Effect of Inorganic Components on Properties of Ceramizable Phenolic Resin Matrix Composites

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Abstract. In order to meet the thermal protection needs of aerospace, a composite material with low cost and good thermal protection effect was prepared. Boron phenolic resin is used as the matrix, and high silica glass fiber cloth is used as the reinforcing filler. The aluminosilicate mineral powder such as glass frit, feldspar powder, kaolin, talcum powder is a ceramic filler, and ceramic phenolic resin matrix composites were prepared by moulding method. The effects of different mineral powders on the properties of composites were investigated. The results show that with the increase of the amount of inorganic filler, the thermal conductivity of the material increases gradually, the high temperature weight loss rate is first increased and then decreased, and the minimum is reached when the filler content is 30%; The results of XRD analysis show that the inorganic filler in the material undergoes ceramization reaction at 1000°C to form a new material cristobalite, which effectively blocks the penetration of oxygen and heat into the material. The ceramic layer formed at high temperature makes the material flow at high temperature and high speed. The scouring resistance and oxidation ablation performance are improved, and it is expected to become a new type of heat-proof material.

1. Introduction

When spacecraft such as returning satellites, spacecraft and deep space detectors re-enter the atmosphere, the surface can reach temperatures above 1000°C under aerodynamic heating [1], therefore, the spacecraft must use a thermal protection system to ensure the internal instruments work properly. The thermal protection method can be divided into endothermic method, radiation method and ablation method according to its protection mechanism [2]. Ablative heat protection is one of the most widely used thermal protection systems, the so-called ablation is the consumption of solid surface materials caused by thermochemical and mechanical processes under the action of heat flow when missiles and aircraft re-enter the atmosphere. Ablative heat protection can be adjusted by its own mass exchange and heat exchange. Under certain pressure and enthalpy, the ablation process can reach a quasi-steady state, that is, the thickness of the affected material is nearly constant [3]. As a typical representative of ablative materials, phenolic resin-based composite materials have been widely used in the thermal protection system of deep space detectors such as the Moon and Mars due to their high heat-proof efficiency, reliable operation, and strong ability to adapt to the heat flow environment [4], early AVCOAT-5026 has been used as a representative of this type of ablation material in the ”Apollo” spacecraft [5].

With the rapid development of the aerospace industry, the traditional phenolic resin-based composite materials can no longer meet the requirements of use, and the phenolic resin matrix must be modified. The ceramizable polymer matrix composite is a new type of fireproof and heat insulating material. Professor Cheng Yibing of Monash University in Australia invented a ceramizable polymer-based composite material. The fireproof material was prepared by adding mica powder, feldspar powder and inorganic clay to silicone rubber and silicon-based resin and successfully applied...
to fireproof cables [6], and commercialized production in Australia. Based on the silicon-based ceramics technology, the special functional materials laboratory of Wuhan University of Technology has taken the lead in the domestic research on the ceramization theory of carbon-based polymers. Polymer matrix composites modified by ceramic powders can be ceramized at high temperature to form ceramic phase [7], which improves the ablation resistance and mechanical properties of the materials. The ceramization of carbon-based resin provides a simple and effective way to modify the phenolic resin. The process is simple, the raw materials are cheap and easy to obtain, and the modification effect is obvious. In this paper, low-cost aluminosilicate mineral powders such as feldspar powder, kaolin and talcum powder were used as ceramic fillers to modify phenolic resin, and ceramsite phenolic resin composites were prepared. The effects of different filler contents on the properties of the materials were studied.

2. Experimental

2.1. Preparation

Dissolving boron phenolic resin and absolute ethanol in a mass ratio of 1:1 to prepare a solution; Weigh a certain amount of ultra-fine kaolin, glass frit, feldspar powder and talc powder into the phenolic resin solution and mix them evenly into a dipping solution. The dipping solution was evenly scraped onto the high silica fiberglass cloth of a certain quality to make a prepreg cloth. After drying, the prepreg cloth was cut and stacked. The prepreg cloth was put into a mold with a demoulding cloth and placed on a hot press at 120°C for 2Mpa for 1h. Then the preg-curing pressure was 5Mpa for 1h, 180°C for 2h, and 200°C for 1h, and then ceramic phenolic resin composites were obtained.

2.2. Performance Testing

Thermogravimetric analysis: Synchronous thermal analyzer model STA449c/3/G produced by NETZSCH, Germany. Test conditions: in a nitrogen atmosphere, the airflow rate is 15 ml/min, the heating rate is 10°C/min, and the temperature range is RT-1200. X-ray diffraction analysis: Bruker's D8ADVANCE X-ray diffractometer, Cu-Kα as the target source, working voltage 40KV, working current 40mA, sweeping angle range: 5~80°, scanning speed: 1°/min. Thermal conductivity test: According to the national standard GB/T 10297-1998, QTM-500 thermal conductivity tester manufactured by Kyoto Electronics Industry Co.Ltd., sample size: (100±1) mm×(100±1) mm×10mm, test temperature is room temperature, heating current: I²=0.625. Model ULTRAPLUS-43-13 field emission scanning electron microscope produced by German Zeiss optical instrument.

3. Results and Discussion

3.1. Effect of Filler on Thermal Conductivity of Materials

Fig. 1 shows the relationship between the thermal conductivity of the material and the change of inorganic filler. It can be seen from the diagram that the thermal conductivity of the material increases with the increase of filler addition. Firstly, because the inorganic filler with high thermal conductivity phase replaces the position of the original resin, the local thermal conductivity of the matrix is higher than that of the surrounding points. As the content of inorganic filler continues to increase, these local high thermal conductivity points will form a thermal conductivity path [8], leading to the increase of the overall thermal conductivity of the material with the increase of the inorganic filler. Gradually increasing. Secondly, the addition of inorganic fillers reduces the porosity of the material to a certain extent, and improves the density of the material. Therefore, the reduction of porosity is also an important factor in the increase of thermal conductivity of the material.
Figure 1. Effect of inorganic filler on thermal conductivity of materials

3.2. Thermal Stability Analysis of Ceramizable Phenolic Resin Matrix Composites

Figure 2 shows the TG (a) and DTG (b) curves of ceramizable phenolic resin matrix composites. It can be seen from Figure 2(a) that the initial decomposition temperature of the ceramsite based phenolic resin composite after the addition of the filler does not change much, and the thermal stability increases at 300-800°C, the residual carbon ratio of the ceramizable phenolic resin composite at 1200°C increased significantly from 76.47% to 83.74%. According to the DTG curve in Figure 2(b), the thermogravimetric curves of ceramizable phenolic resin matrix composites with different content of fillers are divided into room temperature to 300°C, 300 to 800°C, 800°C to 1200°C three stages by 300°C and 800°C. From room temperature to 300°C, the weight loss rate is small at this stage, mainly due to the evaporation of water and the further reaction of unreacted small molecules; in the stage of 300-800°C, the quality has changed significantly. This is mainly due to the obvious pyrolysis of the phenolic resin. With the molecular chain breaking and rearrangement of the phenolic resin, various small molecular gases such as CO, H2O and CH4 are produced [9]. It can be seen from Fig. 2(b) that the phenolic resin composite material after adding the filler has little change before the addition of the filler, indicating that the filler does not participate in or affect the curing reaction of the phenolic resin, and does not substantially increase the cracking peak temperature of the material. At 800-1200 °C, the mass loss rate is significantly reduced. The thermal weight loss at this stage is mainly due to the further cyclization of the benzene ring, which is caused by the cleavage into a structurally complete glassy hydrocarbon atom combined into hydrogen evolution [10].

Figure 2. TG (a) and DTG (b) curves of ceramizable phenolic resin matrix composites
3.3. Analysis of the Microstructure of the Material Section

Figure 3 shows the cross-sectional morphology of a 20% filler phenolic resin matrix composite after treatment at different temperatures. When the heat treatment temperature is 600°C, the composite fibers are debonded with the matrix, some of the fibers are broken, and there are holes left by fiber pulling out and grooves left by fiber shedding. When the heat treatment temperature is 800°C, part of the filler melts at high temperature, filling part of the voids and voids makes the porosity of the material slightly lower. However, due to the high viscosity of the melted liquid at 800°C and the difficulty of flowing, more voids can be observed in the cross section of the material. When the heat treatment temperature is 1000°C, a large number of liquid phases can be observed in the filler melting. The liquid phase flow fills the voids and voids in the material continuously. The melted liquid phase even coats the fiber and matrix, which further reduces the porosity of the material and makes the internal structure of the material more compact.

![Figure 3. Sectional morphology of 20% filler phenolic resin matrix composite after different temperature treatment](image)

3.4. Phase analysis of Ceramizable Phenolic Resin Matrix Composites

Figure 4 is an XRD pattern of a ceramizable phenolic resin based composite at various temperatures. It can be seen from the figure that the XRD diffraction peaks of the materials after treatment at 600°C and 800°C are substantially coincident, and there is no significant change, indicating that the cracking products are substantially the same, and no reaction occurs between the inorganic fillers. The characteristic peaks of Na (AlSi₃O₈) were weakened and the diffraction peaks of high-temperature cristobalite appeared when the heat treatment temperature was 1000°C, which indicated that ceramization reaction took place between fillers, Na (AlSi₃O₈) was consumed and a new high-temperature cristobalite was formed.

![Figure 4. XRD pattern of ceramizable phenolic resin matrix composites at different temperatures](image)
4. Conclusion

With the increase of inorganic fillers, the thermal stability of the material was gradually improved at 1200°C, and the thermal weight loss decreased from 23.53% to 16.26%.

With the increase of heat treatment temperature, inorganic filler melts gradually to produce a large number of liquid phase, filling up the pores produced by pyrolysis, reducing the porosity of the material; at the same time, there is an obvious ceramization reaction between fillers, Na(AlSi3O8) phase is gradually depleted, reaction to produce a new material high temperature cristobalite.

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