, silicon carbide and mica powder in a 10: 1: 8: 1 ratio was weighed for adding in 120g of the resin solution to prepare the resin paste. Next, different quality of zirconia fiber cotton was weighed, and was put into the resin paste for full infiltration to obtain different mass percentages (10wt%,20wt%,30wt%) of bulk molding compound. Then, the bulk molding compounds were put into the oven at 80℃° to remove the alcohol. Finally, the composites were prepared by using flat vulcanizing machine with the temperature at 120℃° for 1h, at 150℃° for 2h and at 180℃° for 1h.

2.3 Performance characterization

The flexural strength of the material before and after sintering was measured by using the universal force testing machine at standard GB/T 9341-2000. And The model of the universal mechanical testing machine is CTM001. The cross-sectional morphology of the samples before and after sintering were tested by using scanning electron microscope which produced by Japan Electronics Co., Ltd. and the electron microscope model is JSM-5610LV. The ablation resistance of the material was characterized by the line ablation rate which was measured by oxygen acetylene ablation test. The phase composition of the sintered reaction product was analyzed by D8 ADVANCE type X-ray diffractometer which produced by Bruker. The firing angle is 5°-80° and the scanning rate is 5°/min.

3 RESULTS AND DISCUSSION

3.1 Analysis of bending strength results

In order to test the mechanical properties of the samples under different temperature conditions, the flexural strength of the samples before and after sintering was tested. The comparison of the flexural strength of composite materials with different fibre contents before and after high temperature sintering at 1400℃ was shown in Figure 1. From the figure, we can see that the flexural strength of the material can reach 19.33MPa before sintering, and the flexural strength of the material can reach 12.03MPa after sintering. And the flexural strength of the material before and after sintering increases with the increase of fibre content, which indicates that the addition of zirconia fibres has played a positive role in the enhancement of the material. In addition, the bending strength of the material after sintering is lower than that of the material before sintering, which may be due to the decomposition of the organic matter in the material during the sintering process, resulting in defects in the material structure. The comparison of the flexural strength of composite materials at different sintering temperatures when the fibre content is 20wt% was shown in Figure 2. It can be seen from the figure that the flexural strength of the material increases with the sintering temperature increasing. This may be due to the fact that the degree of sintering reaction is very low at 1200°C, and the fillers were almost no reaction which caused the fact that there is no dense ceramic phase. But with the increase of temperature, the degree of sintering should be improved and the porosity of the ceramic phase is increased, which leads to the improvement of its mechanical properties.

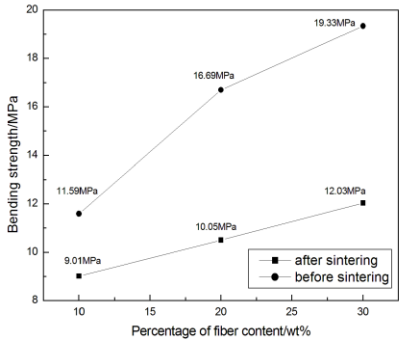

Fig.1 The comparison of the flexural strength of composite materials with different fiber contents before and after high temperature sintering at 1400℃

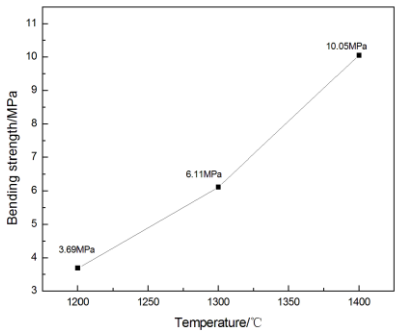

Fig.2 The comparison of the flexural strength of composite materials at different sintering temperatures when the fiber content is 20wt%

3.2 Analysis of the section morphology

In order to observe the interfacial bonding of the composites and the effect after high temperature sintering at 1400℃, the fracture of the bending specimens before and after sintering was carried out by electron scanning microscopy, and the results was shown in Figure 3. The low magnification images of the fracture scanning before and after sintering were shown in Figures A1 and B1, respectively. As can be seen from the figure, the material has a multiphase structure, and the arrangement of zirconia fibres is disordered. The middle magnification images of the fracture scanning before and after sintering were shown in Figures A2 and B2, respectively. It can be seen from Figure A2 that the interface between the zirconia fibres and the boron phenolic resin system is tightly bonded, which indicates that the zirconia fibres were well infiltrated during the preparation process. In the lower left corner of Figure B2, we can see that there is a crystalline structure in the sintered sample, indicating that the material is sintered and crystallized. The high magnification images of the fracture scanning before and after sintering were shown in Figures A3 and B3, respectively. Compared with Figure A3, the structure of material is more compact in Figure B3, which indicates that the filler was integrated into a dense ceramic structure after high temperature sintering.

However, in Figure B3, it can be seen that there is a hole in the material. This is because the liquid phase formed during the sintering process did not fill the entire system.

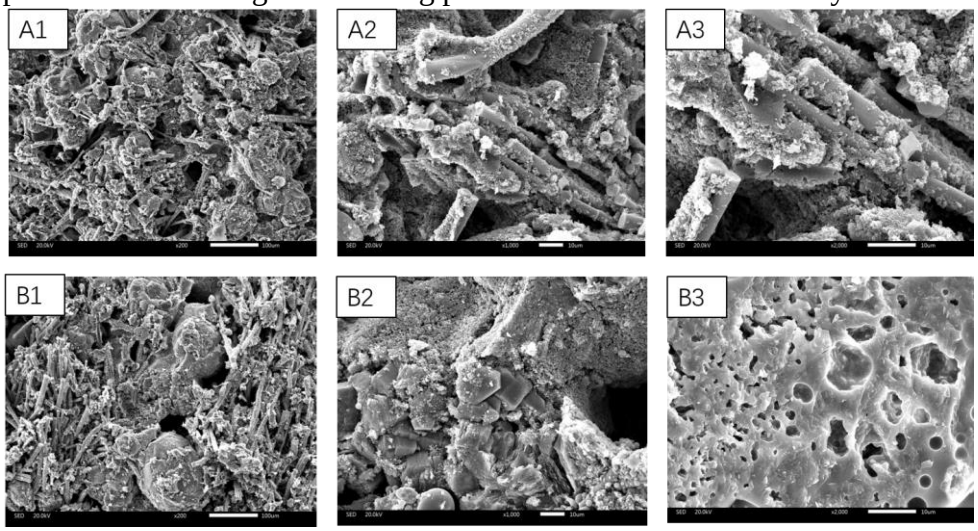

Fig.3 SEM images of the composites before and after sintering at 1400°C

3.3 Analysis of ablation resistance

In order to test the ablation resistance of the prepared ablative composite, the oxygen-acetylene ablation experiments were carried out. And the temperature on the surface of materials was at about 2100C°. The surface morphology of the material after oxygen acetylene flame ablation was shown in Figure 4. We can see that the ablation of the material after oxygen-acetylene flame ablation is very serious when the fiber content is 0wt%, but with the fiber content increases, the material ablation has a gradually improving. The ablation rate of the material under the oxygen-acetylene flame was shown in Table 2. The results show that the line ablation rate is 0.25mm/s when the fiber content is 0wt%, and the fiber ablation rate decreases with the increase of the fiber content. When the fiber content is 30wt%, the line ablation rate is 0.03mm/s, to achieve the best, which indicates that the addition of zirconia fibers makes the corrosion resistance of the material improved.

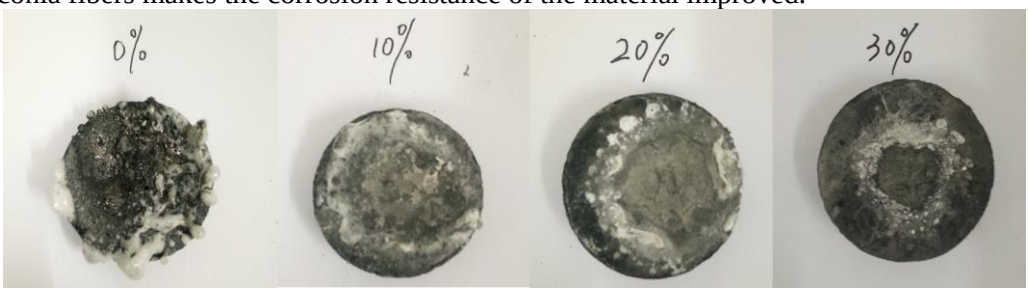

Fig.4 The surface morphology of the material after oxygen acetylene flame

Table 2 The ablation rate of the material under oxygen-acetylene flame ablation

Fiber contents	Linear ablation rate
0wt%	0.25mm/s
10wt%	0.15mm/s
20wt%	0.08mm/s
30wt%	0.03mm/s

3.4 Phase analysis of thermal reaction products

In order to analyze the material phase of the product after sintering at different temperatures qualitatively, the composites after sintering at 1200°C, 1300°C and 1400°C respectively were analyzed by XRD. The XRD spectrum of the material after sintering at 1200℃ was shown in Figure 5. It is found that the main crystal components of the material are zirconium oxide, corundum and silicon carbide. The composition of the material is consistent with that before sintering indicating that the sintering reaction did not occur at 1200°C and the filler was not ceramicized. The XRD spectrum of the material after sintering at 1300℃ was shown in Figure 6. It is found that the main crystal components of the material are zicon, corundum and silicon carbide. The material has a new phase formation, indicating that the conditions of sintering reaction occurred at 1300℃, that is, zirconium oxide reacts with silicon carbide to produce zircon. The XRD spectrum of the material after sintering at 1400℃ was shown in Figure 7. It is found that the main crystal components of the material are zicon, corundum and zirconium oxide. The decrease of silicon carbide content indicates that the degree of ceramicization increased after the temperature increasing, and more silicon carbide was involved in the reaction.

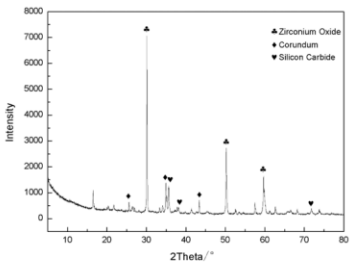

Fig.5 The XRD spectrum of the material after sintering at 1200℃

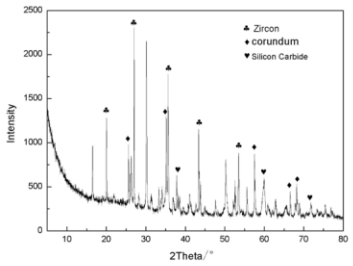

Fig.6 The XRD spectrum of the material after sintering at 1300℃

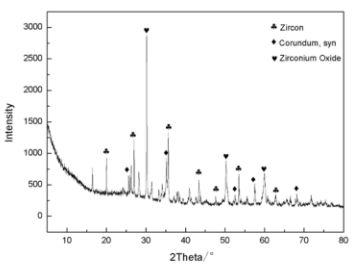

Fig.7 The XRD spectrum of the material after sintering at 1400℃

4 CONCLUSION

(1) With the fiber content increasing, the bending strength of the material increased. When the fiber content is 30wt%, the bending strength of the material is the best, and the bending strength is 19.33MPa.

(2) The ceramic reaction took place in the materials to produce the new phase of zircon after high temperature ablation. Compared with the case of 1200℃ and 1300℃, the ceramic reaction is most well at 1400℃, and the material bending strength is the highest, which can reach 12.03MPa;

(3) Scanning electron microscopy shows that zirconia fiber was well wetted, and after 1400 ℃ sintering, porcelain reaction took place in the materials, and the ceramic crystal was formed. However, since the liquid phase formed after sintering did not fill the whole system, there are holes in the material, resulting in a decrease in the bending strength.

(4) The corrosion resistance of the material after the addition of zirconia fiber is improved, and the oxygen-acetylene line ablation rate is 0.03 mm/s when the fiber content is 30wt%.

In summary, the zirconia fiber reinforced boron phenolic resin for ceramic and high temperature composites have good resistance to high temperature ablation performance, and it also have its excellent mechanical properties, even after high temperature ablation. Moreover, the material preparation process is simple. So, it has good industrial application prospects.

ACKNOWLEDGEMENTS

The authors would like to thank Wuhan University of Technology for supporting this work by the project contract (No. 6141A02022208). Financial support from the Joint Fund Management Office of the Ministry of Education, China, is gratefully acknowledged.

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