EFFECT OF ADDITIVES ON THE OXIDATION RESISTANCE OF CARBON/CARBON COMPOSITE

Xiaoqi Zhu, Zheng Yang and Mokuang Kang
Department of Materials Science and Engineering
Northwestern Polytechnical University, Xi' an, 710072, P.R. China

Abstract

Carbon/Carbon composites (c/c) will oxidize in the air above 400℃. Now, the coating can' t solve the crack problem. The oxidation resistance of c/c can be improved by surface coating as well as by c/c itself. In this paper, some glass ceramic powder such as ZrO_2, B_4C, SiO_2, SiC were added into the c/c matrix according to the orthogonal table. The effect of additives on oxidation resistance was obtained quantitatively by the variance analysis and orthogonal regression. The results showed that it is effective and reliable to use the orthogonal test method to study the effect of additives on c/c. The notability order of additives on the oxidation resistance is: $B_4C > SiO_2 > ZrO_2 > SiC$. The synthetical optimum composition is: ZrO_2 0%, B_4C 10%, SiC 10%, SiO_2 10%. The burning rate of the modified specimen is decreased to one-third of the unmodified one.

Keywords: c/c, burning rate, additives, orthogonal regression, orthogonal table, variance analysis

Introduction

Now, how to increase the oxidation resistance of c/c is a focus problem when used as constructional material at high temperature. The oxidation resistance of c/c can be improved greatly by surface coating. However, problems have not be solved completely, such as cracks in the coating and the matrix due to the difference of thermal expansion coefficient between the matrix and coating. Attention has been paid to the c/c inner self-protection. Combining modification of matrix with coating is the effective approach to remarkably promoting the oxidation resistance of c/c.

The effect of additives on the burning rate of c/c are studied in this paper. Some kinds of glass ceramic powder are selected as additives added in the matrix. Generally, if three levels for four factors are discussed, 81 specimens are needed, which result in a mammoth task to test the specimens one by one. Here, an orthogonal table of $L_9^4(9)$ is used to arrange the experiment in order to get the results rapidly with the least number of specimens.

First, the optimum composition is obtained by the orthogonal test method. Then, the notability of every factor on the burning rate is got by the variance analysis. At last, the regression equations between each factor and the burning rate are deduced.

Experiment

Four kinds of additives ZrO_2, B_4C, SiC, SiO_2 are choosed and defined as factor A, B, C, D. Three levels are adopted for each factor. The experiment is arranged according to $L_9^4(9)$ orthogonal table. Nine specimens are needed.

The main preparation process is shown as Fig. 1. The burning rate of every specimen was measured in 1000℃ for 1 hour using the high-temperature electric resistance furnace and the analytical balance.

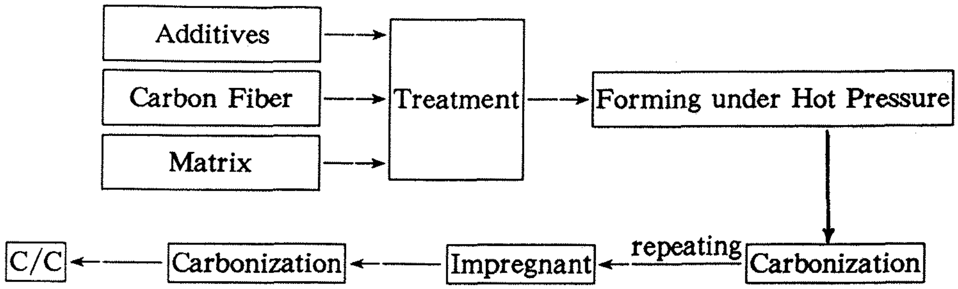

Fig. 1 the Preparation Process of Specimens

Results and Discussion

The results are listed in table 1.

First, we obtain the optimum composition by the orthogonal test method. From table 1, the optimum composition is ZrO_2 0%, B_4C 10%, SiC 10%, SiO_2 10%, i. e. specimen 3. From the results we can see that specimen 3 has the lowest burning rate (0. 06373g/m^2 • s), which is only one-third of specimen 1(0. 17387g/m^2 • s).

Then, we discuss the notability of every kind of additive on the burning rate by variance analysis method.

Table 1 the Content of the Additives and the Burning Rate of Specimens

Factor / Content / Number	A	B	C	D	y_1	y_2	y	$(y_1^2+y_2^2)$	$(y_1+y_2)^2$
1	0	0	0	0	0. 17069	0. 17705	0. 17387	0. 06048	0. 12092
2	0	5	5	5	0. 10352	0. 10352	0. 10352	0. 02143	0. 04287
3	0	10	10	10	0. 05152	0. 07592	0. 06373	0. 00842	0. 01624
4	5	0	5	10	0. 14861	0. 17341	0. 16101	0. 05216	0. 10369
5	5	5	10	0	0. 07354	0. 09900	0. 08627	0. 01521	0. 02977
6	5	10	0	5	0. 11384	0. 07904	0. 09644	0. 01921	0. 03720
7	10	0	10	5	0. 18708	0. 17369	0. 18039	0. 06517	0. 13015
8	10	5	0	10	0. 09404	0. 10696	0. 10050	0. 02028	0. 04040
9	10	10	5	0	0. 11993	0. 10481	0. 11237	0. 2537	0. 05051
I	0. 34111	0. 51527	0. 37081	0. 37251	T=1. 07809				
II	0. 34372	0. 29029	0. 37690	0. 38035					
III	0. 39326	0. 27253	0. 33038	0. 32523					

Note:

1) I 、II 、III : the sum of every burning rate

2) y: the burning rate

3) T= I + II + III : the sum of burning rate

$$S_A^2=\frac{I_A^2+II_A^2+III_A^2}{3}-\frac{T^2}{9}=0.0005756$$

$S_B^2=0.012206$

$S_C^2=0.000426$

$S_D^2=0.000592$

S_i^2: the sum of variance squares for factor i, i=A,B,C,D

$f_A=f_B=f_C=f_D=n-1=2$

f_i: the degree of freedom for factor i

$S_A=S_A^2/f_A=0.2878\times10^{-3}$

$S_B=S_B^2/f_B=0.6103\times10^{-2}$

$S_c = S_c^2/f_c = 0.2130\times10^{-3}$

$S_D = S_D^2/f_D = 0.2960\times10^{-3}$

S_i: the average variance of factor i

We use F—test:

$$\hat{F}_i = \frac{S_i^2/f_i}{S_e^2/f_e}$$

$F_{0.05}(2,18) = 3.55$

The above results are listed in the table 2:

Table 2 the Notability of Every Factor

Factor	$\hat{F}$	Notability
A	2.786	*
B	59.07	* *
C	2.062	
D	2.865	*

From table 2, $\hat{F}_B > \hat{F}_D > \hat{F}_A > \hat{F}_C$. That is to say that the order of factor' s notability of every factor is: $B_4C > SiO_2 > ZrO_2 > SiC$. SiC have no notable effect on the burning rate.

At last, we deduce the regression equations between the content of additives and the burning rate by the orthogonal regression method:

For factor A:

1) Let:

$A_i' = (A_i + h_i - A_1)/H_A = (A_i + 5)/5$

$i = 1,2,3$ h_i: level space length $h_i = 5$

2) $\psi(A') = a_1P_1(A') + a_2P_2(A')$

a_1, a_2: regression coefficients of factor A

$$\hat{a}_j = \frac{1}{l_A \sum_{i=1}^{n} P_j^2(A_i)} \left[\sum_{i=1}^{n} P_j(A_i) y_i\right] \qquad j = 1,2$$

l_A: the repeating number of every level

y_i: the sum of y for factor A

$\hat{a}_1 = 8.69\times10^{-3}, \hat{a}_2 = 7.82\times10^{-3}$

3) $$S_{\hat{i}k}^2 = \frac{1}{\sum_{i=1}^{n} P_k^2(i)} \left[\sum_{i=1}^{n} P_k(i) y_i\right]^2$$

$S_{\hat{a}k}^2$: sum of variance squares for coefficients a

$S_{\hat{a}_1}^2 = 4.53\times10^{-4}$, $S_{\hat{a}_2}^2 = 1.22\times10^{-4}$

For factor B:

$\psi(B') = b_1P_1(B') + b_2P_2(B')$

$\hat{b}_1 = -4.05\times10^{-2}$, $\hat{b}_2 = 3.45\times10^{-2}$

$S_{\hat{b}_1}^2 = 9.82\times10^{-3}$, $S_{\hat{b}_2}^2 = 2.39\times10^{-3}$

For factor C:

$\psi(C') = c_1P_1(C') + c_2P_2(C')$

$\hat{c}_1 = -6.74\times10^{-3}$, $\hat{c}_2 = -8.77\times10^{-3}$

$S_{\hat{c}_1}^2 = 2.72\times10^{-4}$, $S_{\hat{c}_2}^2 = 1.54\times10^{-4}$

For factor D:

$\psi(D') = d_1P_1(D') + d_2P_2(D')$

$\hat{d}_1 = -7.88\times10^{-3}$, $\hat{d}_2 = -1.05\times10^{-2}$

$S_{\hat{d}_1}^2 = 3.72\times10^{-4}$, $S_{\hat{d}_2}^2 = 2.19\times10^{-4}$

$$S_{e_2}^2 = \sum_{i=1}^{9}\sum_{j=1}^{2} y_{ij}^2 - \frac{1}{2}\sum_{i=1}^{9}\left(\sum_{j=1}^{2} y_{ij}\right)^2 = 1.86\times10^{-3}$$

S_{e2}^2: the error variance for repeating test

For the orthogonal regression analysis, $a_1, a_2 \cdots d_1, d_2$ must be evaluated to judge which are dominant factors and which are second factors to make the equations more simple and practical.

In general, F—test is used to judge the notability of the factors. The results are listed in table 3.

$$F_{\hat{k}} = \frac{S_{\hat{j}k}^3}{S_{e2}^2/m(n-1)}$$

$f_{e2} = m(n-1) = 9\times(3-1) = 18$

$F_{0.05}(1,18) = 4.41$

From table 3, only $\hat{a}_1$, $\hat{b}_1$, $\hat{b}_2$, $\hat{d}_1$ are notable, so the regression equations of A, B, D are obtained.

For factor A:

$\psi(A') = \hat{a}_1P_1(A')$

$$P_1(A') = A' - \frac{n+1}{2} = A' - 2$$

$$A' = \frac{A+5}{5}$$

$$\psi(A) = \hat{a}_1\left(\frac{A+5}{5} - 2\right)$$

$= 8.69\times10^{-3}(0.2A - 1)$

Table 3 the Notability Criterion of the Orthogonal Regression Analysis

Coefficient	Sum of Change Squares	$\hat{F}$	Notability
$\hat{a}_1$	4.53×10^{-4}	4.385	*
$\hat{a}_2$	1.22×10^{-4}	1.181	
$\hat{b}_1$	9.82×10^{-3}	95.06	* *
$\hat{b}_2$	2.39×10^{-3}	23.14	* *
$\hat{c}_1$	2.72×10^{-4}	2.633	
$\hat{c}_2$	1.54×10^{-4}	1.496	
$\hat{d}_1$	3.72×10^{-4}	3.601	*
$\hat{d}_2$	2.19×10^{-4}	2.120	

For factor B:

$$\psi(B')=\hat{b}_1P_1(B')+\hat{b}_2P_2(B')$$

$$P_1(B')=B'-2=(0.2B-1)$$

$$P_2(B')=\left(B'-\frac{n+1}{2}\right)^2-\frac{n^2-1}{2}$$

$$=(0.2B-1)^2-\frac{2}{3}$$

$$=0.04B^2-0.4B+\frac{1}{3}$$

$$\psi(B)=1.38\times10^{-3}B^2-1.0863\times10^{-2}B+5.2\times10^{-2}$$

For factor D:

$$\psi(D)=-7.88\times10^{-3}(0.2D-1)$$

From the variance analysis and the orthogonal analysis, SiC have no notable effect on the burning rate of c/c material.

The relationships between additives and the burning rate are shown as Fig. 2, Fig. 3 and Fig. 4.

From Fig. 2, the burning rate increases with the content of ZrO_2. ZrO_2 will not transform into liquid phase until above 2680℃. The difference of thermal expansion coefficient between c/c and ZrO_2 is larger. ZrO_2 can' t heal the cracks. In addition, oxygen penetrating rate of ZrO_2 is high. All these factors have bad effects on the oxidation resistance.

From Fig. 3, when the content of B_4C is lower than 4%, the burning rate decreases with the increasing B_4C.

In the high temperature, B_4C react with O_2:

$$B_4C+4O_2\rightarrow 2B_2O_3+CO_2$$

The intersolubility of B_2O_3 and C is good in the high temperature. The wetting surface energy is lower than 100mJ/m^2 and the viscosity of B_2O_3 is $10^4\sim10^2$ dp • s between 600℃ and 1000℃. So B_2O_3 can form a thin protective film on the surface of carbon. They can also flow into the cracks in the coating or matrix.

Just as Mckee etc. studied in their papers[1], lower content of B_2O_3 can detach the radical on the active part which combine with atom C. So the oxidation resistance is enhanced becaused of the blockade. With the content of B_2O_3 increasing, the protective film is formed, the oxidation resistance increases.

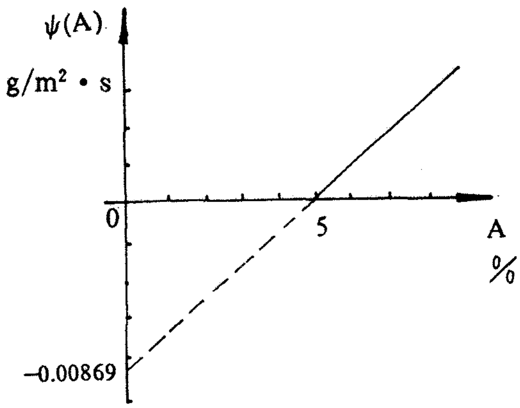

Fig. 2 the Relationship Between the Burning Rate and the Content of ZrO_2

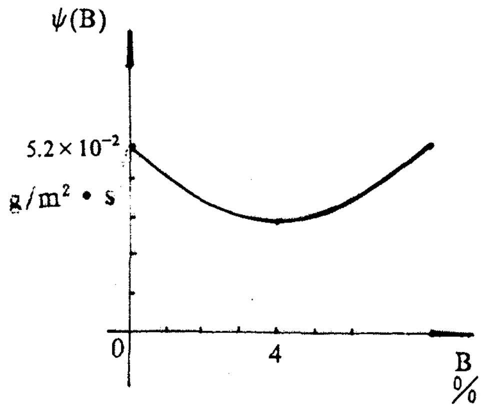

Fig. 3 the Relationship Between the Burning Rate and the Content of B_4C

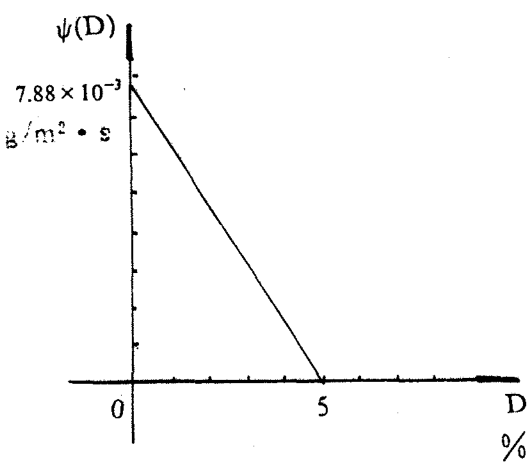

Fig. 4 the Relationship Between the Burning Rate and the Content of SiO_2

When the content of B_4C is higher than 4%, much more B_4C transform into B_2O_3, which result in the volume and cracks increasing. B_2O_3 can' t heal so much cracks, so the oxidation resistance decreases.

From Fig. 4, with the content of SiO_2 increasing, the burning rate decreases. SiO_2 are flowable in the high temperature. They can heal the cracks and have very low thermal expansion and low oxygen penetrating rate. In 1200℃, the oxygen penetrating rate of SiO_2 is about 10^{-13} g • cm^{-1} • s^{-1}[(2)]. All above factors make B_4C have good effects on the oxidation resistance.

Conclusion

① The orthogonal test is an effective and reliable method to study the effect of additives on c/c materials.

② The order of additives notability on oxidation resitance is: $B_4C > SiO_2 > ZrO_2 > SiC$

③ The regression equations between the content of ZrO_2, B_4C, SiO_2 and the burning rate are:

$$\psi(A) = 8.69 \times 10^{-3}(0.2A - 1)$$

$$\psi(B) = 1.38 \times 10^{-3}B^2 - 1.0863 \times 10^{-2}B + 5.2 \times 10^{-2}$$

$$\psi(D) = -7.88 \times 10^{-3}(0.2D - 1)$$

A, B, D stand for ZrO_2, B_4C, SiO_2 respectively.

④ B_4C have notable effect on burning rate. When the content of B_4C is lower than 4%, the burning rate decreases with increasing B_4C. When the content of B_4C is higher than 4%, just on the contrary.

⑤ SiO_2 also have remarkable effect on the burning rate. The burning rate decreases with increasing SiO_2.

⑥ The burning rate increases with increasing ZrO_2.

⑦ SiC have no notable effect on the burning rate.

⑧ The synthetical optimum composition is: ZrO_2 0%, B_4C 10%, SiC 10%, SiO_2 10%. The burning rate of the modified specimen is decreased to one-third of the unmodified one.

Reference

① D. W. Mckee, "Oxidation Resistance of Carbon/Carbon Composites", Carbon, Vol. 26, 1988, P38.

② E. Fitzer, "Structure and Strength of Carbon/Carbon Composites", High Temperatures-High Pressures, Vol. 10, 1989, P29.