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Influence of additives on oxidation resistance of binderless C/C composite①

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Abstract: Experiment of adding B_4C, SiC, and Si powders to improve oxidation resistance of the C/C composites was carried out. The results show that the increase of oxidation resistance is remarkable when the contents of B_4C, SiC, and Si powders are 10%, 10%, and 5% in the composites, respectively. The regularities and mechanism of the effects of the ceramic powders on the oxidation resistance of the composites were also discussed.

Key words: oxidation resistance; binderless; C/C composite
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1 INTRODUCTION

Carbon fibre reinforced carbon matrix composites are advanced materials of high performance, which seem to be excellent structural and functional materials in many fields[1-4]. But their oxidation resistance is poor, and this problem has not been solved so far. Surface coating may fill up the cracks produced by thermal stress, but it will lose the function of oxidation resistance when its surface is destroyed. Self-healing was put forward to overcome the above shortcoming[5-7], and was investigated extensively[8-11]. But there is no report on the self-healing oxidation resistance of binderless carbon fibre reinforced carbon matrix composites. The effects of self-healing on the burn loss of this new kind of composite and anti-oxidation mechanism are investigated in this paper.

2 EXPERIMENTAL

2.1 Preparation of samples

The raw petroleum cokes produced in Jinmen were adopted as the matrix carbon, and carbon fibres were formed by in-situ carbonization of poly-acrylonitrile in the samples. The additives were fine powders of B_4C, SiC and Si. By changing the additives' content, their effects on the oxidation resistance of the samples were studied. The technological route for the sample preparation is shown in Fig. 1. Table 1 is an orthogonal test list for formula design. According to Ref. [11], the contents of additives were selected as three levels of 0%, 5%, and 10%. The mixture of matrix cokes and additives was ground in organic medium. The particle sizes including additives were smaller than 5 μm, the specific surface

Table 1 Orthogonal test design and experimental results

Level	Factor			Mass loss/%	Extreme difference, R
	$w(B_4C)$/%	$w(SiC)$/%	$w(Si)$/%		
1	0	0	0	0.321 4	0.226 0
2	0	5	5	0.172 4	0.077 0
3	0	10	10	0.145 2	0.049 8
4	5	0	5	0.164 8	0.069 4
5	5	5	10	0.151 2	0.055 8
6	5	10	0	0.118 7	0.023 3
7	10	0	10	0.145 1	0.049 7
8	10	5	0	0.139 2	0.043 8
9	10	10	5	0.095 4	0
I	0.352 8	0.345 1	0.293 1		
II	0.148 5	0.176 6	0.146 4	T = 0.594 8	
III	0.094 5	0.073 1	0.155 3		
Extreme difference (better level)	0.086 4 (10%)	0.090 6 (10%)	0.048 9 (5%)		

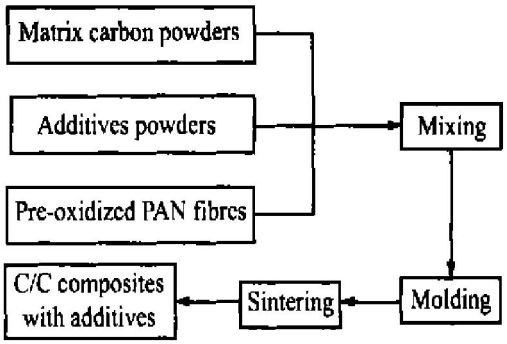

Fig. 1 Technological route of sample preparation

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area was 84 561 cm^2/g, and the length of fibres underwent surface treatment was 3 – 5 mm. The max molding pressure was 250 MPa. Sintering was conducted at 2 000 ℃ in atmosphere of Ar with a pressure of 9 MPa.

2.2 Tests

The samples are oxidized in a high temperature oven at 1 100 ℃ for 1 h, and the atmosphere is the air of normal pressure. The mass change is measured with FA1104 electronic balance, then the rate of the oxidation mass loss can be calculated according to the following equation:

$$A = (m_1 - m_2)/m_2$$

where A is the rate of oxidation mass loss; m_1 is the mass of the sample before oxidation, g; m_2 is the mass of the sample after oxidation, g. Samples are also observed with KyKy-2000 scanning electron microscope.

3 RESULTS AND DISCUSSION

3.1 Formula optimization

Table 1 shows the effects of contents of additive powders on the oxidation mass loss of in-situ carbonization binderless C/C composites. According to the principle of orthogonal test and the selected contents of additive powders, $L_9(3^4)$ orthogonal list is determined, in which there are experiments of 9 groups, and 3 parallel experiments are fixed up in each group. Thus, 27 samples are prepared, and the average oxidation mass loss of each group is put in the orthogonal list, from which the optimization formula for this kind of composite can be obtained as 10% B_4C, 10% SiC and 5% Si. That is sample No. 9. Its oxidation mass loss is the lowest among all the samples, only 1/3 that of sample No. 1 without any ceramic powders. The result shows that the additive powders can greatly improve the oxidation resistance of binderless C/C composites.

The same conclusion can be obtained from the SEM morphologies of the sample No. 9 before and after oxidation at 1 100 ℃ (as shown in Figs. 2 and 3), from which the morphological difference can be observed, but the difference is not obvious. There is no evident increase in oxidation tunnels (micro-pores) after oxidation.

3.2 Effects of different additives on oxidation resistance

The effects of three kinds of additives on oxidation resistance of the samples are shown in Fig. 4, from which it can be seen that the order of effectiveness of the additives on enhancement of oxidation resistance is SiC > B_4C > Si when the samples are oxidized at 1 100 ℃ in 0.1 MPa air. Furthermore, the effects become more obvious

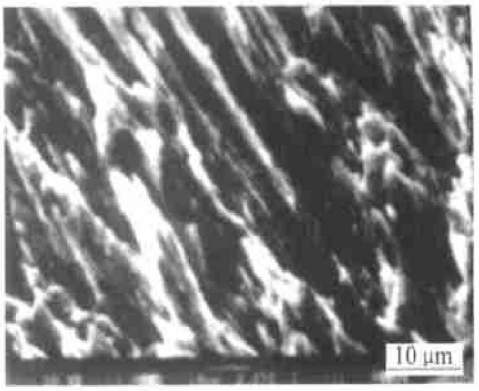

Fig. 2 SEM photograph of sample No. 9 before oxidation

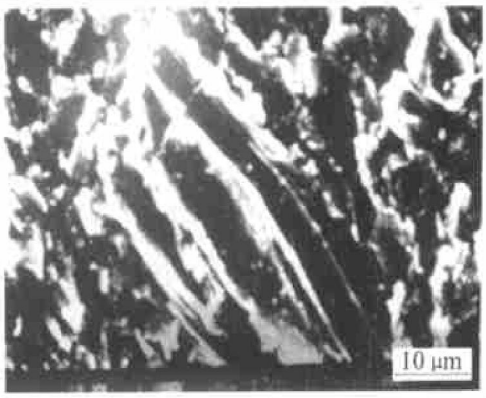

Fig. 3 SEM photograph of sample No. 9 after oxidation

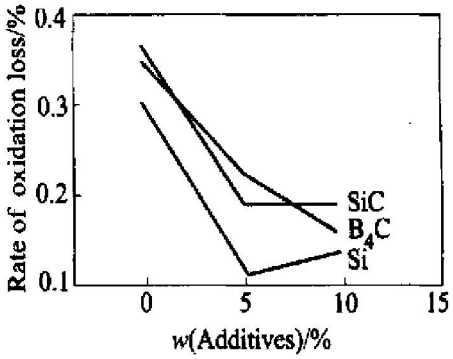

Fig. 4 Relationship of oxidation mass loss and contents of additives

with the increase of B_4C and SiC contents. The effects of all the three additives become greater in the content range of 0% – 5%, and the oxidation resistance gets worse when the content of Si is more than 5%.

3.3 Role of additives in oxidation of composites

The relationship of oxidation mass loss and contents of additives is shown in Fig. 4.

1) B_4C can react with CO at 0.1 MPa when the temperature is below 1 585 ℃[12] to form $B_2O_3(l)$ and C (s):

$$B_4C + 6CO \rightarrow 2B_2O_3(l) + 7C(s) \quad (1)$$

The melted B_2O_3 blocks the pores and coats the particles and fibres of the matrix. It becomes a protective coating to prevent oxygen further entering the samples. Because of the expansion during the formation of $B_2O_3(l)$ and $C(s)$, the samples get denser, thus improves their oxidation resistance.

2) SiC takes an important part in the oxidation resistance of the C/C composite. During the samples are sintered, SiC can react with CO to form $SiO_2(s)$ and $C(s)$, that is

$$SiC(s) + 2CO(g) \rightarrow SiO_2(s) + 3C(s) \quad (2)$$

Gibbs free energy of which can be expressed as follows[12]:

$$G = 6.2 \times 10^5 + 11.43t + \lg t + 303.5t - 38.3t \lg p(CO) \quad (3)$$

where t is the reaction temperature, $p(CO)$ is the partial pressure of CO.

This reaction can go on when the temperature is lower than 1 800 ℃ at 0.1 MPa, and the reaction temperature gets lower with the increase of pressure. A part of the formed $SiO_2(s)$ and $C(s)$ will deposit on the surface of the sample and stop up the pores, thus improve the oxidation resistance. And another part of the formed SiO_2 will dissolve in melted B_2O_3 to form glass, which coats on the surfaces of the matrix carbon particles and carbon fibres, and prevents them from oxidation. However, the solubility of SiO_2 in melted B_2O_3 is limited. When it gets saturated, the role of the glass will not change remarkably. This is the reason why the oxidation resistance of the material will not increase distinctly with the increase of the content of SiC when it is greater than 5%.

3) Si may react with C at high temperature because of its high activity. The reaction is as follows:

$$\begin{aligned} &C(s) + Si(s) \rightarrow SiC(g) \\ &2Si(s) + CO(g) \rightarrow SiC(g) + SiO(g) \quad (4) \\ &SiO(g) + 2C(s) \rightarrow SiC + CO(g) \end{aligned}$$

Their Gibbs free energies are less than zero[13], so the reaction may go rightward. The ultimate product is SiC whether with the presence of CO or not. From reaction(4), it can be seen that the presence of SiC is of benefit to the oxidation resistance of samples. However, when the content of Si powders is more than 5%, the speed of the reaction $2Si(s) + CO(g) \rightarrow SiC(s) + SiO(g)$ is accelerated, and $SiO(g)$ content increases, which makes SiO (g) quickly escape from the sample, thus the pores increase, and the oxidation resistance gets worse.

4 CONCLUSIONS

1) The oxidation resistance of the in-situ carbonized binderless C/C composites with pre-oxidized fibres comes up to the highest value when the adding contents of B_4C, SiC and Si are 10 %, 10%, and 5% respectively.

2) SiC and B_4C can evidently improve the oxidation resistance of the C/C composites, and it gets better with the increase of B_4C and SiC contents. The effect of B_4C is more obvious when its content is less that 5%, and it becomes gentle when more than 5%.

3) The oxidation resistance is enhanced with the increase of content of Si when it is less than 5%, and dropped when more than 5%.

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