Proceedings of the 4th International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/58/20240719

Review on preparation technology of carbon-based ultra-high temperature resistance ceramic fibers

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Abstract. The rapid development of hyper-sonic vehicles has put forward an urgent demand for ultra-high temperature resistance ceramic fibers ceramic matrix composites. The properties of ultrahigh-temperature ceramic matrix composites made of carbon-based ultra-high temperature resistance ceramic fibers are excellent. Therefore, the preparation processes of several commonly used carbide-resistant ultrahigh-temperature ceramic fibers are described in detail. This review compares the advantages and disadvantages of five common methods (Molten-salt synthesis method, Chemical Vapor Reaction Method, Chemical Vapor Deposited method, Sol-Gel Method & Polymer-Derived method) for preparing ceramic fibers, summarizes the preparation methods that should be used in the face of different preparation requirements, and evaluates the improvement and prospect of each method. Among them, the polymer-derived method, as the most difficult and effective preparation method, has been given great hope by material scientists.

Keywords: Carbon Fiber, Ultra-High Temperature Resistance Ceramic Fiber, Preparation.

1. Introduction

The hot end parts in the field of machinery manufacturing and aerospace are faced with the challenges of high temperature, ablation and complex working environment. The ultra-high temperature resistance ceramic fiber has been widely used in the preparation of ultra-high temperature resistance ceramic matrix composite materials due to its advantages of high strength, good toughness, excellent high temperature resistance and close thermal expansion coefficient with the ceramic matrix [1].

Ultrahigh temperature ceramics are often made of metal carbides, nitrides or borides such as Hf, Ta, Zr and Ti, these compounds have excellent properties such as a high melting point, high strength, high modulus and oxidation resistance [2, 3].

Carbon fiber has high specific strength, high specific modulus, and good chemical stability at high temperatures in vacuum, but it will be oxidized when it reaches 360 °C in oxygen. SiC, HfC, TaC and other carbides are more difficult to be oxidized at high temperatures, and are commonly used as ultra-high temperature ceramic fibers. At present, the commonly used preparation methods of carbide ultra-high temperature ceramic fiber include Molten-salt synthesis method (MSS), Chemical Vapor Reaction (CVR), Chemical Vapor Deposited method (CVD), Sol-Gel method and Polymer-Derived method(PD). In this paper, the different preparation processes of carbide resistance to ultra-high temperature ceramic fibers are reviewed. By comparing the advantages and disadvantages of different

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preparation methods, it is beneficial to prepare low-priced and excellent-performing high-temperature resistant ceramic fiber.

2. Molten-salt synthesis method

The MSS method refers to the use of chloride, sulfate, and other salts with low melting points that do not chemically react with reactants as reaction media. When the temperature of the system is higher than the melting point of the mixed salt, the liquefied molten salt will become the site of reaction. The reaction product is obtained by using water to dissolve the salt at the end of the reaction, and is often used as a synthetic powder, block and coated fiber.

V.S. Dolmatov and S.A. Kuznetsov use NaCl-KCL-K_2MeF_7 as a molten salt system to react metal and molten salt at 1073-1023K for 6 to 24 hours, and finally produce uniform thickness, non-adhesive niobium carbide and tantalum carbide coating on the surface of carbon fiber [4]. When Loic Constantin and his team used the molten salt method to prepare Cr_3C_2 and TiC composite ceramic coatings, they found that the order in which different metals react with carbon fibers depends on their solubility, reactivity, and diffusion properties in the molten salt. In the experiment, carbon fiber reacts with Cr to form Cr_3C_2, and Ti not only reacts with carbon fiber to form TiC, but also reacts with Cr to form Ti-Cr coating, which blocks the generation of Cr_3C_2 after a period of time. When all Ti reacted to form TiC, Cr continued to react with carbon fiber to form Cr_3C_2, and finally formed a multi-layer ultra-high temperature ceramic coating on the surface of carbon fiber. The results show that the multilayer coating produced by this method has better resistance to high temperature and ablation [5]. In summary, the preparation time of molten salt synthesis is short, the production method is simple, the reaction temperature is low, and multiple layers of coating with different structures can be prepared, which is convenient to improve the performance of carbon fiber according to the demand.

3. Chemical Vapor Reaction Method

Chemical Vapor Reaction (CVR) is a method that takes the matrix fiber as the starting core material and reacts between gas and solid at high temperature to transform the matrix fiber into the target ceramic fiber. This method was first applied to the preparation of BN and SiC fibers. Wang et al. first obtained B_2O_3 fiber by melt spinning, and then partially nitrided the B_2O_3 fiber by heat treatment at 1000°C under NH_3 gas [6]. Finally, the fiber was completely nitrided by heat treatment at 2000°C under N_2 gas to obtain BN fiber with a diameter of about 5μm. Its tensile strength and elastic modulus are 1.2GPa and 85GPa, respectively. Ryu et al. took PAN-based carbon fiber as the template and Si powder and SiO_2 powder as the silicon source [7]. SiO gas was generated by the reaction of Si and SiO_2 at high temperature, and then SiO gas diffused to the surface of C fiber and reacted with C fiber to transform into SiC fiber. This SiC fiber maintained almost the same shape as the original C fiber, but there were pores on the fiber surface. It can be used as a catalyst carrier material.

In general, although the ceramic fiber obtained by the CVR method is continuous, the conversion process is too long. In order to speed up the conversion rate, the matrix often uses porous fiber, which makes the strength and modulus of the ceramic fiber product low and cannot meet the requirements of use.

4. Chemical Vapor Deposited method

CVD is a method to prepare ultra-high temperature resistant ceramic fibers by controlling the nucleation and growth of small molecular compounds on the surface of the fibers by gasification of small molecular compounds as reaction materials. This method can better retain the mechanical properties of the original fiber because the original fiber does not participate in the chemical reaction.

Chen and his team prepared a TaC coating on the surface of carbon fibers by chemical vapor deposition, which is uniform and dense with an intact crystal structure. The authors pointed out that the layer has excellent thermal stability and corrosion resistance, and can be widely used in high temperature and easy corrosion environment [8]. Monteleone's team prepared the TiC mesophase coating in carbon fibers by chemical vapor deposition. The coating is a pure TiC phase that binds very tightly to the carbon fiber matrix. Although this method has good fiber properties, it has high requirements for reaction conditions and is easy to have defects in the preparation process, so it is difficult to large-scale production [9].

5. Sol-Gel Method

Sol-Gel method is to hydrolyze and condense insoluble metal compounds to obtain a three-dimensional network structure of oxide colloids, and then to prepare gel fibers, gel fibers after drying and pyrolysis to obtain the required ceramic fibers. The method has strong designability, good chemical uniformity and high stability, and is beneficial to the formability of fibers.

Hasegawa prepared ZrC and Si-Zr-C fiber materials by this method. The results show that the chemical formation and structure of the product can be controlled by changing the proportion of the polymer. The appropriate proportion can prepare the fiber with uniform and fine coating, so that the preparation of ceramic fiber is flexible and controllable [10]. In another paper, tantalum powder, hafnium powder and carbon source were centrifugally mixed and a fibrous structure with uniform thickness and excellent properties was obtained at high temperature. The fiber obtained by this method has excellent high temperature resistance [11].

In general, the sol-gel method has a low cost and relatively simple process, but the ultra-high temperature ceramic fiber prepared by it has large porosity and poor mechanical properties. It is not suitable for preparing ultra-high temperature ceramic fiber but can be used to prepare fiber surface modified oxide coating.

6. Polymer-Derived method

The organo-derived (PD) method was pioneered by Yajima in Japan in the 1970s. In this method, the polymer precursor is first constructed, then spun and molded, and high strength continuous ceramic fiber is obtained by firing at high temperature. The HfC and TaC ultra-high temperature ceramic fibers synthesized by Matech Global Strategic Materials Company in the United States have excellent high temperature resistance, which is a typical representative of the method [12, 13]. Similar to the preparation of SiC fiber by PD method, it is first through the synthesis of thermal curable or photocurable liquid ultra-high temperature ceramic precursor, and then the liquid precursor through spinning, non-melting and high temperature heat treatment, you can get continuous HfC, TaC ultra-high temperature ceramic fiber, but the relevant technical details are not reported. A new type of oxygen-free poly-zirconium carbosilane (PZCS) was synthesized by sodium shrinkage method using zirconium dichloride and dichlorodimethylsilane as Zr and Si sources. Then the PZCS were fused spinning, crosslinking and sintering at high temperature to obtain the ZrC-SiC multiphase ceramic fiber with a diameter of about 15μm. In addition, the precursor of PZBCS was obtained by mixing PZCS with PBN (polycyclic borazane), and the ZrC-ZrB_2-SiC multiphase ceramic fiber was prepared accordingly. Compared with ZrC-SiC multiphase ceramic fiber, ZrC-ZrB_2-SiC multiphase ceramic fiber has better antioxidant properties [14].

The PD method can realize the controllable design of ultra-high temperature ceramic fiber composition and the preparation of continuous long fiber, but the synthesis of organic precursor is very important in the process of preparing ultra-high temperature ceramic fiber by PD method, and the non-melting treatment method, high temperature firing and other factors have an important influence on the subsequent fiber composition structure. As one of the most possible methods to prepare ultra-high temperature ceramic fibers with excellent properties, the technical realization of this method is very difficult and needs further breakthrough.

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Table 1 Comparison of preparation methods of several ultra-high temperature ceramic fibers.

Method	Temperature	Complexity	Time-consuming	Cost	Property
CVR	high	Relatively complicated	Long time	Relatively high	Relatively bad
CVD	relatively high	complexity	relatively long	high	Excellent
Sol-Gel	high	complexity	Long time	High	Ordinary
PD	high	complexity	Long time	Relatively low	Better quality
MSS	Low	easy	Short time	low	better quality

The advantages and disadvantages of different methods for preparing ceramic fibers are shown in Table 1.

7. Conclusion

The MSS method excels in producing cored structural ultra-high temperature ceramic fiber with a straightforward process, low reaction temperature, and enhanced fiber strength, yet controllable preparation of ceramic coating on carbon fiber surfaces is still challenging. In contrast, while the CVR product fiber is continuous due to material choice, its mechanical properties are subpar. The CVD method yields fibers with commendable mechanical properties and high-temperature resistance, but its intricate process and stringent condition control make large-scale production problematic. The Sol-Gel method, being cost-effective and uncomplicated, unfortunately results in fibers with high porosity, compromising their mechanical strength. On the other hand, the PD method stands out for its controllable preparation of linked long fibers; despite its high process complexity, the end product showcases superior performance, marking it as a pivotal focus in current scientific research.

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