Research and Development of UHT Ceramic Composites

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Abstract: Due to many excellent properties of UHT ceramics, such as high melting point, high hardness, high thermal conductivity, it has been more and more widely studied and used. Based on this, this paper analyses and discusses the research of ultra-high temperature ceramic composite with excellent properties. In this paper, the research progress of the preparation of UHT ceramic composites is introduced firstly, then the properties of UHT ceramic composites are analyzed, finally the future research of UHT ceramic composites is prospected.

1. Introduction

At present, the research on transition metal UHT ceramic composites is relatively mature, such as boride and nitride. Due to its wide application in structure, electron, wear-resistant and catalytic materials, carbide ceramic high-temperature structural materials have become one of the research hotspots and development trends in ultra-high temperature environment. Because of the low toughness and the lack of oxidation property of ceramic composite materials, it needs matrix ceramic materials, or adding reinforcement phase, which can not only enhance its anti-oxidation ability but also improve its thermal shock performance.

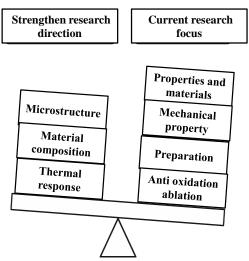


Figure 1. Current research status of UHT ceramic composites

At present, the research on UHT ceramic composite mainly focuses on the following aspects shown on the left side of Figure 1, while the research on the relationship between the thermal response, material composition, microstructure and the properties of UHT ceramic composite is still insufficient. Therefore, it is of great practical significance to strengthen the research on the content shown on the right side of the picture for improving the comprehensive performance of environmental adaptation of the material.

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2. Preparation of UHT ceramic composite

The densified UHT ceramic composite mainly has several sintering methods as shown in Figure 2. Among the several sintering methods shown in the figure, HP is the most commonly used sintering method at present. The advantages and disadvantages of HP, SPS, RHP and PS are shown in Table 1 below. In this chapter, these sintering methods will be analyzed in detail.

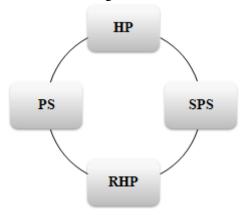


Figure 2. Densification of UHT ceramic composite

Table 1. Advantages and disadvantages of different preparation methods of UHT ceramic materials

	HP	SPS	RHP	PS
Advantage	Good uniformity	Short time Grain size	Low sintering temperature and raw material cost	Low cost, near net shape
Disadvantage	Long time. High cost	Expensive sintering equipment	Component content cannot be adjusted arbitrarily	High sintering temperature and remarkable grain growth

2.1 Hot pressing sintering

The increase and coarsening of ultra-high temperature ceramic grains will lead to the decrease of sintering driving force and looseness, which is generally caused by impurities on the surface of the original powder, especially oxide impurities. Because the high oxygen content will lead to the evolution of fine pores in the ultra-high temperature ceramic composite, in order to densify the ultra-high temperature ceramic composite, the first step is to reduce the oxide impurities to reduce the low oxygen content. The reduction of oxide impurities is usually achieved by introducing carbon or nitride, but the amount of both should be strictly controlled according to the amount of oxide in the material, otherwise it will backfire. For example, excessive addition of carbides will lead to excessive carbon content, which will not only reduce the mechanical properties of UHT ceramic composite, but also reduce the strength of the material.

In addition, unlike the introduction of carbon or nitride to improve the HP performance of UHT ceramic composites, the hot sintering (HP) performance can also be improved by promoting the rearrangement and mass transfer of particles. This is mainly achieved by adding metals. Similarly, the amount of metal additives also needs to be strictly controlled; otherwise, the mechanical properties of UHT ceramic composites will also be reduced.

2.2 Spark plasma sintering

The introduction of electric field can also promote the densification of UHT ceramic composites, which is because the diffusion, transfer and growth of material grain boundaries can be achieved by the introduction of electric field. Because of the advantages of SPS, it is more and more used in the manufacture of high temperature ceramic composites. On the one hand, because temperature can affect the process of grain growth (promote grain growth), so as to promote the densification of materials; on the other hand, SPS method can rapidly heat up, so as to reduce the sintering time. In addition, SPS can lead to the self-discharge of the material particles, thus eliminating the defects on the particle surface, reducing the impurities on the particle surface, and controlling the structure of the material. It can be seen that the above factors can finally densify the high temperature ceramic composite. The main disadvantage of SPS is that the equipment is relatively expensive and the initial investment is high.

2.3 Reactive hot press sintering

Another way to densify UHT ceramic composites is through in-situ reaction. Among them, the original reaction can be carried out under pressure or without pressure, so as to prepare dense ultrahigh temperature ceramic composite materials. Generally speaking, it can be prepared by in-situ reaction of zirconium, boron carbide and silicon, and the content of each component in UHT ceramic composite can be adjusted by changing the proportion of raw materials. Zirconium hydride or zirconia can be used instead of zirconium and silicon carbide. In the preparation of zirconium borate based ultra-high temperature ceramic composites, boron, boron oxide and carbon can be used instead of boron carbide.

In addition, the composites with higher purity can also be synthesized by SHS, because the Gibbs free energy of in-situ reaction is generally lower. However, in the preparation process, attention should be paid to control the reaction process and heating rhythm to prevent overheating reaction.

2.4 Pressure-less sintering

Compared with the hot pressing sintering (HP), the pressureless sintering (PS) has a significant advantage, that is, it can make mechanical components only after a small amount of processing. The material manufacturing cost of PS technology is relatively low, and its application in the preparation of ultra-high temperature ceramic composite mainly includes several sintering methods as shown in figure 3.

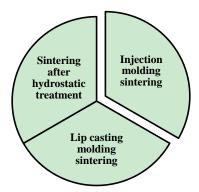


Figure 3. The preparation methods of ultra-high temperature ceramic composite

In addition, in order to ensure the compactness of the materials, the working temperature of pressureless sintering is higher, or sintering aids are used to reduce the negative effect of pressureless working conditions on the compactness.

3. Properties of UHT ceramic composites

3.1 Mechanical properties of UHT ceramic composites

Because the material composition, powder purity and particle size have a direct impact on the mechanical properties of ultra-high temperature ceramic composite, the impurities with low melting point will reduce its high temperature performance, so it is necessary to eliminate the material. In addition, the characteristics of grain boundary will directly affect its high-temperature performance, so it is necessary to use high-purity powder raw materials to ensure its high-temperature performance. Because SPS method can ensure the high purity of particle surface, the high temperature properties of UHT ceramic composite prepared by SPS method are better, that is, its strength and mechanical properties are not different from those at low temperature.

3.2 Anti oxidation / ablation properties and thermal response of UHT ceramic composites

The relationship between the ablation resistance and temperature of UHT ceramics is very large, so the introduction of silicide can greatly improve the ablation resistance of zirconium borate and hafnium borate. As the silicon dioxide produced by the oxidation of silicon carbide can make up the structural gap of ZrO2, its introduction will greatly improve the oxidation resistance of the material. In addition, after adding silicon carbide, the oxidized product can produce a dense protective film, which can isolate oxygen and prevent the material from further sampling.

The oxidized SiO₂ can cover the surface of the material and/or fill the pores of ZrO₂, which can form the skeleton structure and play a good role in anti-oxidation protection. The oxidation reaction of SiC is shown in Figure 2.

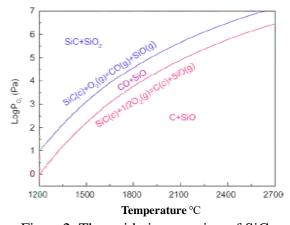


Figure 2. The oxidation reaction of SiC

4. Research prospect of UHT ceramic composites

4.1 Improvement and development of preparation technology

There are many methods to prepare ceramic matrix composites, but carbide ceramics have higher melting point than boride ceramics, so the preparation technology and equipment are required. In addition to the continuous improvement of the preparation process of ceramic composite materials, the development of new preparation methods and processes is one of the main ways to obtain high-

performance composite materials. As mentioned before, the addition of carbides can significantly improve the comprehensive properties of UHT ceramic composites, so it is widely used in the preparation of ceramic matrix composites. However, its high melting point puts forward more restrictions on the preparation equipment of the material, which makes the preparation process more complex and costs more. Therefore, it is necessary to continuously optimize and innovate the preparation process and methods of UHT ceramic composite materials. The above limitations also guide the development direction of the preparation process in the future: reducing the process cost and simplifying the process flow.

4.2 Types and selection of reinforcement materials

According to the characteristics of the material, the selection of appropriate reinforcement material is the key factor to improve the performance. When choosing reinforcement materials, we should try to match the elastic modulus and thermal expansion coefficient with the matrix materials, so as to maximize the potential and role of reinforcement materials. According to the requirements of performance in practical application, different types of reinforcement materials are selected. Because the high temperature properties of ceramic matrix composites will be directly affected by additives, the proportion and type of materials are important factors to further improve their high temperature properties. In addition, the components of the added materials should be strictly matched with the ceramic matrix composite materials to maximize the guarantee of the performance improvement after adding, without any new negative impact. Based on this, the focus of future work is to study which materials are introduced to further improve the properties of UHT ceramic composites.

4.3 Improvement of high temperature properties of materials

At the same time of solving the brittleness problem of ceramics, the future research also focuses on the high-temperature properties, such as high-temperature mechanical properties, thermal shock resistance, anti-oxidation and ablation properties. With the development of the brittleness of ceramics and the potential performance advantages of ceramic composites, UHT ceramic composites will play a greater role in the development of aerospace industry in the near future. Because of the natural brittleness of ceramics, the application of UHT ceramic composites is limited. Therefore, more attention should be paid to the high temperature properties of UHT ceramic composites in the future. With the continuous improvement of high-temperature properties such as mechanics and impact resistance, ultra-high temperature ceramic composites will be widely used in the future and play an important role in more fields.

Conclusions

Ultra high temperature ceramic composite materials have excellent high temperature comprehensive properties. Through the design and control of microstructure, the damage tolerance and reliability of ultra-high temperature ceramic composite materials are greatly improved, which lays the foundation for the application of ultra-high temperature ceramic materials. With the deepening of research and development and the continuous improvement of production technology, the research, production and application of UHT ceramic matrix composites will be more extensive. Due to the remarkable properties of ultra-high temperature ceramic composite, its application range is more and more extensive. The research on sintering method, oxidation resistance and thermal response of ultra-high temperature ceramic composite is more and more in-depth. With the deepening of the research on the control of its microstructure and the continuous innovation of its

preparation process, the improvement of the high temperature performance and damage tolerance of UHT ceramic composite materials in the future will surely play an important role in more fields.

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