

Research on the Preparation and Properties of ZrC Ceramic Composites

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In this study, we used the preparation of organic zirconium precursors as the start work, and use PIP technology as a matrix modification technology. Selecting ZrC (zirconium carbide) and SiC as the ceramic phase, we prepared C/C-ZrC composite material and C/C-ZrC-SiC composite materia. At the same time, we made a study on the microstructure of ceramic materials before burning. The effect of the impregnation pyrolysis treatment on the composition of the zirconium carbide ceramic composites and the mechanical properties were also studied.

1. Introduction

Concerning the history of human evolution, the material is an important basic substance to measure a country's development level in the science, technology, economy and national defense, and an essential milestone for the progress of the whole society and symbol of civilization (Kenta et al., 2016). (Liu, 2015) It has been an increasingly urgent demand for aerospace and national defense to search for cutting-edge technologies such as ultra-high-temperature ceramic materials that suffer extreme conditions, as the existing refractory metal, graphite materials, carbon/carbon composite materials, and other traditional high-temperature-resistant ceramic materials all fail to meet the above needs. Therefore, the research and development of new high-temperature-resistant ceramic materials has become a pressing task.

Ultra-high-temperature (UHT) resistant ceramics refer to the first-class ceramic materials featuring high melting point, high heat stability, low linear expansion coefficient, high thermal conductivity, high electric conductivity, and high hardness that can be used in the ambient temperature of more than 2000 °C. The most widely studied UHT-resistant ceramics are mainly carbide ceramics and boride ceramics (Hu et al. 2015).

Carbide ceramics generally refer to refractory metal carbides, and ZrC is considered to be very promising UHT materials. It has sound stability, hardness, and strength at high temperature stability, as well as corrosion resistance, making itself an ideal material in high temperature (Li et al., 2015). At present, there are two ways to introduce high-temperature ceramics into carbon/carbon composite materials. One is the matrix modification technology, which is to introduce high-temperature ceramics into the matrix of carbon/carbon composites. The other is the surface coating technology, which is to prepare a high-temperature ceramic layer on the surface of carbon/carbon composites to protect the materials.

Therefore, it is necessary to conduct the modification research on the ZrC ceramic materials (Li et al., 2015). ZrC is a typical face-centered cubic crystalline (see Fig. 1 for the crystalline structure), whose crystalline properties make it a promising material in many applications, such as cutting tools, wear-resistant parts, mechanical industrial furnaces, etc. In particular, due to the low-neutron absorption section and sound radiation resistance, it is used as the core material in nuclear reactor (Zhang, 2011). The basic properties of ZrC are shown in Table 1.

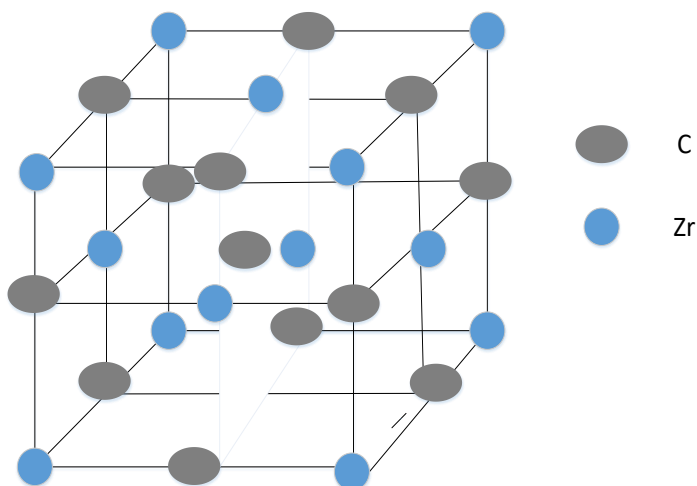


Figure 1: Crystal structure of ZrC

Table 1: The Basic properties of ZrC

Crystal structure	Face three-dimensional
Lattice constant	A=0.4685
Density(g/cm ³)	6.90
Formed Heat	-184.3
Hot Melt(J/mol.K)	45.6
Thermal expansion coefficient (*10 ⁻⁶ K ⁻¹)	6.59
Capture area (m ²)	Na=0.016*10 ⁻²³
Crush strength(Mpa/M)	3.4*10 ⁵

Based on the basic properties of the ZrC, this paper holds that to realize the oxidation and ablation resistance of ZrC ceramic composite under the extreme condition of UHT, matrix modification and surface coating technologies shall be combined as a try to make a breakthrough so as to meet the end application requirements.

Therefore, this study began with the preparation of the precursors of organic zirconium, and applied the PIP technology for the matrix modification for the first time to prepare C/C-ZrC composite materials and C/C-ZrC-SiC composites with ZrC (ZrC) and SiC as the ceramic phases. Then, the pre-ablation micro-structure, mechanical properties, and the effect of infiltration and pyrolysis on ZrC ceramic composites were studied.

2. Experiments

2.1 Experiment Reagents and Equipment

2.1.1 Precursors of Organic Zirconium (POZ)

The POZ was independently synthesized by the laboratory, and can dissolve in organic solvents such as xylene, toluene and ethanol. The ceramic yield was about 25% under pyrolysis at high temperature in inert atmosphere.

2.1.2 Other Experiment Reagents and Equipment

The other major reagents and main instruments used in this research are shown in Table 2.

Table 2: Other major reagents and major equipment

Equipment name	Type	Reagent name	Type
Oven	DZ-1BCII	Xylene	AR
Glass reactor	FZB-150	Ethanol	AR
Magnetic stirrer	XYT-15	Argon	Purity 99.99%

Rotary evaporator	NEC4911	Nitrogen	Purity 99.99%
Vacuum pump	WSP-180	Carbon fiber	7K,12K-PAN

2.2 Preparation Process of ZrC Ceramic Composites

2.2.1 Overall Design Ideas of Materials

C/C-ZrC and C/C-ZrC-SiC composites can be prepared by POZ with the PIP matrix modification technology (Liu, et al, 2015., Simonenko, 2011). And then ZrC composite materials can be made by the two composites with the surface coating technology, as shown in Fig.2.

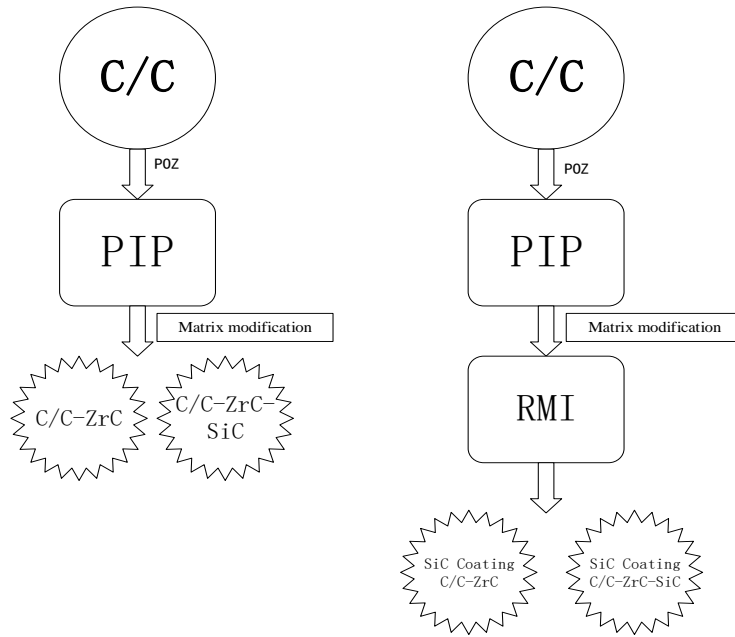


Figure 2: The preparing scheme of the Zirconium carbide ceramic composite materials

2.2.2 ZrC Ceramic Composite Matrix Modification Preparation by Infiltration and Pyrolysis Method

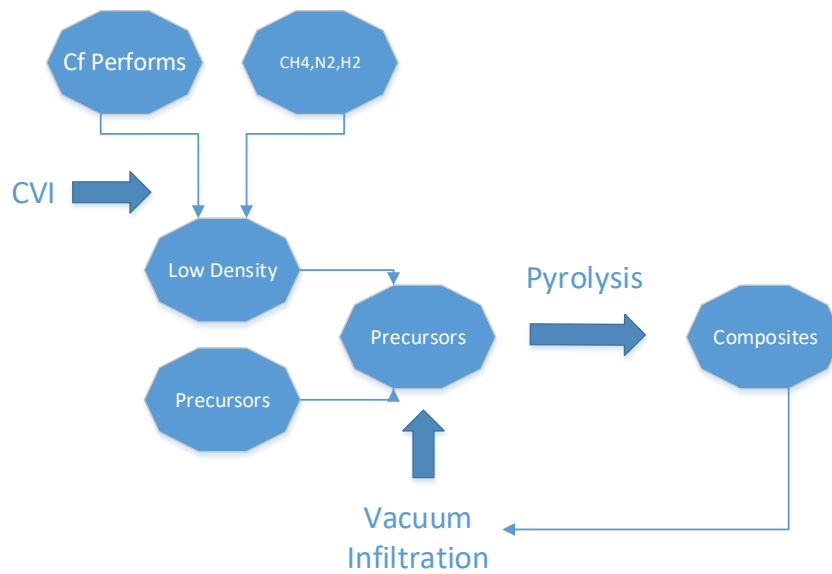


Figure 3: Schedule of the experiment

The PIP process was used to introduce the ceramic phase into a sample of low-density carbon-carbon composite material cut to a certain size. The process is shown in Fig. 3 (Tao et al., 2013).

The specific procedures are as follows. Prepare a certain concentration and ratio of the organic precursor xylene solution as the precursor solution, put the carbon-carbon composite sample with a lower density in the vacuum infiltration pump, vacuumize the pump, and infiltrate the precursor solution into the composite matrix for 60 minutes. The vacuum infiltration device is mainly made of the circulator bath vacuum pump, the atmospheric funnel, and the peeling dryer. After the infiltration, the sample was removed from the infiltration solution and baked for 10 hours in the supply box, with the baking temperature of 70°C. After drying, the sample suffered pyrolysis in a small graphitization furnace under the protection of N₂ gas at the temperature rise rate of about 5°C / min and the pyrolysis temperature of 1600°C, with the holding time of about 1 hour. After the pyrolysis, the sample was cooled to room temperature with the furnace. Then polish the sample surface with the abrasive paper, and repeat infiltration and pyrolysis processes. After several infiltration and pyrolysis, the sample achieved the desired density (Li et al, 2012).

3. Performance of ZrC Ceramic Composites

3.1 Microstructure of ZrC Ceramic Composites

The microstructure of the pre-ablation composite prepared by multiple infiltration and pyrolysis processes is shown in Fig.4. With a large number of tiny particles in different shapes and sizes, the sample's surface has relatively poor density with obvious pores. It can be seen from the enlarged picture that the single particles on the surface have better crystallization performance, and the smaller particles are more compact and complete but with more obvious pores.

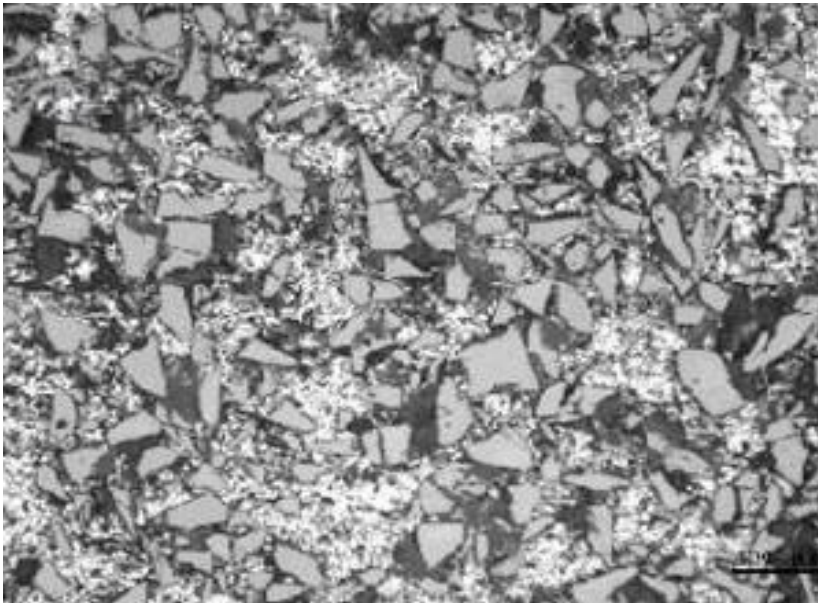


Figure 4: Photograph of the surface of C/C-ZrC composites before ablation test

3.2 Influence of Infiltration and Pyrolysis on the Composition of ZrC Ceramic Composites

Figure 5 shows the density and porosity of ZrC ceramic composites before and after pyrolysis at 1400-2200°C.

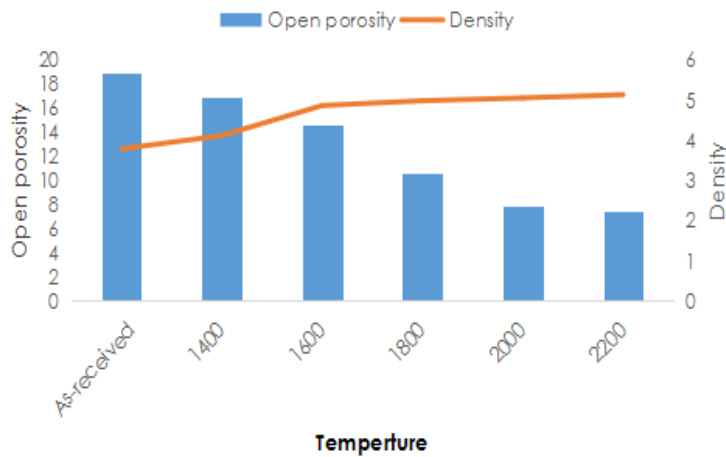


Figure 5: Density and open porosity of C/C-ZrC composites

After pyrolysis treatment, the density of the material increased while the porosity decreased. The higher the pyrolysis temperature was, the greater the density of the material increased and the larger the porosity decreased. After heat treatment at 2200°C, the density of the material increased from 3.87 g/cm³ to 4.98 g/cm³, and the porosity decreased from 19.57% to 8.57%. When the temperature was further increased, the density and porosity of the material remained basically unchanged.

3.3 Influence of Infiltration and Pyrolysis on the Mechanical Properties of ZrC Ceramic Composites

Figure 5 is the curve of the relation between the composite flexural strength retention rate and pyrolysis temperature (1400-2200°C) of C/C-ZrC composite materials. It can be seen that as the pyrolysis temperature increases, the flexural strength retention rate of the material gradually decreases. When the heat treatment temperature was 1400°C, the flexural strength retention rate of the material was 94%. When the temperature was raised to 1600°C, the flexural strength retention rate of the material dropped to 75%. When the temperature reached 2200°C, the retention rate was only 45%.

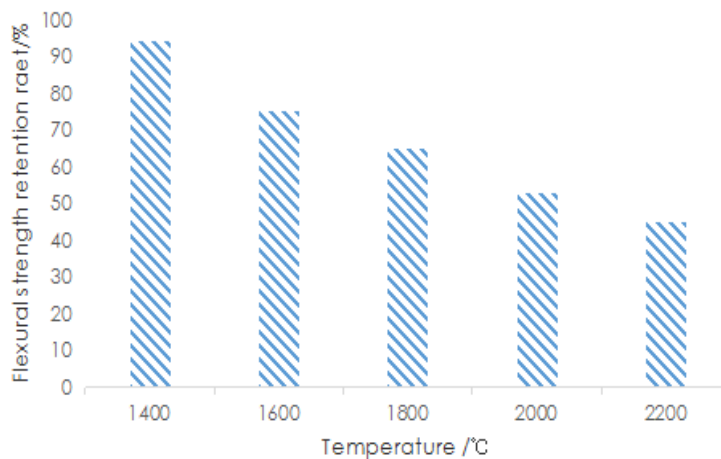


Figure 6: Flexural strength retention rate of C/C-ZrC composites after dealing with immersion pyrolysis

The reason for the strength changing characteristics of ZrC ceramic composites shown in Fig. 5 is mainly related to the influence of the temperature of the infiltration treatment on the composition and structure of the material. The high-temperature infiltration treatment leads to the increase in the porosity of the material, the destruction of the ZrC matrix structure, and the damage of the carbon fiber. At 1400°C, the material composition, structure and fiber properties changed little, so the material could maintain a high strength. After 1600°C heat treatment, a large amount of melt loss between the ZrC grains led to a significant increase in the material porosity and weakened load transfer capacity of the matrix. Also, the fiber was eroded by the melt, so the flexural strength retention rate decreased to 75%. When the heat treatment temperature reached 2200°C,

the porosity of ZrC ceramic composites increased, and the damages to the matrix structure and the carbon fiber were more serious, leading to more significant decline in the flexural strength with the flexural strength retention rate of only 45%.

4. Conclusion

In this study, we used the preparation of organic zirconium precursors as the start work, and use PIP technology as a matrix modification technology. Selecting ZrC (zirconium carbide) and SiC as the ceramic phase, we prepared C/C-ZrC composite material and C/C-ZrC-SiC composite materia. At the same time, we made a study on the microstructure of ceramic materials before burning, the effect of the impregnation pyrolysis treatment on the composition of the zirconium carbide ceramic composites and the mechanical properties were also studied.

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