Article ID: 1003-6326(2005)06-1346-05

Anti-oxidation mechanism of SiC-B$_4$C-C composites①

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Abstract: Mixture of green petroleum coke, B$_4$C and SiC together with short carbon fiber were employed as starting materials, the mixture was press-formed without any binder after grinding, dense and homogeneous binderless SiC-B$_4$C-C(carbon/ceramic) composites were then obtained after sintering. Composites thus prepared possess excellent anti-oxidation property, that is, mass loss less than 1% within the temperature range from 900 to 1 100 ℃ for 10 h. Anti-oxidation mechanism was also discussed from the viewpoint of thermodynamics, excellent anti-oxidation property of materials thus prepared can be discribed to 1) solid SiO$_2$ formed from SiC, which restrains the filtering of oxygen and simultaneously, its volume expansion brought about by the reaction takes roles both walling up the original pores and making the material more compact; 2) liquid B$_2$O$_3$ from the reaction of B$_4$C not only makes the combination with C, B$_4$C and SiC tighter through forming solid solution, but also effect of reaction SiC(s) + 2CO(g) = SiO$_2$(s) + 3C(s) is an expansive process, which improves the microstructure of the material.

Key words: SiC-B$_4$C-C composites; anti-oxidation; mechanism

CLC number: TQ 050.4 **Document code:** A

1 INTRODUCTION

C/C composites with excellent properties of carbon fiber and matrix carbon widely used in metallurgy, machinery, electric, nuclear energy and aeronautics and space, are a kind of fast growing and prosperous new material. Recently it has been used as exhausting pipe for rocket and missile owing to its good anti-thermal-shock property, but the obvious shortcoming of it limits its application, that is, the nearly half mass loss of its binder during heat treatment process makes this material have high porosity and low strength, especially low anti-oxidation property[1]. To overcome that disadvantage, protection film such as dipping phosphate or borate is employed, or SiC or B$_4$C (or other carbide) is doped to form a SiC-B$_4$C-C (carbon/ceramic) composite[2-6]. These improvement methods are effective to promoting its high-temperature anti-oxidation property, mechanical strength and thermal conductivity. Adding SiC as protection coating in inert atmosphere at 1 450 ℃ was discussed[6], Chinese scholars[7] also mentioned SiC as composite coating and its protecting ways; others [8] proposed TiC/SiC protection coating layer. While that increases its preparation cost and producing period, and makes it difficult for industrial production.

In this paper, the authors discuss a new process in which green petroleum coke, SiC and B$_4$C powder were mixed, and ground, then formed without binder (which can be called binderless forming), and compact carbon/ceramic were obtained after sintering. This approach, characterized by its simplicity and short processing period, can prepare SiC-B$_4$C-C (carbon/ceramic) composites with both excellent anti-oxidation property and high strength[9-11]. The oxidation mass loss (the indicator of anti-oxidation index), and further the anti-oxidation mechanism with regard to thermodynamics were also discussed.

2 EXPERIMENTAL

2.1 Preparation of specimens

The raw materials used are as follows: Jingmen green petroleum coke (prepared with postponing method, with average diameter 5 μm), pre-oxidized PAN carbon fiber (Shanghai Carbon Plant, average length 3-5 mm), and SiC and B$_4$C ceramic powder (ground to 1-2 μm). Milling SiC and B$_4$C ceramic powder (in various ratios) with the green petroleum powder 24 h, adding in carbon fiber, and then model pressed. Heat treatment was carried out in N$_2$ atmosphere at 2 000 ℃ sintering at 1 100 ℃, the carbon/ceramic composites were

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① **Foundation item:** Projects(03WHY3018; 03JKY1018-2) supported by the Natural Science Foundation of Hunan Province

Received date: 2005-03-18; **Accepted date:** 2005-09-26

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obtained, Table 1 gives the composition of the specimens, followed by processing flow chart (Fig. 1).

Table 1 Composition of specimen (mass fraction, %)

Specimen No.	Green coke	B$_4$C	SiC	w(B$_4$C) : w(SiC)
1	66	17	17	1 : 1
2	64	6	30	1 : 5
3	57	5.4	37.6	1 : 7
4	35	5	60	1 : 12

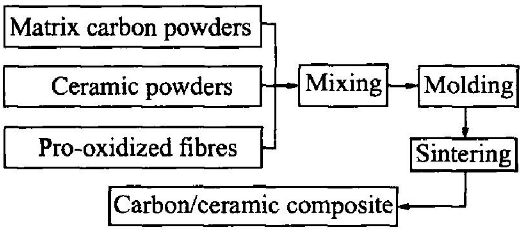

Fig. 1 Processing flow chart

2.2 Testing of prepared specimens

Oxidation mass loss was tested at different oxidation temperatures and oxidation times at the same air flow (50 mL/min). The oxidation temperatures were arranged at 900, 1 000, 1 100 and 1 200 ℃ respectively with the specimen dimension of 40 mm × 10 mm × 10 mm. Phase analysis and testing were carried out by X-ray diffractometry (XRD) and its microstructure was analyzed with scanning electronic microscopy (SEM). Thermodynamic mechanism of the anti-oxidation property was discussed on the basis of these tests.

3 EXPERIMENTAL RESULTS

3.1 Anti-oxidation property at different temperatures

Fig. 2 reveals that oxidation mass loss increases with the increase of temperature obviously for specimen No. 1, while No. 2 has a lower loss —less than 1% below 1 100 ℃; No. 3 and 4 have greater mass loss at lower temperature but smaller loss at higher temperature, oxidation time for all specimen is 10 h. Therefore it can be seen that specimen No. 2 possesses a good anti-oxidation property both at lower and higher temperatures.

3.2 Anti-oxidation property at different times

Fig. 3 is drawn based on the above experimental results, which indicates the relationship between oxidation mass loss and oxidation time of specimen No. 2. Oxidation mass loss of the four specimens varying with the oxidation time can be shown in Fig. 3, which is obvious that the oxidation mass loss at lower temperature (900 ℃) is higher than that at higher temperature (1 200 ℃) at air flow of 50 mL/min and respective oxidation time of 5, 10 and 15 h.

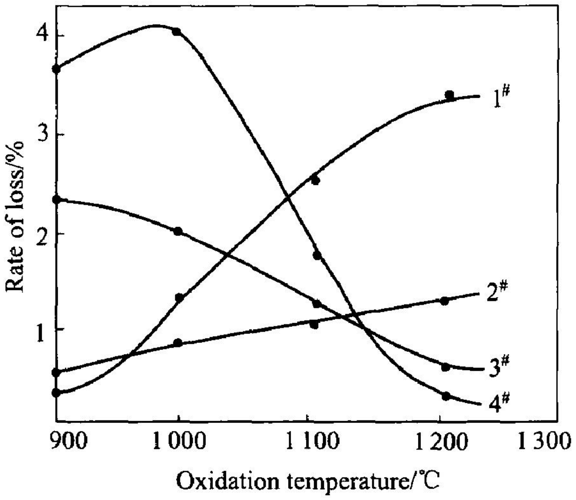

Fig. 2 Oxidation mass losses at different temperatures

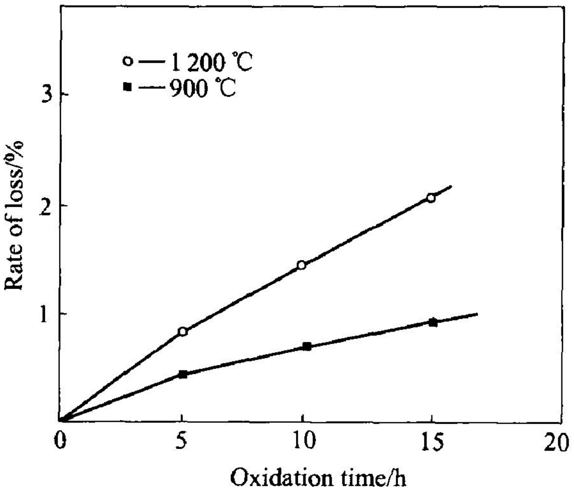

Fig. 3 Oxidation mass losses at different oxidation times

Figs. 4 (a) and (b) illustrate the SEM images of the specimen before and after oxidation (heat treatment 10 h), which shows the change of microstructure, but not much difference happens after heat treatment, the surface micro-porosity does not alter. The above discussion indicates that it is the SiC and B$_4$C ceramic additives, not the short oxidation time contributes most to the improvement of the increase of the anti-oxidation property of C/C composites. Products without ceramic additives have an oxidation mass loss [1] as high as 45% and high porosity even at the oxidation time of 2 h at 550 ℃.

4 DISCUSSION OF OXIDATION MECHANISM

4.1 Oxidation model

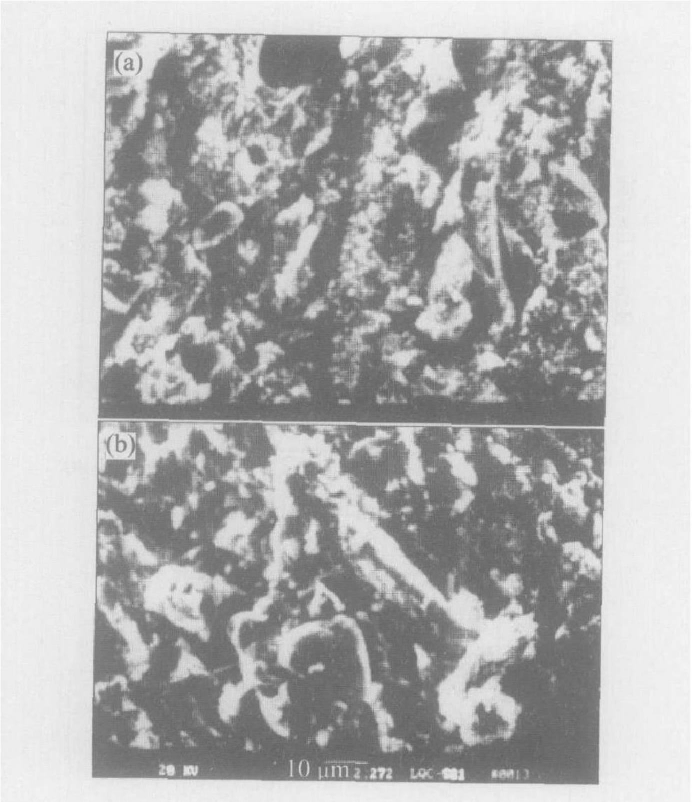

Fig. 4 SEM images before and after oxidation mass loss
(a) —Before oxidation; (b) —After oxidation

It is generally accepted that the multi-phase oxidation reaction takes place on the active surface, that is, the so called oxidation centers. The most common oxidation centers are cavity, dislocation (line defect), the other structural defects and the edge atoms, the adding of ceramic additives makes the oxidation process more intricate. The oxidation process can be simplified in Fig. 5[12]: when the right side of C/C composites has already decarbonized, its carbon has been oxidized. The newly formed pore together with the original one becomes the diffusion path (dashed line). In this case the oxidation process of carbon can be thought as: oxygen passes through the surface of the composites, enters the inner part of the material through diffusion path, then reacts with carbon when it reaches the gas-solid interface, and the reacted product-carbon dioxide passes out along the diffusion path. Therefore, through the above brief discussion, the additive candidate should possess the following two characteristics, they are: 1) it has a greater affinity with oxygen than that with carbon atom and 2) the compound(s) formed with O_2, CO, or carbon brings about a change of microstructure of the composites, such as an increase of density, a wall-up of pores and a slow-down of the diffusion of reactant(s). Experimental results illustrate that the additives employed possess the above characteristics.

Fig. 6[12] show the relation line between the reaction (between ceramic powder and oxygen) free energy and temperature, which reveals that the affinity between ceramic powders employed and oxygen are all greater than that between carbon and oxygen, thus ceramic powder(s) is preferentially oxidized prior to carbon (powder and fiber) to form an oxidation protection film, which hinders much diffusion path, and that is why it restrains the further oxidation.

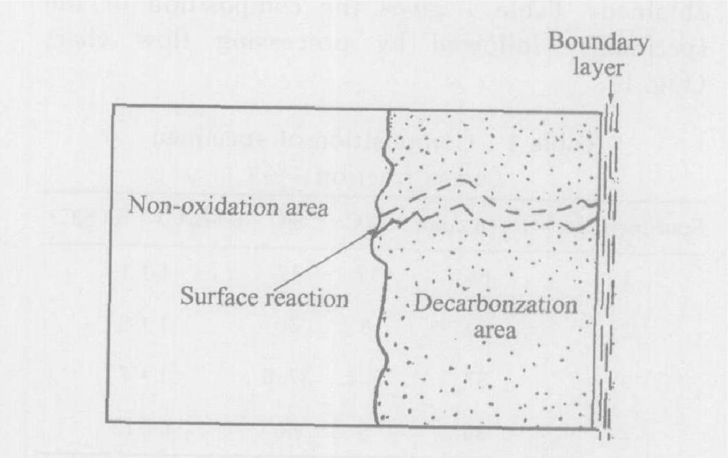

Fig. 5 Oxidation model of C/C composites

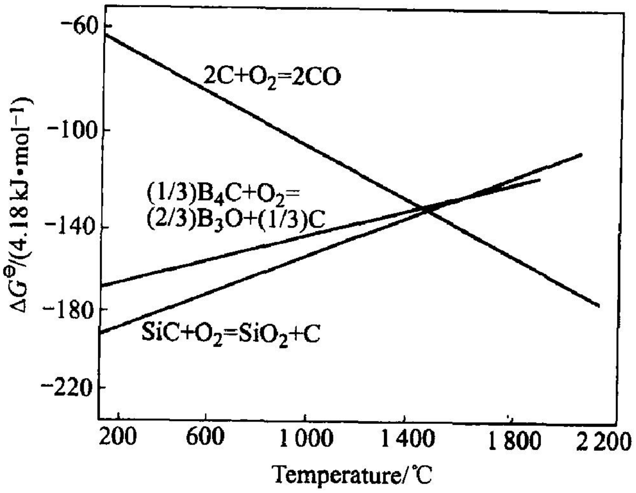

Fig. 6 Standard oxidation reaction free energy of related atoms in carbon product reaction system

4.2 Thermodynamic analysis

XRD pattern in Fig. 7 shows the mineral (phase) composition of specimen before oxidation; it contains C, SiC, B_4C and B_2O_3. The formal three compositions are raw materials by all appearances, while B_2O_3 is the product of reaction between B_4C and oxygen, which is the basis of thermodynamic analysis.

1) Reaction mechanism of SiC

Fig. 8[13] shows the significant role of SiC on anti-oxidation. SiC is thermally unstable at 1 800 K and $p(CO) = 1$ MPa, and forms $SiO_2(s)$ and C(s) as follows:

$$SiC(s) + 2CO(g) = SiO_2(s) + 3C(s) \qquad (1)$$

with a free energy

$$\Delta G^{\ominus} = -616\,297 + 11.43\,T\lg T + 303.5\,T -$$

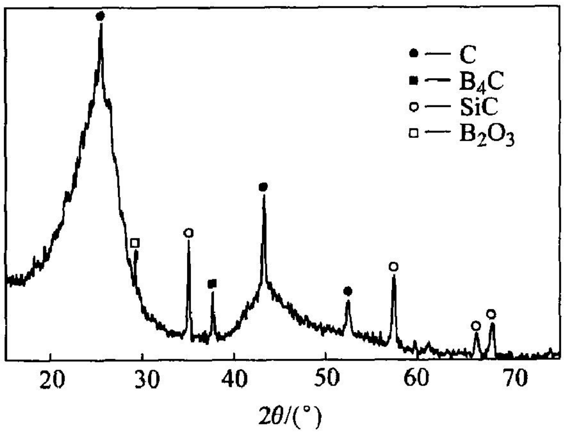

Fig. 7 XRD pattern of specimen before oxidation

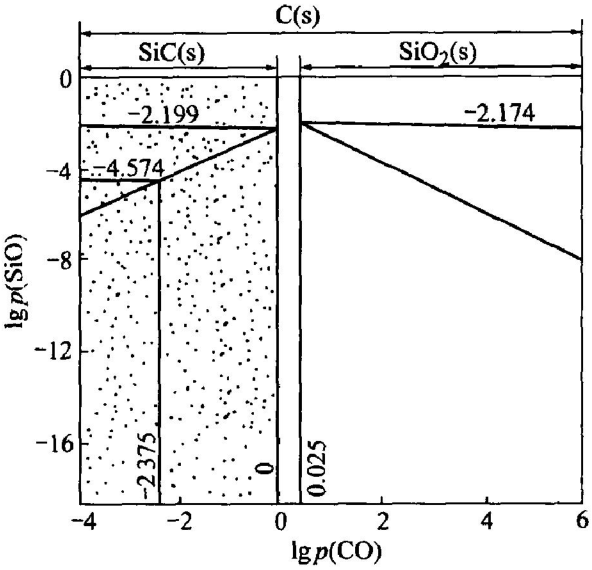

Fig. 8 SiO_2-SiC-C phase diagram at 1 800 K and different CO pressures

$$38.31T\lg p(\mathrm{CO})$$

When $p(\mathrm{CO}) = 1$ MPa, and the temperature is lower than 1 100 ℃, all the $\Delta G^{\ominus}$ values are less than zero, that is, when the temperature is not higher than 1 100 ℃, the above reaction tends to proceed from left to right. Description is[10]: first, SiC(s) reacts with CO(g) to form C(s) and SiO(g):

$$\mathrm{SiC(s) + CO(g) = SiO(g) + 2C(s)} \qquad (2)$$

Carbon formed deposes onto the surface of SiC, which increases $p(\mathrm{CO})$ and decreases $p(\mathrm{SiO})$, while gaseous SiO diffuses and reacts with neighboring CO to form SiO_2 and C(s) as follows:

$$\mathrm{SiO(g) + CO(g) = SiO_2 + C(s)} \qquad (3)$$

The above reaction makes CO reduced to carbon, and SiO_2 formed enwraps on the surface of C, B_4C and SiC to restrain oxidation infiltration and inhibit further oxidization of carbon, simultaneously, the volume expansion of formed SiO_2 and C wall up in the original cavity, which increases the density and anti-oxidation ability of the material.

2) Reaction mechanism of B_4C

Fig. 9[13] is an illustration of thermodynamic stable areas of various phases in B-O-C system. It can be see that B_4C remains stable at 1 327 ℃ only on condition that $\lg p(\mathrm{CO}) \leqslant 1.285$: while in oven, B_4C is stable at 1 000 ℃ with partial pressure approximately 0. 1 MPa and reacts with CO and O_2 as follows[14]:

$$\mathrm{(1/3)B_4C(s) + O_2(g) = (2/3)B_2O_3(l) + (1/3)C} \qquad (4)$$

$$\mathrm{(1/2)B_4C(s) + 3CO(g) = B_2O_3(l) + (7/2)C(s)} \qquad (5)$$

$$\mathrm{(1/2)B_4C(s) + 2CO(g) = B_2O_2(g) + (5/2)C(s)} \qquad (6)$$

$$\mathrm{(1/4)B_4C(s) + CO(g) = BO(g) + (5/4)C(s)} \qquad (7)$$

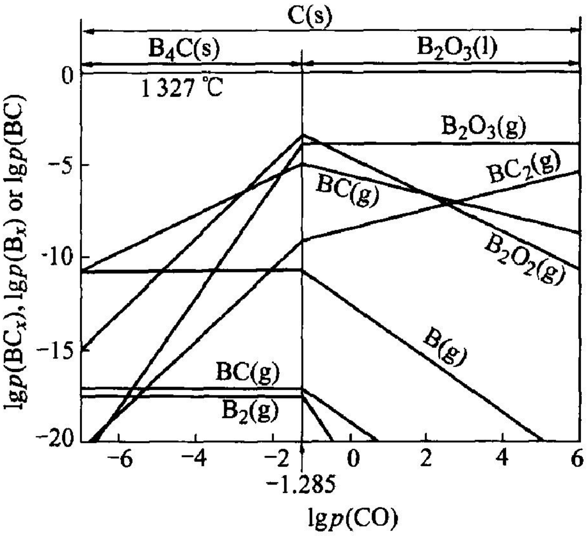

Fig. 9 Equilibrium partial pressure and stable solid state phase in B-O-C system at 1 600 K

With the proceeding of these reactions, the partial pressure (p(CO)) near B_4C powder decreases, CO in the environment diffuses onto B_4C particle surface and makes the above reactions go on. At the same time, the formed B_2O_3(g) and BO(g) diffuse into environment and reacts with CO(p(CO) = 1 MPa):

$$\mathrm{B_2O_2(g) + CO(g) = B_2O_3(l) + C(s)} \qquad (8)$$

$$\mathrm{BO(g) + (1/2)CO(g) = (1/2)B_2O_3(l) + (1/2)C(s)} \qquad (9)$$

Reactions (8) and (9) make CO reduced to carbon, and B_2O_3 exists in liquid phase; simultaneously, reaction (1) causes an expansion of the reacting system, which walls up pores. B_2O_3 liquid filters into pores through capillary, and carbon in pores more firmly combines with other carbon atoms in liquid through dissolution, separating out and sintering to form a solid solution, and the formed solid solution further walls up pores to prevent oxygen to filter. Material thus prepared has a more compact inner structure and of course, better anti-oxygenic property.

Within the temperature range of 9 000－1 200 ℃, SiO_2 formed exists in solid state, B_2O_3 liquid, there is also a eutectic liquid of both which takes role of composite protecting film; among which, B_2O_3 and the eutectic liquid dominate in increasing anti-oxidation ability.

5 CONCLUSIONS

1) Powder mixture of green petroleum, $B_4C$and SiC, in certain proportion, after grinding and then with the adding of short carbon fiber, can prepare high mechanical strength C/C composites with excellent anti-oxidation property, that is, mass loss less than 1% within the temperature range from 900 to 1 100 ℃. This binderless and direct model press process is also characterized by its simple processing procedure.

2) The excellent anti-oxidation property of the materials prepared in the above way is due to a) the solid SiO_2 formed from SiC, which restrains the filtering of oxygen and also, its volume expansion brought about by the reaction takes roles both walling up the original pores and making the material more compact; b) the liquid B_2O_3 formed fom the reaction of B_4C not only makes the combination with C, B_4C and SiC tighter through forming solid solution, but also effects of equation (1) being an expansive process, which improves the microstructure of the material.

3) The anti-oxidation property indicated by the oxidation mass loss of C/C composites prepared with binderless process deteriorates with a) the increase of temperature at selected heating time and, b) the prolongation of oxidation time under certain temperature.

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(Edited by PENG Chao-qun)