Improvement of Oxidation Resistance of the C/C Composites with Coating of Glass Forming Materials

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Improvement of Oxidation Resistance of the C/C Composites with Coating of Glass Forming Materials

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1.1. Advantages and Applications of Carbon/Carbon Composite

The mechanical, chemical, thermal and electrical properties of traditional materials are being pushed ever closer to their intrinsic limits. Many thousands of years of effort are required to research and develop new and advanced materials with which to face the engineering demands of the next century. These materials usually take the form of complex composite structures, applying the benefits of a number of materials drawn together from a spectrum of available metals, ceramics and polymers.

Designers of weight sensitive structures, such as aircraft and racing cars, make extensive use of fiber-reinforced polymer composites. The composites used have been mainly those based on continuous carbon fibers and, to a lesser extent, glass and aramid. The use of composites in Formula 1 motor racing is particularly advanced; all of the vehicles making up the grid are totally dependent on composites and consist of up to 75 percent carbon fiber-reinforced epoxy.

Carbon/carbon composites are a specialized family of fiber-reinforced composites in which both the matrix and reinforcing fibers are carbon. They are produced in an attempt to combine the advantages of fiber-reinforced composites, such as high specific strength, stiffness and fiber-plane toughness, with the refractory properties of engineering ceramics. Their properties include chemical inert, biocompatibility, thermal stability as a solid, high resistance to thermal shock (as a result of high thermal conductivity and low thermal expansion) and, most importantly, retention of mechanical properties at high temperatures.

One of the most attractive features of fiber-reinforced composite materials is that their extreme anisotropy can be exploited in tailoring their properties to suit a specific application. This offers a more efficient use of materials than simply that resulting from, for example, higher specific strength and stiffness. Composites can be made in a wide variety of forms, from unidirectional to multidirectional, 3-dimensional, using performs. Variations of fiber orientation result in diverse mechanical and other properties. Carbon fibers may be produced with a wide variety of attributes, depending on the choice of precursor and processing conditions, thus extending the possible diversity of composite response.

Research and development efforts in the United States, Japan, France and the United Kingdom have tended to concentrate on military and aerospace components. The first applications of carbon/carbon composite were in rocket motor components and the heat
shields of re-entry vehicles. The most famous application of carbon/carbon composite is the application in the leading edges and nose-cone of the Space Shuttle. Properties of interest are retention of mechanical performance at high temperatures, high thermal conductivity and good resistance to thermal shock.

The major use of carbon/carbon at present is for brake materials, because of its low weight and excellent wear resistance and friction behavior. Carbon/carbon composites have good compatibility with living tissue and the composite's modules is close to that of bone. If a carbon/carbon prosthesis is embedded in bone it will be porous enough for bone and tissue to grow into and anchor. Most recently carbon/carbon has found applications in industry. The material has been used to make heating elements for furnaces, high temperature fasteners, moulds for superplastic metals forming, glass making equipment, and so on[31. Carbon/carbon composites could be used in high-performance jet engines if the problems of oxidation can be solved. They would make the engines smaller and lighter and allow them to operate at higher temperatures, thus making them more efficient. Despite a number of research programs very little progress has been made in this area.

The present and predicted applications of carbon/carbon composite are many and varied, but the true potential of these materials will only be met if the problems of prohibitive costs and oxidation resistance are fully addressed.

1.2. Protection for the Oxidation of Carbon/Carbon Composites

Carbon/carbon composites can withstand temperatures of up to 3000°C in vacuum or inert atmospheres. But carbon materials have very poor oxidation resistance in oxidizing atmosphere even at temperatures as low as 500°C[7]. If we would discuss the history of oxidation of carbon, it should have returned to the beginning of human civilization. Here, for the modern applications, efforts to protect carbon bodies from oxidation has still spent more than a half century.

The works that are significant to current efforts are highlighted in Fig. 1.1. A 1934 US patent is of major importance and describes a coating system for graphite articles composed of a surface conversion to SiC and vitreous glaze overlay coatings based on alkali and alkaline earth additions to the traditional glass former. A number of later patents pertaining to electrode applications claim effective graphite protection by the use of discrete ceramic coatings and by internal ceramic modifications of the graphite. Work on graphite oxidation protection culminated in the early 1960s with extensive studies for rocket propulsion and reentry applications. Experiments using iridium coatings and the development of hot-pressed graphite materials with ceramic additions were significant in
Figure 1.1. Evolution of carbon oxidation protection
this period\cite{61}. 

Work on oxidation protection for C/C composites started in the early 1970s with the development of the shuttle orbiter thermal protection material. The shuttle C/C composite is made from low strength and modulus carbon fibers. The coating system was very similar to that described in the 1934 patent cited earlier and was composed of a SiC conversion layer and silicate glaze overlay\cite{1, 3, 61}. This coating system worked well on the relatively high-thermal expansion C/C under conditions of rapid heating and cooling where times at temperatures over 1000°C were minimal.

1.2.1. Investigations on the Oxidation of Carbon Materials and C/C Composites

A number of researches have been done to understand the oxidation mechanism of carbon materials and to search the appreciated materials, methods against to the oxidation for carbon materials, graphite materials and C/C composites.

Yasuda and his colleagues worked on C/C composites for many years. As a part of their works, the oxidation behavior of the composites has been studied at 650°C to 850°C\cite{81}. Yasuda found that the rate of oxidation increased with temperature but decreased with time. He suggested that the matrix had a faster rate of oxidation and a slower oxidation of the fiber follows. Goto’s findings showed that the rate of oxidation was controlled by diffusion at higher temperature and was controlled by a chemical reaction at lower temperature\cite{93}.

The effects of heat-treatment on the oxidation of C/C composites were investigated by Ragan, Emmerson and other researchers\cite{10-12}. The results suggested that oxidation resistance of the composite increased with increasing heat treatment temperature up to 2250°C, but at 2650°C the oxidation resistance decreased to which was similar to that of the composite heat-treated at 1800°C. Ragan proposed that the increased oxidation resistance had generally been attributed to thermal annealing of active sites due to graphitization, micropore collapse, and the decrease of catalytic impurity contents due to sublimation at high heat-treatment temperature. For the oxidation behavior of the composite treated at 2650°C went against trend, it was possible that high stresses associated with matrix “stress graphitization” around fibers and the general structural re-ordering to more graphitic forms of carbon at the highest heat-treatment temperature produced an increase in active site concentration hence decreased oxidation resistance. However, a simple relationship between oxidation and graphitization or the high stresses could not be established. The reason was that the oxidation was influenced by many structural factors, such as porosity, active site, impurity and extent of graphitization. It was difficult to determine a simple relationship between the oxidation rate and any single
factor among them.

Thrower investigated the effects of oxidizing environment\textsuperscript{[12]}. The oxidation rate of graphite increased with the increase of the partial pressure of oxidative gases. In his investigation, it was found that the rate was increased by the flow rate from 9.2 to 13.8 cm\textsuperscript{3}/sec, but then decreased by further increasing to 15.3 cm\textsuperscript{3}/sec. The surface roughness might be changed by the change of the flow rate. It was suggested that the oxidation behavior depended not only on the structural factors but also on the factors of oxidative environment.

1.2.2. Investigations on Additives and Coatings for Oxidation Resistance

Many of the present and predicted applications of the materials demand operation for extended period in oxidizing atmospheres of up to 1000°C, even to 2000°C. The future potential of C/C composites is, therefore, very much depended on the development of oxidation protection. The most sensible way of achieving this is to attempt to ensure that the carbon does not get exposed to high temperature oxygen. This is achieved by applying the refractory coatings which act as a diffusion barrier to oxygen.

The glass forming inhibitors, such as B\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}, play a very important role in this field. The use of borate glaze is a time-honored oxidation-protecting system for graphite with patents granted in 1934, and addition of glass-forming additives to matrix precursors is a widely used oxidation protection route in the production of C/C composites\textsuperscript{[13-14]}. However, this composite possesses insufficient oxidation resistance to appear alone at temperature higher than 800°C. The addition of SiO\textsubscript{2} as glass forming additive improves the oxidation resistance of C/C composites at higher temperature.

Many other inhibition additives have been investigated in a wide range\textsuperscript{[9, 15-20]}, such as oxides of P, Cr, Al, Be, Y, Ce, borides or carbides of Zr, Si, Cr, Ti, Hf, Nb, V, Ta, Mo, W, and so on. Meanwhile, the current researches in protective coatings are based on the use of silicon ceramics as the primary oxygen barrier. These ceramics are combined with internal glass forming inhibitors, such as SiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}, which are used to seal thermal stress cracks and other defects arising from the difference of thermal expansion between coating and substrate.

With multi-component oxidation-protective system, the oxidation resistance of the composites is more complex. Mizutani investigated the oxidation resistance of metal borides dispersed in the SiC-B-C ceramics at 1500°C\textsuperscript{[17]}. With his researches, Mizutani proposed that the vaporization of oxides, like oxides of Mo, V, W, Nb and B, and the formation of thin protective layer of oxides improved the oxidation resistance of the substrate material. The samples containing the additives of NbB\textsubscript{2} and WB showed a better
oxidation resistance at 1500°C.

In order to identify the promising material combinations for structural applications in oxidizing environments at high-temperature, Mehrotra investigated the oxidation behavior with a large number of material combinations at the temperature range of 1600°C to 2200°C. The material combinations included AlN-ZrB, AlN-AlB₂, MoSi₂-ZrB₂, MoSi₂-HfB₂, SiB₆-ZrB₆, SiB₆-HfB₂, TiC-HfB₂, TiN-ZrO₂, TiN-HfO₂, SiB₆-ZrO, SiB₆-HfO₂, ZrC-ZrO₂ and HfC-HfO₂. The results indicated that compounds in the systems MoSi₂-HfB₂ appeared to have the best stability in air at the temperature lower than 1600°C.

By the addition of ZrC and/or ZrB₂, the oxidation resistance of C/SiC-B₄C has been reported. Ogawa’s research showed that the optimal rate of SiC/SiC-B₄C was between 60 wt%–87 wt% for the oxidation resistance of the C/SiC-B₄C composite. With X-ray and EPMA analysis, after oxidation at 1000°C-1400°C, it was presented that addition of ZrB₂ or ZrC seemed to accelerate the dissolution of SiO₂ into B₂O₃ at high temperature, and formed a relatively homogeneous protective film containing Si-rich glass phase. Kobayashi’s work emphasized on the effects of environment atmosphere on the oxidation behavior of C/B₄C/SiC at 600°C-1400°C. It was found that the oxidation behavior depended strongly on the nature of protective layer form on the surface by oxidation. Several environment factors, temperature and time of oxidation, the oxygen partial pressure, and moisture content, had very serious effects on this layer.

1.3. Theoretical Analysis of the Oxidation Protection

1.3.1. Basic Concepts on the Oxidation of C/C Composites

It is known that the oxidation of carbon by CO₂ or water vapor has been studied in relation to “Boudouard’s reaction” and the gasification of coal. At moderate temperature, the rate-controlling steps of the following two reactions were considered chemically in nature.

\[
\begin{align*}
C(s) + CO_2(g) &= 2CO(g) \\
C(s) + H_2O(g) &= CO(g) + H_2(g)
\end{align*}
\]

The rates of the chemical reactions increase exponentially with temperature and, eventually above 1200°C, the rate-controlling step usually changes to the diffusion of gaseous species through the stagnant layer close to the solid carbon. Considering carbon
composites are usually used in air, and therefore, the reaction would proceed by

\[ C(\text{fibers or matrix}) + O_2(g) = CO_2(g) \]  \hspace{1cm} (1-3)

The Gibbs energy change of Eq.(1-3) has a very large negative value and the reaction would proceed always with a big driving force even at low oxygen partial pressures.

Generally, oxidation kinetics fits approximately with parabolic law, as the following function\textsuperscript{[23]}

\[ K_p = C \exp\left(-\frac{Q}{RT}\right) \]  \hspace{1cm} (1-4)

where \( K_p \) is the parabolic rate coefficient, \( Q \) the activation energy, \( R \) the gas constant and \( T \) the absolute temperature. At a certain temperature, obviously, the change of \( K_p \) depends on the change of \( Q \). The activation energy \( Q \) is sensitive to the structure of carbon or graphite. It is meaning that the ordering of carbon atoms or higher graphitization will induce a higher value of \( Q \), and further lower the oxidation rate. In fact, the oxidation rate is most sensitive to the microstructure of carbon materials or C/C composites when we consider the oxidation behavior of those materials without any resistant treatment. However, in the investigation of oxidation resistance, this kind of sensitivity is reduced when carbon materials or C/C composites with a better treatment of oxidation resistance. Rang and Emmerson made some interesting researches on this subject in their works\textsuperscript{[10]}. After comparison between the oxidation behaviors of C/C composite with and without ZrB\(_2\) at treatment temperatures, 850\(^\circ\)C, 1000\(^\circ\)C, 1800\(^\circ\)C, 2250\(^\circ\)C and 2650\(^\circ\)C, respectively. The oxidation behaviors were similar between both composites, although a small improvement in overall oxidation scale. The oxidation behavior of the inhibited matrix composites appeared unaffected by reaction of the inhibitors with the matrix at temperatures above 2300\(^\circ\)C.

1.3.2. Rate Limiting of the Oxidation

In the presence of a protective oxide film on the surface, the oxidation of a substrate involves the following four steps. At steady state, the rates of all the steps in series (e.g., 1, 2, and 4) would be the same.

1. Gas phase diffusion across the boundary layer: Oxygen has to diffuse across the boundary layer at the surface.
2. Gas diffusion through cracks: If the oxide film is cracked, the oxygen can diffuse through it to the substrate/oxide film interface. The diffusion coefficient depends on the crack diameter. For large diameters, the diffusion coefficient would be the same as the bulk gas diffusion coefficient. However, for small diameters, where the mean free path of the gas molecules is of the same order as the crack size, the gas molecules bounce against the walls. This reduces the effective diffusion coefficient, and transport occurs by a process called Knudsen diffusion. The protective film does not have to be an oxide. For example, it could be silicon carbide covered by a thin film of silica. Oxygen will then diffuse through cracks in silicon oxide followed by diffusion through cracks in silicon carbide.

3. Condensed phase diffusion: If the oxide film is nonporous, oxygen has to diffuse through it to oxidize the substrate. The transport mechanism depends on the defect structure of the oxide.

4. Reaction at the interface: The oxygen arriving at the substrate/oxide interface reacts to form an oxidation product of the substrate.

The diffusion steps (1, 2, and 3) discussed above for oxygen would also apply to gaseous reaction products, such as carbon monoxide, which would have to diffuse out of the system. The reaction rate could again be limited by any of the first three steps involving the outward transport of the reaction product, instead of the inward transport of the oxidizing species, namely oxygen.

Any of the four steps listed above could control the overall reaction rate. The rate limiting step is the one that has the lowest virtual maximum rate. If two or more steps have virtual rates of the same order, the reaction would be under a mixed control. It is not difficult to understand that the investigation of oxidation resistance is to find some materials and technique to avoid the carbon material from oxidizing environment and limit the diffusion of oxygen from oxidizing environment to the carbon substrate. Previous investigations made success in the protection of carbon materials from oxidation at lower temperatures by forming an oxide film on the surface of carbon materials. But it can not protect the materials from the diffusion of oxygen through the cracks or pores in the oxide film, especially at higher temperatures. For the investigation on oxidation resistance at higher temperatures, it is more concerned with the limiting of the diffusion of oxidation gases.

Consider first the diffusion across the boundary layer. The transport rate \( J \) across the boundary layer can be expressed from Fick's first law as

\[
J = -D \frac{\Delta C}{\delta}
\]  

(1-5)
where $\delta$ is the boundary layer thickness, and $\Delta C$ is the concentration gradient across it. The boundary layer thickness is a function of many variables, such as gas velocity, temperature, and pressure. The diffusion coefficient is also a function of many variables. Two variables of particular interest for oxidation in gas turbines are temperature ($T$) and pressure ($P$), which influence the gas phase diffusion coefficient in the following manner 

$$D_b \propto \frac{T^{3/2}}{P}$$

(1-6)

where $D_b$ is the bulk gas diffusivity, and the temperature $T$ is expressed in degrees Kelvin.

Considering diffusion through cracks and pores, the effective diffusion coefficient ($D_e$) is related to both the bulk ($D_b$) and Knudsen diffusivities ($D_k$) by the following relation,

$$(D_e)^{-1} = (D_b)^{-1} + (D_k)^{-1}$$

(1-7)

The Knudsen diffusivity through pores can be further expressed as

$$D_k = \frac{4}{3} \left( \frac{8RT}{\pi M} \right)^{1/2} \frac{L}{2}$$

(1-8)

where $r$ is the pore radius and $M$ is the molecular weight of the diffusing species.

Diffusion through cracks is somewhat more complicated than through pores. For diffusion through pores, the effective gas diffusivity is lower than bulk gas diffusivity due to collisions of gas molecules with the pore walls, which become important for small pore sizes. Whereas wall collisions can occur all along the pore, they can occur in cracks only along the width. Thus, for cracks with the same width as the diameter of pores, the wall collisions would be lower for cracks. Consequently, both the Knudsen and the effective gas diffusivities for cracks would be somewhat higher than for pores.

In the case of smaller pores or microcracks, the gas diffusion rate is limited by the Knudsen diffusion. Many investigations have been done to find some materials or technique to decrease or seal the pores and microcracks. Among those investigations, the effective one is the inhibition or coating base on $\text{B}_2\text{O}_3$ and $\text{SiO}_2$. 
1.3.3. General Mechanism of Inhibition on the Oxidation of Carbon Materials or C/C Composites.

The oxidation of C/C composite always begin at the active sites, pores, or along with the cracks of C/C composite[27-28]. Carbon materials have been inevitable to include cracks, stresses, pores and other defects with active sites due to the thermal expansion after graphitization. In these sites, carbon atoms have an active state with lower activation energy for oxidation. Once in the oxidizing atmosphere, they will react with oxygen atoms easily at relatively low temperatures. Oxidation inhibitor or coating will protect these defects from the attempt of oxygen.

The current researches in protective inhibition is based on the use of silicate and/or boride, primarily SiC and B4C, as the primary oxygen barrier. They are coupled with internal glass forming inhibitors, such as B2O3 and SiO2, which are used to seal thermal stress cracks and other defects arising from the difference of thermal expansion between coating and substrate. It is known that boride can be oxidized to form B2O3 easily in oxidizing atmosphere. B2O3 has much lower melting point at 450°C[20], although its boiling point higher than 1500°C. At about 800°C, B-rich glaze phase starts to form on the matrix surface. But the higher volatility and flow viscosity of B2O3 will be increased and decreased respectively with the increasing of temperature. That can increase the oxygen diffusion across the protective layer and damage the oxidation resistance of C/C composite. Silicate will be oxidized to SiO2 at about 1200°C. Formation of Si-rich glaze phase provide the protective layer again. It is impossible for one sealant to give a acceptable oxidation rate. This has led to the development of duplex protection. If some appropriate additives are contained, the temperature range of SiO2 dissolution in B2O3 can be enlarged[11]. A kind of relative impermeable protective layer will enhance the oxidation behavior of C/C composite at a larger temperature range from 600°C to 1400°C.

For all the reports on this field, the system used at present are able to provide protection reasonable well below 1400°C, but are inappropriate at higher temperatures owing to the volatilization of the glass sealant. Protective coatings of this type are particularly susceptible to thermal cycling and the effects of moisture, both of which may be lead to spalling.

The upper limit for the use of silicon ceramics is 1800°C[29]. Protective systems being capable of operating in the 1400°C-1800°C region are beginning to emerge, but a great deal of further research is still required. The long term goal of operating C/C composites at temperature above 1800°C in the oxidizing environments will require multi-layer coatings of a number of refractory materials if a good thermomechanical and chemical stability are to be achieved.
1.4. The Processing Technology of C/C Composites

In currently, there are a few kinds of processions to be adopted for fabrication and addition of inhibition additives into C/C composites:

1) Solid Phase Sintering Processing

The powder sintering processing is a general used processing in C/C composites production. Carbon fiber, matrix materials and addition powder mixed together. After grinding of the powder mixture and compacting it under a certain pressure, calcination and heat treatment at a certain temperatures in nitrogen or other non-oxidizing atmosphere are carried out in the way of a traditional method for making ceramics. The distribution of the protective depends strongly on the mixing and the size of the powder.

2) Gas Phase Impregnation

The chemical vapor deposition (CVD) method deposits pyrolitic carbon and other metalorganic polymers directly onto a fiber perform by thermal decomposition of a gas containing carbon or other elements. In the isothermal technique, which is by far the most prevalent CVD manufacturing processing, the fiber substrate is radiantly heated by an electrical resistance furnace, so that the gas and substrate are maintained at a uniform temperature. There is a tendency for preferential deposition on the sample's exterior surfaces. This results in the formation of a crust, requiring machining and multiple infiltration cycles. The processing difficulties associated with maintaining the thermal and pressure gradient methods mean that they are generally only employ to densify single artifacts. Many researches of composite coating have been used CVD technique[30-32]. However, CVD is extremely efficient at filling small pores but poor at filling large holes.

3) Liquid Phase Impregnation Processing

Liquid phase densification aims to exploit the technology developed for the conventional fiber-reinforced composites industry to produce components. This is followed by some forms of heat treatment to convert the polymer or oligomeric matrix to carbon. In the present investigation of oxidation resistance, the inhibitions or coatings, like B$_2$O$_3$, SiO$_2$ and polycarbosilane, were introduced by the technique of liquid phase impregnation such as sol-gel technique[1, 33-35].

With present researches on the C/C composites with high oxidation resistance, multilayer coating on the surface of C/C composites was reported[31]. That also gave rise to combination of the use of two or more processing. Wu and his colleagues used a combined processing of resin impregnation, CVD and reaction sintering to make an
oxidation resistant film on the C/C composite surface and showed the comparison among the different procedures\cite{36}.

### 1.5. Purpose of the Present Study

Although many programs have been made, very little progress were obtained in previous investigations of oxidation resistance for C/C composites. Especially at higher temperatures, simple additives or single protective layer are not enough to meet the needs of modern applications. The further improvement of oxidation resistance requires new protective coating system. This system includes choosing new materials for oxidation resistance, adapting new technique to improve efficiency of additives or coating and adjusting the layer structure for the multi-layer protection to improve the stability of protective layer in oxidation process. Therefore, the present study is emphasized on trying a multi-coating that included LaB$_6$-Si coating, polycarbosilane impregnating and SiO$_2$ coating by sol-gel technique to improve the oxidation resistance of C/C composite at the temperature range from room temperature to over 1200°C. In this study, the works are divided into following steps:

1. Oxidation behavior of C/C composite and its mechanical properties
2. Effects of LaB$_6$ coating on the oxidation of C/C composite
3. Effects of SiO$_2$ coating on the oxidation of C/C composite
4. Improvement of oxidation resistance of C/C composite at high temperature by LaB$_6$-Si/polycarbosilane/SiO$_2$
References

18. G. M. Mehrotra, Report 1991, Order No. AD-235958,
36. T. M. Wu, W. C. Wei, S. Hsu, Carbon, 29(1991), 1257
Chapter 2. EFFECT OF HEAT-TREATMENT

2.1. Introduction

The incentive to use C/C composites in high temperature structural materials evolves from the superior specific strength and enhanced service temperature capability of these composites. As described previously, C/C composite exhibits strength-density ratio in excess of superalloys and ceramics at temperatures above 1000°C. However, the rapid reaction of carbon with oxygen at temperatures as low as 500°C causes rapid degradation of the composites[1].

It is well known that carbon material reacts with many other materials. From a physical point of view reactions with oxygen are of particular interest, as they have been used to investigate structure features. For improving the oxidation resistance of C/C composites, most researches are focused on conducting many oxide or nonoxide compounds as glazes or diffusion-barrier coating with different processes[1-3]. Meanwhile, processing of C/C composites often requires a heat treatment for graphitization at temperatures above 2000°C to gain required dimensional-weight stability and fracture toughness. A few works were made on the effect of this treatment on the physical and mechanical properties, and oxidation behavior of C/C composites[4-6].

As the beginning study of the oxidation resistance of C/C composites, the basic physical properties and oxidation behaviors of C/C composites should be understood. In this chapter, the effects of heat-treatment on the volume density, porosity and the bending strength will be described. The changes of oxidation behavior of C/C composites resulting from graphitization up to 2700°C will also be described. Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and nitrogen adsorption (B.E.T.) techniques will be used to evaluated the changes of microstructure.

2.2. Experimental Procedure

2.2.1. Materials Processing

The C/C composites used in this study were manufactured by Nippon Carbon Company. Two kinds of C/C composites, commercial name CCM-190C and CCM-290C respectively, were used in the present study. CCM-190C was made from PAN-based carbon fibers and a carbonized phenolic resin impregnated matrix. CCM-290C was made from acrylic staple fibers and also a carbonized phenolic resin impregnated matrix. Both
kinds of C/C composites were woven in a two-dimensional fiber mat lay-up, as shown in Fig. 2.1 (a) and (b). The principle physical properties supplied by the company were summarized in Table 2.1. 2000°C heat-treatment was carried out for both as-received C/C composites. In order to understand the effects of heat-treatment, in this study, both kinds of C/C composites were treated at 2200°C, 2500°C, and 2700°C respectively for 1 hr in Argon (2.5 cm³/min).

![Morphologies of the C/C composites of 2-D fiber mat lay-up used in present study (a) CCM-190C and (b) CCM-290C](image)

Figure 2.1. Morphologies of the C/C composites of 2-D fiber mat lay-up used in present study (a) CCM-190C and (b) CCM-290C
Table 2.1. General physical properties of C/C composites in this study

<table>
<thead>
<tr>
<th></th>
<th>CCM-190C</th>
<th>CCM-290C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Density (g/cm³)</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>300</td>
<td>70</td>
</tr>
<tr>
<td>Bending Strength (MPa)</td>
<td>160</td>
<td>120</td>
</tr>
<tr>
<td>Compress Strength (MPa)</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>Resistivity (μΩ•cm)</td>
<td>2200</td>
<td>2500</td>
</tr>
<tr>
<td>Specific Heat (JKg⁻¹K⁻¹)</td>
<td>720</td>
<td>750</td>
</tr>
</tbody>
</table>

2.2.2. Test Procedure

The volume densities and porosity of both kinds of C/C composites were measured with Archimedes Method (in distilled water) at room temperature. The values of volume density (Dv) and porosity (Po) were calculated from the following equations,

\[
D_v = \frac{W_a}{(W_c - W_b)} \cdot D_w \quad (2-1)
\]

\[
Po = \frac{(W_c - W_d)}{(W_c - W_b)} \quad (2-2)
\]

where \(W_a\) is the sample weight after the sample was out of water, dried and then cooled to room temperature. \(W_b\) is the sample weight after the sample was soaked in boiled water and then cooled to room temperature. \(W_c\) is the sample weight after the sample was out of water and then cooled to room temperature. \(D_w\) is the density of water at room temperature. In the present experiment, the room temperature is 25.1°C, \(D_w = 0.9971\) g/cm³. The porosity calculated in this study is concerned with the open pores in C/C composites.

The bending strength was determined by four-point bending technique. The size of the sample used in bending test was about 4 x 5 x 40 cm, loading weight 500 N and crosshead speed 0.5 cm/sec. The values of bending strength (σb) were calculated from equation (2-3).
\[ \sigma_s = \frac{3P}{2wt^2}(L - l) \]  

(2-3)

where \( P \) is the maximum loading, \( w \) is the width of sample, \( t \) is the height of sample, \( L \) and \( l \) are support length and length of loading points that were 3 cm and 1 cm in present test, respectively.

Oxidation of both kinds of C/C composites with different heat-treatment temperatures were studied under programmed heating of up to 1200°C in flowing air (30 cm³/min dry air, 10 cm³/min nitrogen). The weight loss relative to temperature and time were carried out during the present experiment where the weight loss with temperature was done in the heating rate of 2.5°C/min. All the samples were made in size of 4 x 5 x 1.6 mm and cleaned ultrasonically in ethanol before oxidation. Data collection and temperature control proceeded with a computer.

For the C/C composites with different heat-treatment temperatures, specific surface areas and diameters of pores were measured by B.E.T. technique. All samples with different heat-treatment temperatures were characterized using XRD in CuKα and SEM. In order to understand the effect of heat-treatment on graphitization, values of \( Lc_{(002)} \) and \( d_{(002)} \) spacing were calculated in following equations,

\[ Lc_{(002)} = \frac{K\lambda}{\beta \cos \theta} \]  

(2-4)

and

\[ d_{(002)} = \frac{\lambda}{2 \sin \theta} \]  

(2-5)

respectively, where \( K \) is the Scherrer constant, \( \beta \) the real half-width of the XRD peak in the unit of radian, \( \lambda \) the wave length, \( \theta \) is Bragg angle.

2.3. Effect of Heat-treatment Temperature on Graphitization

Table 2.2 showed the calculation results of \( Lc_{(002)} \) and \( d_{(002)} \) from XRD analysis. With increase of heat-treatment temperature, the values of \( Lc_{(002)} \) increased and \( d_{(002)} \)
decreased for both kinds of C/C composites. Generally in the study of graphitization, the values of Lc(002) and d(002) response to the change of structural ordering of carbon materials or graphitization of carbon materials. Value of Lc(002) responds to the ordering range of carbon structure, and value of d(002) responds to the ordering degree of carbon structure. The improvement of the graphitization of carbon materials would give rise to the increase of both the ordering range and the ordering degree that would be represented by the increase of the value of Lc(002) and the decreasing of the value of d(002)\textsuperscript{[7]}. In the present study, improvement of graphitization was shown with the increase of heat-treatment temperature for both kinds of composites.

<table>
<thead>
<tr>
<th>Table 2.2. Results of XRD analysis on two kinds of C/C composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>H.T.T. (°C)</td>
</tr>
<tr>
<td>Lc(002) (Å)</td>
</tr>
</tbody>
</table>

2.4. Effects of Heat-treatment Temperature on the Physical and Mechanical Properties

Figure 2.2 showed the dependence of volume density of both kinds of C/C composites with heat-treatment temperatures. The values of volume density of CCM-190C was shown to be higher than that of CCM-290C. With the increase of heat-treatment temperature, the value of volume density of both CCM-190C and CCM-290C were shown to enhance slightly. Figure 2.3 showed the changes of porosity of two kinds of C/C composites with heat-treatment temperatures. Considerable increase of the porosity for both C/C composites was shown with the increase of heat-treatment temperature. Generally, the porosity of CCM-290C was shown to be higher than that of CCM-190C. It is known that C/C composite is a kind of porous material. Along with the improvement of graphitization, a slight increase of the density raised from the densification of the composite. Meanwhile, the generation of cracks or pores induced an increase of the porosity.
EFFECT OF HEAT-TREATMENT

**Fig. 2.2.** Changes of volume densities of C/C composites with the increase of heat-treatment temperature

**Fig. 2.3.** Change of porosities of C/C composites with the increase of heat-treatment temperature
Figure 2.4 was the dependence of bending strength with heat-treatment temperature. A significant decreased tendency was shown for both C/C composites with increase of heat-treatment temperature. The parameter of bending strength is sensitive to the microstructure of materials, such as impurities and cracks. For composite materials, the bending strength is not only depended on the strength of fiber and matrix material, but also depended on the strength of the combination of fibers and matrix. In spite of improvement of graphitization that would generally benefit for enhancing of bending strength of carbon materials, the bending strength of C/C composites decreased with the significant increase of pores or cracks, as shown in Fig. 2.3.

Fig. 2.4. Changes of bending strength of C/C composites with the increase of heat-treatment temperature

Meanwhile, two kinds of fracture behaviors were observed in present experiments, as shown in Fig. 2.5 (a) and (b). For CCM-190C, the fracture is likely due to the pullout of fibers that the crack extended along with fibers. For CCM-290C, a typical brittle fracture of brittle material was shown that the crack crossed the fibers and matrix. Figure 2.6 (a) and (b) showed load-displacement curves for CCM-190C and CCM-290C, respectively. In case of CCM-190C, the nonlinear loading curve first became evident at about 90% of the fracture load and the stepping effect as the loading decreases after the peak fracture load, as shown in Fig. 2.6 (a). In case of CCM-290C, a linear loading
curve and sudden crack down were shown in Fig. 2.6 (b). It was recognized that the area under the loading curve was responded to the toughness of material\[8-10\]. From this different of fracture behaviors, better toughness was shown in CCM-190C and better bending strength in CCM-290C.

Figure 2.5. Morphologies of the fractures of two kind C/C composites (a) CCM-190C and (b) CCM-290C
Figure 2.6. Load-displacement behaviors of two kind C/C composites
(a) CCM-190C and (b) CCM-290C
2.5. Effect of Heat-treatment Temperature on Oxidation Behaviors

2.5.1. General Oxidation Behavior of C/C Composites with Different Heat-treatment Temperatures

Generally, it is reasonable to consider that the graphitization of C/C composites were improved with increase of heat-treatment temperature in present experiments. The improvement of graphitization would give a relative stable microstructure for C/C composites that would be benefited for the oxidation resistance of these composites. However, oxidation resistance of carbon materials is not simply dependent on graphitization of carbon materials only.

Figure 2.7 and Figure 2.8 showed the oxidation of CCM-190C and CCM-290C with different heat-treatment temperatures. The oxidation for both kinds of composites occurred appreciably at about 550°C-600°C. The anomalous oxidation resistance with heat-treatment temperatures were found for both kinds of C/C composites. For both kinds of C/C composites, the C/C composites heat-treated at 2200°C and 2700°C were shown the best oxidation resistance and the one heat-treated at 2000°C was the worst. Obviously, the improvement of oxidation resistance was not agreement with the improvement of graphitization of C/C composites. Figure 2.9 (a) and (b) showed the SEM photos of CCM-190C and CCM-290C after oxidation (response to 30-40 wt% weight loss). It was clear that the oxidation of fibers were faster than that of matrix for CCM-190C, while for CCM-290C, the oxidation of matrix were faster than that of fibers. For both kinds of composites, it was found that corrosion pits distributed on fibers and matrix. This is meaning that oxidation reaction would begin at the active sits in the structure of carbon. In fact, the improvement of oxidation resistance for non-protective carbon materials is depended on the decrease of active sits in carbon materials for reacting with oxygen\(^\text{[11]}\). Many factors would affect the number of active sits in carbon materials, such as graphitization, pores, impurities, defects and stress. In the present experiment, the increase of heat-treatment temperature gave a improvement of graphitization of C/C composites and benefited the decrease of impurities and defects in the composites that would give rise to decrease of active sits. Meanwhile, the porosity was increased, as shown in Fig. 2.3, that would give rise to increase of active sits due to the increase of effective surface for oxidation reaction. There were two contradictory factors to affect oxidation behaviors of C/C composites with the increase of heat-treatment temperature. It was considered that these contradictious factors made the anomalous oxidation behaviors with the increase of heat-treatment temperature, as shown in Fig. 2.7 and 2.8.
Fig. 2.7. Weight loss of C/C Composites (CCM-190C) with different heat-treatment temperature, air flow 30 cm$^3$/min, rate of rising temperature 2.5°C/min
Fig. 2.8. Weight loss of C/C Composites (CCM-290C) with different heat-treatment temperature, air flow 30 cm$^3$/min, rate of rising temperature 2.5°C/min
It was interested to notice that, for both kinds of composites, the oxidation behaviors at lower temperature range (below 800°C) were different with that at higher temperature. Below 800°C, in the case of CCM-190C, the worst oxidation resistance was shown in the C/C composite heat-treated at 2500°C instead of the one heat-treated at 2000°C; in the case of CCM-290C, the C/C composite heat-treated at 2000°C was shown the best oxidation resistance and the one heat-treated at 2200°C was shown to be the worst. This difference were shown clearly in Figure 2.10 and 2.11 that were the relationship between weight loss and time for CCM-190C and CCM-290C at 780°C, respectively. It was considered
that there was still a serious effect at the beginning of oxidation. This effect would decrease with the proceeding of oxidation and had an anomalous change with the increase of heat-treatment temperature.

Fig. 2.10. Isothermal oxidation of C/C Composite (CCM-190C) with different heat-treatment temperatures, Air 30 cm$^3$/min, at 780°C.

Fig. 2.11. Isothermal oxidation of C/C Composite (CCM-290C) with different heat-treatment temperatures, Air 30 cm$^3$/min, at 780°C.
2.5.2. Effect of Strain-stress on Oxidation Behavior of C/C Composites with Different Heat-treatment Temperatures

Figure 2.12 (a) and (b) showed the SEM photographs of CCM-290C with 2000°C and 2200°C heat-treatment after oxidation (weight loss about 10 wt%). For the one heat-treated at 2200°C, it was found that the microcracks existed in carbon matrix and these microcracks were usually located nearby fibers. The traces of oxidation corrosion principally gathered in the microcracks areas, as shown in Fig. 2.13.

Figure 2.12. Morphologies of the C/C composites with different heat-treatment temperatures, (a) at 2000°C and (b) at 2200°C, after about 10 wt% weight loss in air flow
As described above, with the improvement of graphitization, ordering of carbon atoms was undergone along with the increase of porosity and cracks. This ordering of carbon atoms would give rise to strain or stress in the microstructure of carbon material\textsuperscript{[7]}. For the strain-stress behavior with the graphitization, an empirical theory was developed by Jenkins\textsuperscript{[12-13]}. The relationship of strain-stress was represented as following,

\[ \varepsilon = A\sigma + B\sigma^2 \text{ (when } \varepsilon < \varepsilon_m \text{ or } \sigma < \sigma_m \text{)} \quad (2-6) \]

The removal of this stress gives a relationship as following,

\[ \varepsilon_m - \varepsilon = A(\sigma_m - \sigma) + \frac{1}{2} B(\sigma_m - \sigma)^2 \quad (2-7) \]

where \( \varepsilon \) and \( \sigma \) are strain and stress, \( \varepsilon_m \) and \( \sigma_m \) are the maximum strain and the concerned stress, \( A \) and \( B \) are constants independently of the specimen history, but are depended on conditions of stress and temperature. From equation (2-7), it is not difficult to understand that the stress would be released when stress \( \sigma \) was up to \( \sigma_m \). According to the Griffith fracture theory, a release of stress would induce an increase of surface energy that was...
meaning the generation of microcracks or the extension of microcracks[14]. Considering the subsequent strain up to the previous maximum after a release of stress, the relationship of strain-stress was given by

\[ \varepsilon - \varepsilon_0 = A\sigma + B\sigma^2 \]  

(2-8)

where \( \varepsilon_0 \) is the reminded strain after removal of the stress. From the equations above, it is easy obtained

\[ \varepsilon_0 = \frac{1}{2} B\sigma_m^2 \] and \( \varepsilon_m - 2\varepsilon_0 = A\sigma_m \)  

(2-9)

Obviously, the change of stress was anomalous with the improvement of the graphitization of carbon material. With the improvement of graphitization, the value of strain would change repeatedly from \( \varepsilon_0 \) to \( \varepsilon_m \). Figure 2.14 shown the possible behavior of microcrack with increase of heat-treatment temperature. With Assumption that the shape of microcracks just like that shown in Figure 2.13, \( \sigma_i, \varepsilon_i \), and \( \omega_i \) were the initial strain, stress and width of microcrack in as-received sample. With increase of heat-treatment temperature, when \( \sigma_i < \sigma < \sigma_m \) or \( \varepsilon_i < \varepsilon < \varepsilon_m \), graphitization of carbon would increase of stress and strain that gave rise to the increase of the width of microcrack, \( \omega > \omega_i \). When \( \sigma = \sigma_m \) or \( \varepsilon = \varepsilon_m \), stress would be released by the extension of microcrack and \( \sigma \) or \( \varepsilon \) would decrease to \( \sigma_0 \) or \( \varepsilon_0 \). Whereas, the width of microcrack would decrease from the maximum value (\( \omega_m \)) to a lower value \( \omega_0 \) that was responded to \( \varepsilon_0 \).

To the oxidation of carbon material, higher stress or larger strain would give an increase of the concentration of active sites that decreased the oxidation resistance of carbon material. However, this effect would decrease with the proceeding of oxidation due to the change of the surface area and the structural loss of carbon material. In order to understand the change of strain or stress with heat-treatment temperature, the average pore size was measured by B.E.T. technique. Table 2.3 shown the changes of density (D), specific surface area (Sa), pore volume per gram (V) and average pore radius (R). Because the variety of pores and cracks in C/C composite, the value of R was not directly equal to the width of microcrack in the composite. However, it qualitatively represent the
Fig. 2.14. Simulation of the extension of microcracks in carbon material with the increase of heat-treatment temperature.
Table 2.3. Results of B.E.T. analysis on two kinds of C/C composites

<table>
<thead>
<tr>
<th></th>
<th>CCM-190C</th>
<th>CCM-290C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H.T.T. (℃)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>1.924</td>
<td>1.933</td>
</tr>
<tr>
<td>2200</td>
<td>1.987</td>
<td>1.977</td>
</tr>
<tr>
<td>2500</td>
<td>2.155</td>
<td>2.040</td>
</tr>
<tr>
<td>2700</td>
<td>2.240</td>
<td></td>
</tr>
<tr>
<td><strong>D (g/cm³)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.26</td>
<td>19.80</td>
<td>10.75</td>
</tr>
<tr>
<td>15.09</td>
<td>15.75</td>
<td>13.77</td>
</tr>
<tr>
<td>14.99</td>
<td>21.15</td>
<td>27.13</td>
</tr>
<tr>
<td>17.62</td>
<td>17.62</td>
<td>17.62</td>
</tr>
<tr>
<td><strong>V (cm³/g)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>0.22</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>R (μm)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>0.06</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>0.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tendency of the change of microcrack width. Comparing Fig. 2.10 and 2.11 with data in Table 2.3, it was found that the higher value of R were responded to the worse oxidation resistance and the lower value of R to the better oxidation resistance for both kinds of C/C composites. With the description above, it is most likely that the change of stress or strain in the composites by graphitization gave the most important effect on the oxidation of C/C composites at lower temperature. In spite it is impossible to establish a strict mathematical relationship simply between oxidation and stress, because there are many other factors to affect the oxidation behavior, such as impurities and network structure, and these factors would influence each other within the oxidation process. With the data in present study, it was believed that an important effect of strain or stress in graphite structure was existed on the oxidation of C/C composites with different heat-treatment temperatures.

2.6. Conclusion

Two kinds of C/C composites (CCM-190C and CCM-290C) was undergone by the heat-treatment at 2000℃, 2200℃, 2500℃ and 2700℃. XRD characterization showed the increase of Lc(002) and the decrease of d(002) with the increase of heat-treatment temperature. It was evident that the graphitization of C/C composites were improved with enhanced heat-treatment temperature. Along with the improvement of graphitization, the volume densities of C/C composites increased with densification proceeding of carbon and the porosity tended to increase with generation of cracks. With the increase of heat-treatment temperature, the bending strength for two kind composites tended to decrease due to the increase of cracks.
The effect of heat-treatment temperature on the oxidation behaviors of C/C composites was discussed in this study. With improvement of graphitization by increasing of heat-treatment temperature, contradiction effects on oxidation behaviors of C/C composites were generated. The ordering of structure was benefit to lowering active sites; whereas, the increase of cracks and the generation of stress increased active sites and the concentration of active sites. With the contradictory effects, anomalous oxidation behaviors with the increase of heat-treatment temperature were shown in the present study. Generally, the C/C composites heat-treated at 2200°C and 2700°C were shown the best oxidation resistance and the one heat-treated at 2000°C was the worst.

With theories of Griffith and Jenkins and the data from measurement by B.E.T. method, the effects of strain-stress were analyzed on the oxidation behaviors at lower temperature. It is suggested that the oxidation behavior of C/C composites at lower temperature were considerably influenced by the repeatedly change of strain-stress with increasing of heat-treatment temperature. In spite it was difficult to establish a simple relationship between oxidation and the change of strain-stress, a qualitative analysis was applied to explain this relationship in this experiment.
References

Chapter 3. IMPROVEMENT OF THE OXIDATION RESISTANCE OF THE LaB₆-COATED C/C COMPOSITES

3.1. Introduction

Many investigations\(^1\) have been reported on oxidation behavior of carbon materials including C/C composites with and without antioxidation treatments. In the case of unprotected C/C composites, it was suggested that the enhancing graphitization of C/C composites would improve oxidation resistance of C/C composites\(^1\). The oxidation rate was controlled by diffusion of oxygen above 1000°C with the apparent activation energy about 10-16 kJ/mol and by chemical reaction below 700°C with the apparent activation energy of 140-180 kJ/mol. In the intermediate temperature range, the oxidation rate was controlled by both chemical reaction and the diffusion of oxygen. The transition temperature moved to higher temperature with the increase of heat-treatment temperature\(^2\)\(^-\)\(^6\).

In the case of coated C/C composite, the oxidation processes include gas-phase diffusion across the boundary layer at the surface, diffusion through cracks, diffusion through the protective condensed phase and chemical reaction at the interphase between oxide and substrate. It was reported that a few materials, like B₂O₃ and P₂O₅, really retard the rate of oxidation of carbon. However, most compounds and metals are regarded as catalysts and can lower the oxidation kinetics at the temperatures up to 700°C and 850°C for long-term and short-term applications\(^9\). B₂O₃ is not stable at higher temperatures because of its high volatility. Greene and Margrave calculated the values of the vapor pressures for various boron oxide species based on thermodynamic data\(^10\). The results of their works suggested that the vapor pressure of HBO₂ was over 1 mmHg (at P₁₁₀ = 1 atm) at 900°C; the vapor pressure of B₂O₃ was about 10⁻² mmHg at 1000°C and 1 mmHg at 1400°C.

To find protective materials with high temperature strength and stability for carbon materials, metal borides have been investigated in many works\(^11\)\(^-\)\(^14\). With inspecting the previous investigations, it was not found that lanthanum boride had been used as a protective coating on C/C composites. It had been reported the additions of lanthanum or lanthanum boride would affect on the graphitization of carbon materials after high temperature treatment\(^15\)\(^-\)\(^16\). In this chapter, lanthanum boride was coated on the C/C composites and heat-treated at 500°C and 2000°C, respectively. With the kinetic calculation, the oxidation behaviors of the C/C composite coated with lanthanum boride were discussed. The effects of diffusion of lanthanum and boron to the C/C composites were also discussed with XRD and energy dispersion X-ray analysis (EDX).
3.2. Fabrication of the LaB₆ Coating on C/C Composite

The C/C composites of CCM-290C with the final heat-treatment of 2200°C was used in this study. Lanthanum boride powder (Lot. No. 89305) with a median size of 2.06 µm was received from Japan New Metals Company. For the coating of lanthanum boride (LaB₆), the LaB₆ slurry was made by mixing LaB₆ powder with polyethylene (a binder) in the volume ratio of 1:10. The amorphous boron powder (Lot. No. 40729-84) with a median size of 1.73 µm was obtained from Rare Metallic Co. Ltd.

Figure 3.1 showed the process chart of LaB₆-coated C/C composites. The C/C composites were cut with a diamond wheel into specimens with the size about 4.0 x 5.0 x 1.6 mm. All the specimens were dipped in LaB₆ slurry and dried at 300°C. Then the C/C specimens were divided into two groups; one group of the specimens was heated at 500°C (C/C-LaB₆-LT), another group was heated at 2000°C (C/C-LaB₆-HT). In the present experiments, the additive weight of LaB₆ was about 8 wt%.

Measurements of the weight change by oxidation for the composites with and without LaB₆ were carried out in a vertically mounted furnace in flowing air between 700°C and 1200°C. The specimen was held in a platinum wire cage suspended on steel wire links from the mass balance. After loading the specimen, the chamber was purged.
with argon until the desired reaction temperature was reached. When the temperature reached the preset value, the argon was turned off and dry air with a flowing rate of 30 cm³/min was turned on to begin the oxidation reaction. The control of the furnace temperature and the collection of kinetic data were carried out with a computer. The oxidation rate was calculated in \( \ln(\frac{\Delta W}{W_0}) \), as a function of reciprocal temperature, \( \frac{1}{T} \) K⁻¹, where \( W_0 \) is the initial weight of the C/C composite (about 49 mg). At the initial stage, the reaction chamber was not equilibrated with air and the relationship between the weight loss and the time was nonlinear. Thus, in this work, the reaction rate was calculated after 10 wt% oxidation had taken place, when a linear relationship was observed\(^{31}\).

In order to understand the effects of LaB₆ on graphitization of the carbon material, the C/C composites added with LaB₆ were characterized by Energy Dispersion X-ray analysis (EDX, 20 kV) and X-ray diffraction analysis with CuKα radiation at 30 kV and 20 mA. The quantitative analysis of X-ray was also carried out in this work. The conditions of quantitative X-ray analysis were divergence and scattering slit of 1/6°, receiving slit of 0.15 mm, time constant of 4 sec., scale factor of 8 and multiplier of 1.0. The values of \( Lc(002) \) and \( d(002) \) were calculated in \( \frac{K\lambda}{\beta \cos \theta} \) and \( \frac{\lambda}{2 \sin \theta} \), respectively, where \( K \) is the Scherrer constant, \( \beta \) the line width at half maximum intensity, \( \lambda \) the wave length and \( \theta \) the Bragg angle.

3.3. Oxidation of the LaB₆ in Flowing Air

In order to understand oxidation behavior of LaB₆, the weight changes of LaB₆ and amorphous boron powders were measured under the same conditions in air. Figure 3.2 shows the weight changes of LaB₆ powder and boron powder with temperature in flowing air of 30 cm³/min at the heating rate of 2.5°C/min. It was shown that two materials varied obviously in oxidation behavior.

It is observed that boron powder began to oxidize about 300°C, while LaB₆ powder began to oxidize about 500°C. The rate of the weight gain for boron powder became fastest at the temperature range between 500°C and 600°C. The weight change indicated that boron powder was completely converted to oxides at about 1100°C. The oxidation product, B₂O₃, lowered the rate of weight gain at the temperature range from 600°C to 1000°C. Above 1000°C, the rate of weight change was affected by the volatilization of boron oxide. On the other hand, the fastest rate of weight gain of LaB₆ powder was
observed at the temperature range between 700°C and 800°C. Similarly, oxidation products lowered the rate of weight gain at the temperature range from 800°C to 1000°C. Above 1100°C, the rate of volatilization of B₂O₃ was almost balanced by the rate of conversion of LaB₆ to lanthanum oxide and B₂O₃. LaB₆ powder was completely oxidized at about 1300°C. A higher resistance against oxidation was observed obviously for LaB₆.

![Graph showing weight gain of boron and LaB₆ powder in flowing air](image)

**Fig. 3.2.** Weight gain of boron and LaB₆ powder in flowing air (30 cm³/min)

### 3.4. Diffusion of Lanthanum and Boron

With the analysis of XRD, it was not found that carbides of lanthanum or boron appeared in both C/C composites coated LaB₆ at 500°C and 2000°C, C/C-LaB₆-LT and C/C-LaB₆-HT, except the diffraction peaks of LaB₆ and graphite. Figure 3.3 showed the X-ray diffraction pattern of C/C-LaB₆-HT. Figure 3.4 (a) and (b) showed the results of EDX analysis for C/C-LaB₆-LT and C/C-LaB₆-HT. In case of C/C-LaB₆-LT, it was observed that LaB₆ powder was located on the surface of C/C composite and the thickness of the layer of LaB₆ powder was about 20μm. Serious pores were found in the layer of LaB₆ powder. The concentration profile of lanthanum indicated that LaB₆ did not exist inside of the C/C composite, as shown in Fig. 3.4 (a). Different with the case of
Fig. 3.3. X-ray diffraction pattern of the C/C composite coated with LaB₆ at 2000°C (C/C-LaB₆-HT)

Fig. 3.4. Results of EDX analysis of the C/C composites coated with LaB₆ at different temperatures: (a) at 500°C (C/C-LaB₆-LT), (b) at 2000°C (C/C-LaB₆-HT)
The effect of the diffusion of lanthanum and boron on the graphitization of the C/C composite was investigated with XRD analysis. Table 3.1 showed the values of $L_c(002)$ and $d_{(002)}$ of C/C-LaB$_6$-HT comparing with the values of the uncoated C/C composites with different heat-treatment temperatures. With the increase of heat-treatment temperatures, values of $L_c(002)$ and $d_{(002)}$ of the uncoated C/C composites tended to increase and decrease respectively. Comparing to that of the uncoated C/C composite with 2200°C heat-treatment, both values of $L_c(002)$ and $d_{(002)}$ of C/C-LaB$_6$-HT were observed to be enhanced.

The graphitization of carbon materials would enhance the oxidation resistance because the structure of carbon materials became stable\cite{11-21}. It has been known that ordered structure and non-ordered structure coexisted in graphitized carbon materials and the structural change from ordering structure to non-ordered structure is continuous. In the X-ray analysis of graphitization, the value of $L_c(002)$ is relative to the size of graphitic domain or the range of the ordered structure; the value of d-spacing is relative to the interplanar distance of the layer structure of graphitic domain. If only considering the effect of heat-treatment temperature on the graphitization, the improvement of the graphitization of carbon materials would give rise to the increase of the value of $L_c(002)$ and the decreasing of the value of $d_{(002)}$. While, in the case of the effect of impurities on the

<table>
<thead>
<tr>
<th>Temp.*</th>
<th>2000°C</th>
<th>2200°C</th>
<th>2500°C</th>
<th>2700°C</th>
<th>2200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_c(002)$ (Å)</td>
<td>280</td>
<td>280</td>
<td>540</td>
<td>590</td>
<td>320</td>
</tr>
<tr>
<td>$d_{(002)}$ (Å)</td>
<td>3.415</td>
<td>3.404</td>
<td>3.373</td>
<td>3.369</td>
<td>3.450</td>
</tr>
</tbody>
</table>

* "Temp." is corresponding to the final treatment temperature of the C/C composites.
3.5.1. Oxidation Resistance of the C/C Composite Coated with LaB₆ at 500°C

The weight changes with temperature in air for the uncoated C/C composite and the C/C-LaB₆-LT were shown in Fig. 3.5. The curve of the C/C-LaB₆-LT apparently shifted about 150°C to higher temperature side. The X-ray diffraction profiles of the C/C-LaB₆-LT before and after oxidation was shown in Fig. 3.6. Before oxidation, only graphite and LaB₆ were found in the specimens. After oxidation, graphite was burned off and LaB₆ was converted to La-B-O oxides that were showed the weak and the broad peaks at angles between 10° and 25° in 2θ. The Arrhenius plots of the oxidation rate for the uncoated C/C composite and the C/C-LaB₆-LT were shown in Fig. 3.7. Two steps of oxidation rates were observed with transition temperature about 900°C for both specimens. As many other investigators reported that the rate-limiting step for the oxidation of C/C composites...
OXIDATION OF LaB₆-COATED C/C COMPOSITE

Fig. 3.5. Weight loss with temperature of the uncoated C/C composite and C/C-LaB₆-LT in flowing air (30 cm³/min)

Fig. 3.6. X-ray diffraction patterns of C/C-LaB₆-LT before and after oxidation
at low temperature range is relative to the chemical reaction on the carbon surface. The oxidation rate at high temperature range becomes controlled by oxygen diffusion through pores and adsorption at active sites. This gives a lower activation energy as the temperature increases. From the Arrhenius plots in Fig. 3.7, the values of apparent activation energies were estimated to be about 125 kJ/mol at lower temperature and about 20 kJ/mol at higher temperatures for the uncoated C/C composite, and about 160 kJ/mol at low temperature and about 75 kJ/mol at high temperature for the C/C-LaB$_6$-LT.

The addition of LaB$_6$ effectively decreased the oxidation rate of the C/C composite at the temperatures below 1000°C. As shown in Fig. 3.2, LaB$_6$ was almost all, at least partially, converted to lanthanum oxide and B$_2$O$_3$ at the temperature range between 700°C and 800°C. The stable lanthanum oxide is known not to be an active catalyst for carbon oxidation and boron oxide is a potent inhibitor$^{15-17}$. It is likely that above 500°C molten B$_2$O$_3$ formed from the LaB$_6$ particles and blocked active sites on the carbon surface that would be oxidized rapidly. Comparing with the oxidation behavior of the uncoated C/C composite, the effect of oxidation resistance still existed above 900°C for the C/C-LaB$_6$-LT. The reason was the vaporization of B$_2$O$_3$ and the film of molten B$_2$O$_3$ was formed due to complete oxidation of LaB$_6$ particles$^{17}$. This became the barrier for the diffusion of oxygen to the surface of the C/C composite and enhanced the apparent
activation energy of oxidation.

In this work, no attempt has been made to measure the isothermal oxidation rates quantitatively as the observed kinetics would obviously depend on such physical factors as surface area, crystal structure and stoichiometry, which would vary from one preparation to another. Nevertheless, the general conclusions can be made that LaB₆ began to oxidize at the temperature about 500°C and converted completely to the oxides at the temperature about 1300°C. In the flowing air, LaB₆ converted to the stable oxides including lanthanum that was not catalytically active to the oxidation of C/C composite. With the presence of boron oxide, LaBo showed effective resistance to oxidation and this effect would give a more stable structure of the C/C composites and lower active sites in the C/C composite. Thus, much higher value of the apparent activation energy of oxidation at lower temperatures was expected for C/C-LaB₆-HT, about 210 kJ/mol, as shown in Fig. 3.10. At higher temperatures, the Arrhenius plots were almost parallel between the plots of C/C-LaB₆-HT and C/C-LaB₆-LT. The value of the apparent activation energy of C/C-LaB₆-HT was calculated to be about 80 kJ/mol. Similar to the case of C/C-LaB₆-LT, because of the oxidation of LaB₆ particles, the forming of the film of molten B₂O₃ and the appearance of volatilization of B₂O₃ retarded the diffusion of oxygen to the C/C composite. While in the case of C/C-LaB₆-HT, more complete coating layer was formed due to the diffusion of lanthanum and boron on the surface of C/C composite. That induced further lower diffusion rate of oxygen and shifted the transition temperature to 825°C.

3.5.2. Oxidation Resistance of the C/C Composite Coated with LaB₆ at 2000°C (C/C-LaB₆-HT)

The isothermal oxidation at 700°C and 1000°C for the untreated C/C composite, the C/C-LaB₆-LT and C/C-LaB₆-HT were shown in Fig. 3.8 and Fig. 3.9, respectively. Comparing to C/C-LaB₆-LT, the further improvement on oxidation resistance was illustrated by C/C-LaB₆-HT. An analogous set of Arrhenius plots was shown in Fig. 3.10 to compare the oxidation behavior of C/C-LaB₆-HT with that of C/C-LaB₆-LT. As discussed above, the diffusion of LaB₆ improved the graphitization of C/C composite and formed the diffusion layer beneath the surface of the C/C composites. It is suggested that this effect would give a more stable structure of the C/C composites and lower active sites in the C/C composite. Thus, much higher value of the apparent activation energy of oxidation at lower temperatures was expected for C/C-LaB₆-HT, about 210 kJ/mol, as shown in Fig. 3.10. At higher temperatures, the Arrhenius plots were almost parallel between the plots of C/C-LaB₆-HT and C/C-LaB₆-LT. The value of the apparent activation energy of C/C-LaB₆-HT was calculated to be about 80 kJ/mol. Similar to the case of C/C-LaB₆-LT, because of the oxidation of LaB₆ particles, the forming of the film of molten B₂O₃ and the appearance of volatilization of B₂O₃ retarded the diffusion of oxygen to the C/C composite. While in the case of C/C-LaB₆-HT, more complete coating layer was formed due to the diffusion of lanthanum and boron on the surface of C/C composite. That induced further lower diffusion rate of oxygen and shifted the transition temperature to 825°C.
Fig. 3.8. Weight loss with time of the C/C composites with and without LaB₆ coating, at 700°C, in flowing air (30 cm³/min)

Fig. 3.9. Weight loss with time of the C/C composites with and without LaB₆ coating, at 1000°C, in flowing air (30 cm³/min)
3.6. Conclusion

In this study, LaB$_6$ has been used as protective coating material to be fabricated on the C/C composites. With the TG analysis, it was shown that LaB$_6$ began to oxidize at the temperature about 500°C and converted completely to the oxides at the temperature about 1300°C. In the flowing air, LaB$_6$ converted to the stable oxide of lanthanum oxide that was not catalytically active to the oxidation of C/C composites. In the case of C/C composite coated with LaB$_6$ at 500°C, LaB$_6$ showed effective resistance to oxidation below 900°C, due to the boron oxide blocking the active sites on the carbon surface. This effect extended above 1000°C with the formation of the oxide film of lanthanum and boron. Under the present experimental conditions, the apparent activation energies were calculated to be 160 KJ/mol at lower temperatures and about 75 KJ/mol at higher temperatures.

In the case of the C/C composites coated with LaB$_6$ at 2000°C, the diffusion layer of lanthanum with thickness of about 10 μm was found beneath the surface of C/C composite by EDX analysis. With the XRD and TG analysis, it was applied that the diffusion of lanthanum and boron was benefit for the structural ordering of carbon and removed the active sites in the C/C composites. A further improvement of oxidation
resistance was shown with the apparent activation energies of 210 kJ/mol at lower temperatures and 80 kJ/mol at higher temperatures.

The simple and traditional technique, dip-coating in LaB₆ slurry and heat-treatment at high temperature, was used to fabricate the LaB₆ coating on C/C composites. The cracks and pores in the coating and C/C composite could not be completely sealed by this technique. The experimental results in this study suggested that the effective resistance of LaB₆ retarded the oxidation of C/C composites, but did not protect the C/C composites from the onset of oxidation completely.
References

12. W. Mackee, Carbon, 26(1986), 659
17. D. W. Mckee, Carbon, 24(1986), 331
4.1. Introduction

Advantages of sol-gel processing for glass and glass-ceramics are well documented in the literature. Sol-gel processing is especially ideal for composites fabrication because of the ease with which fibers can be impregnated with a matrix. Furthermore, fiber performs in net shape can easily be infiltrated with liquid matrix, thereby alleviating the undesirable need for impregnated tows or fabrics.

The use of glasses and glass-ceramics as the matrix phase or coating in composites is attractive because of their good flowing ability during densification and oxidation\[1-3\]. However, the conventional slurry processing is not amenable to net shape fabrication. Moreover, it requires a higher process temperature than does sol-gel processing. A higher process temperature increases the possibility of fiber degradation and detrimental fiber/matrix/coating interfacial reactions\[4-6\].

Sol-gel processing is not without some disadvantages\[4\]. Compared with powder processing, starting materials are more expensive and densification is accompanied by greater shrinkage. Also, the sol-gel processing requires a longer process cycle time and some of the ingredients used may need more stringent health precautions. It usually takes about 2 to 3 hr to prepare a solution and an additional 5 to 24 hr to age and dry the resulting gel\[5-7\].

To carbon materials, several literature mentioned that sol-gel would be possibly potential technique to improve protective coatings to oxidation\[8-11\]. It had been not found to protect C/C composite from oxidation by using sol-gel processing. This chapter described a sol-gel processing technique that had been used to process a silicon oxide coating on C/C composite. It also described the oxidation behaviors of SiO₂-coated C/C composites with different concentrations of precursor solutions. The changes of structure and phases were characterized by SEM and XRD analysis.

4.2. Fabrication of the SiO₂ Coating

4.2.1. Preparing of Precursor Solutions

In present study, the conventional method was used to prepare the precursor solution.
Equal mols of tetraethoxysilane [Si(OC₂H₅)₄] (Kadayama Kagaku Industry LTD., 95 wt%, No. 09-2460) and ethanol solvent (C₂H₅OH) (Wako Junyaku Industry LTD., 99.5 wt%, No. 057-00451) was mixed and stirred at room temperature. Diluted water (H₂O), which included 6.3 wt% HN₃ (Wako Junyaku Industry LTD., 70 wt%, No. 143-01326) as catalyst of hydrolysis, was added into the precursor solution, the mole ratio of H₂O/Si(OC₂H₅O)₄ being 5. The solution obtained was warmed and held at 65°C for 45 min for partial hydrolysis. Then a monophase and transparent solution was formed. With the requirement of this study, the precursor solutions of different concentrations was made by diluting of C₂H₅OH, as shown in Table 4.1.

Table 4.1. Precursor Solutions Used in This Study

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>Si(OC₂H₅)₄ (mol.)</th>
<th>C₂H₅OH (mol.)</th>
<th>H₂O* (mol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>1</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>No. 2</td>
<td>1</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>No. 3</td>
<td>1</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>No. 4</td>
<td>1</td>
<td>22.5</td>
<td>5</td>
</tr>
<tr>
<td>No. 5</td>
<td>1</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>No. 6</td>
<td>1</td>
<td>30</td>
<td>5</td>
</tr>
</tbody>
</table>

* H₂O contains 6.3 wt% HN₃

4.2.2. Materials Used for Dip Coating

The C/C composite used for dip coating was CCM-290C as described in Chapter 2, the final heat-treatment temperature was 2200°C in argon. Before the C/C composites used in this experiment, dip coating of SiO₂ was carried out on carbon material that was made from pitch carbon and phenol (both supplied from Nippon Carbon Co.). As shown in Fig. 4.1, pitch carbon was heat-treated firstly at 500°C in nitrogen for 2 hr. After milling into powder, the sample of carbon material was pressed in size of 41.4 x 6.4 x 4.8 mm under 330 kgf/cm². The carbon samples were carbonized at 1000°C for 2 hrs in nitrogen, then impregnated in the phenol solution under 6.8 x 10⁻³ Kgf/cm² for 10 mins. The phenol solution was made of phenol and ethanol in volume ratio of phenol/ethanol 1:5. Four cycles of carbonization-impregnation were carried out in this experiment.
Finally, the carbon samples were graphitized at 2200°C in argon for 1 hr. The graphitized samples had a volume shrinkage of 79.6 wt% compared with that of the samples before carbonized. Figure 4.2 showed the morphology of the carbon sample after graphitization.

Fig. 4.1. Process chart of carbon material in this study

Fig. 4.2. Morphology of carbon sample after graphitization
4.2.3. Deposition of the SiO$_2$ Coating

Figure 4.3 showed the schematic diagram of the dip coating process. Both samples of C/C composite and carbon material were cut in size of $4 \times 5 \times 1.6$ mm. Samples were dipped in the SiO$_2$ precursor solution at room temperature for 15 mins, then taken out and placed in a semi-closed container filling a few mount of ethanol to let the solvent evaporated in a moderate speed. The drying process lasted for 48 hrs in room temperature. Then, heat treatment was carried out at 800°C for 0.5 hr in nitrogen. Four cycles of this process were conducted for every sample.

The oxidation behaviors of carbon samples with and without coatings in different concentrations of the SiO$_2$ precursor solutions were measured with a TG instrument. The morphologies of SiO$_2$ coatings on sample surfaces was characterized by SEM.

Fig. 4.3. Schematic diagram of dip coating process in this study
4.2.4. Chemistry of the Process

The main chemical reactions are as following,

\[ \text{Si(OEt)}_4 + \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + \text{EtOH} \]  \hspace{1cm} (4-1)

\[ \text{Si(OH)}_4 \xrightarrow{\Delta T} \text{SiO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (4-2)

As hydrolysis proceeds polycondensation of the hydrolysis products takes place according to the reactions,

\[ \text{Si(OEt)}_4 + \text{H}_2\text{O} \rightarrow (\text{EtO})_3\text{SiOH} + \text{EtOH} \]  \hspace{1cm} (4-3)

\[ 2(\text{EtO})_3\text{SiOH} \rightarrow (\text{EtO})_3\text{Si-O-Si(OEt)}_2 \text{OH} + \text{EtOH} \]  \hspace{1cm} (4-4)

\[ n(\text{EtO})_3\text{Si-O-Si(OEt)}_2 \text{OH} \rightarrow (\text{EtO})_3\text{Si}-[\text{OSi(OEt)}_2]_{2n-1}\text{OH} + (n-1)\text{EtOH} \]  \hspace{1cm} (4-5)

From equation (4-3), (4-4) and (4-5), it was shown that ethanol not only acts as a solvent but also is involved in the chemical reaction through ethanol exchange. The amount of ethanol have a considerable effect on the chemical equilibrium and process rate of hydrolysis and polycondensation. Thus, the adjusting of EtOH was an important method to control the coating properties [2]. Figure 4.4 showed the weight change in aging time of precursor solution No. 2 and No. 3. Obviously, the quick weight loss was shown in the case of the precursor solution with higher concentration.

Further polycondensation and heat-treatment would give rise to the product of SiO\(_2\) gel, chemical reaction was shown as following,

\[ (\text{EtO})_3\text{Si}-[\text{OSi(OEt)}_2]_{2n-1}\text{OH} + \text{H}_2\text{O} \rightarrow \text{HO(EtO)}_2\text{Si}-[\text{OSi(OEt)}_2]_{2n-1}\text{OH} + \text{EtOH} \]

\[ \xrightarrow{\Delta T} O(\text{EtO})_2\text{Si}-[\text{OSi(OEt)}_2]_{2n-2}\text{OSi(OEt)}_2 + \text{H}_2\text{O} \]

\[ \xrightarrow{\Delta T, \text{2nEtOH}} 2n\text{SiO}_2 + 4n\text{EtOH} \]  \hspace{1cm} (4-6)

Thermogravimetric analysis (TG) was carried out to study the weight loss behavior of the sonogel. The sample was heated at 10°C/min to 1000°C in flowing air.
Fig. 4.4. Weight changes with aging time of precursor solution of No.2 and No.3

Fig. 4.5. Weight loss with temperature of sonogel in flowing air (30 cm$^3$/min)
The aluminun oxide was used as substrate. Before TG experiment, the sample had been aged for about 24 hrs and subsequently dried at 70°C. Figure 4.5 showed the TG trace for the sonogel. The weight loss at the temperature up to 90°C was only about 3% of the initial weight possibly as a result of desorption of H₂O and EtOH. Above 90°C the sonogel loosed weight rapidly until about 300°C. The weight loss over this range was about 17% and was mainly due to pyrolysis and carbonization of organic residues in the gel. The total weight loss of about 20% was found over 800°C.

4.2.5. Morphologies of SiO₂ Coatings

The morphologies of the SiO₂ coatings on carbon samples and C/C composites were observed by SEM. The cracks were generated during drying process. Serious cracks were found in the SiO₂ coatings on both carbon samples and C/C composites, as shown in Fig. 4.6 and 4.7. Because polarized solutions generally have a bad wettability to be coated on carbon materials, it was wished that the cracks would be decreased by coating cycles and control of drying time. By using lower concentration of precursor solutions and repeatedly coating, the SiO₂ coating layer was improved in the present experiment.

In the case of using higher concentration of precursor solution, larger cracks were found in the SiO₂ coating layer, as shown in Fig. 4.6 (a) and 4.7 (a), and these cracks were not sealed by coating cycles. It was implied that the precursor solution was tended to gather on the gel blocks instead of to flow into the cracks between the gel blocks during the second and following coating cycles. With the decreasing of the concentration of precursor solution, the cracks were flowed partially by the precursor solutions during coating cycles, as shown in Fig. 4.6 (b), and the more smooth coating was shown in Fig. 4.7 (b).

Another important factor that affected the coating, especially in the case of using higher concentration of precursor solution, was the roughness of the surface of carbon samples and C/C composites. Both carbon sample and C/C composite were porous materials. The most amount of precursor solution flowed into the cracks or pores in the materials rather than located on the surfaces of samples, as shown in Fig. 4.6 (c) and 4.7 (c). It was also found that the coating covered the larger pit on the surface of carbon sample, as shown in Fig. 4.8. Further serious cracks and gathering of SiO₂ gel were shown around the pit. Thus, further decreasing of the concentration of precursor solutions did not give a more improvement of the coatings. The optimum concentration of precursor solutions was 1:20 of Si(OEt)₄/EtOH.
Fig. 4.6. Morphologies of SiO₂ coating on carbon samples in different precursor solutions
(a) Precursor solution No.2 (EtOH/Si(OEt)₄ of 15)
(b) Precursor solution No.3 (EtOH/Si(OEt)₄ of 20)
(c) Precursor solution No.4 (EtOH/Si(OEt)₄ of 22.5)
Fig. 4.7. Morphologies of SiO$_2$ coating on C/C composites in different precursor solutions
(a) Precursor solution No.1 (EtOH/Si(OEt)$_4$ of 10 )
(b) Precursor solution No.3 (EtOH/Si(OEt)$_4$ of 20 )
(c) Precursor solution No.4 (EtOH/Si(OEt)$_4$ of 22.5)
OXIDATION OF SiO₂-COATED CARBON MATERIALS

Fig. 4.8. Morphology of the section of SiO₂-coated carbon sample, precursor solution No.3

Fig. 4.9. Change of coating thickness with different precursor solutions

Fig. 4.9. Change of coating thickness with different precursor solutions
Measured from SEM photograph of sample section, the change of the coating thickness with the concentration of precursor solution was shown in Fig. 4.9. Different from carbon samples, the coating was shown to be more difficult to wet along the carbon fibers, as shown in Fig. 4.7 (c). Figure 4.10 shown the photograph of Energy Disperse X-ray analysis (EDX) that clearly showed Si distribution located beside the carbon fiber.

4.3. Oxidation Behaviors of Carbon Samples and C/C Composites with the SiO₂ Coating

XRD analysis results of SiO₂-coated carbon material was shown in Fig. 4.11. No peak of crystallized SiO₂ was found that SiO₂ was believed to exist in amorphous form. Figure 4.12 showed the weight loss with increasing temperature for different SiO₂-coated carbon samples in flowing air (30 cm³/min). Because of the existence of cracks in the coating, the weight loss of all samples began at about 600°C that was the same with the carbon sample without any coating. With the decreasing of the concentration of precursor solution, the oxidation resistance of SiO₂-coated carbon samples was improved gradually. When the concentration of precursor solution was decreased over 1:20 of Si(OEt)₄/EtOH, the oxidation resistance went down to that was similar with the samples dip-coated with higher concentrations of precursor solutions. This result was agreement with the coating morphology described above. Similar changes of oxidation resistance was illustrated in SiO₂-coated C/C composites, as shown in Fig. 4.13.
Figure 4.14 showed the weight change with time at 800°C and 1100°C for the C/C composite without coating and SiO₂-coated C/C composite by the precursor solution of Si(OEt)₄/EtOH of 1:20. Figure 4.15 showed Arrhenius plots for these two kind composites. Both composites with and without SiO₂ coating were shown two steps of oxidation behaviors. The transition temperature was about 900°C. Due to the partial coverage of SiO₂ coating on the surface of C/C composites, the effective area for oxidation was decreased that made the oxidation of SiO₂-coated C/C composite lower than that of the C/C composite without coating. In lower temperature range, the Arrhenius plot of SiO₂-coated C/C composite was paralleled with the plot of C/C composite without coating. It was suggested that the control of oxidation rate was the same between C/C composites with and without SiO₂ coating, the chemical reaction on the surface of carbon. In the higher temperature range, the oxidation rate was controlled by diffusion of oxidizing gases for both kind composites. While, in the case of SiO₂-coated C/C composite, the diffusion was difficult comparing the case of C/C composite without coating, because the diffusion would undergo through the cracks in the coating.

Fig. 4.11. X-ray diffraction patterns of C/C composite with SiO₂ coating
Fig. 4.12. Weight loss with temperature of carbon samples with SiO₂ coating in different precursor solutions, (-) carbon without coating, (---) in precursor solution No.1, (----) in precursor solution No.2, (-----) in precursor solution No.3, (-----) in precursor solution No.4, (-----) in precursor solution No.5, (-----) in precursor solution No.6.
Fig. 4.13. Weight loss with temperature of C/C composites with SiO$_2$ coating in different precursor solutions, (---) C/C composite without coating, (---) in precursor solution No.1, (---) in precursor solution No.2, (---) in precursor solution No.3, (---) in precursor solution No.4, (---) in precursor solution No.5.
Fig. 4.14. Oxidation of C/C composites with and without SiO₂ coating at different temperatures: (-o-) without coating, (-□-) with SiO₂ coating

Fig. 4.15. Arrhenius plots of C/C composites with and without SiO₂ coating ( -o-) without coating, ( -□-) with SiO₂ coating
4.4. Conclusion

A series of SiO$_2$ precursor solution were prepared by adjusting the ratio of Si(OM)$_4$/EtOH. With the stable precursor solutions, SiO$_2$ coating was fabricated on carbon sample and C/C composite by dip-coating technique. For all the samples, the cracks were generated in the coatings during the pyrolyzing process. It was not successful to seal these cracks by coating cycles. The reasons were that the polarized solution had a bad wettability on carbon materials and the very rough surfaces of samples made the coating not to be uniformed. The coatings on both carbon samples and C/C composites were improved by decreasing the ratio of Si(OM)$_4$/EtOH. While, the improvement of the coating was not always agreement with the decreasing the ratio of Si(OM)$_4$/EtOH. When the ratio of Si(OM)$_4$/EtOH decreased over 1/20, the SiO$_2$ coating was hardly formed because most solution flowed into the cracks, pores and pits in the samples. In the present study, the optimum molar ratio of Si(OM)$_4$/EtOH for coating both carbon sample and C/C composite was found in 1/20. Comparing the carbon sample and C/C composite, it was also found that the coating on C/C composites was more difficult than that on carbon samples, especially on the carbon fibers.

XRD analysis showed that amorphous SiO$_2$ coating was formed on both carbon sample and C/C composite after 800°C heat-treatment. In spite of the existence of serious cracks, the effects of SiO$_2$ coating by sol-gel technique was shown in this study. Corresponding to the forming of SiO$_2$ coating, for both carbon samples and C/C composites, the best of oxidation resistance was observed in the samples by dip-coating in the precursor solution of Si(OM)$_4$/EtOH being 1/20. With TG analysis, it was suggested that the oxidation resistance by the SiO$_2$ coating was due to the decrease of effective surface of carbon for oxidation and the barrier of the diffusion of oxidation gases by the cracks at higher temperatures.

The results on the SiO$_2$-coated carbon materials in this study applied that it was not successful to protect C/C composites from the onset of oxidation. Further improvement of coatings would need to be carried out for enhancing the oxidation resistance of C/C composite.
References

2. B. Samuneva, V. Dozhukharov, Ch. Trapalis and R. Kranold, J. Mater. Sci., 28(1993), 2353
Chapter 5. ÓXIDATION RESISTANCE OF THE C/C COMPOSITE WITH MULTI-COATING

5.1. Introduction

The investigation on the oxidation resistance of C/C composites is very important for their applications. Especially, much of the attention has been focused on developing these materials for use as high-temperature structural components in advanced gas-turbine engines. The requirement on the oxidation resistance of C/C composites is much more urgent and strict. It was wished that a well oxidation resistance would be effective over 1000°C and even up to 1800°C in oxidizing environment. The development of an effective oxidation resistance system for carbon materials including C/C composite has been in progress for more than 50 years, and many different materials have been tried[1-6]. While, any single coating or protective layer can not meet the requirement of modern application. It is generally accepted that in order to protect C/C composite from oxidation over high temperatures, a multi-coating system is required. The main advantage in the development of a multi-coating coating is the possibility of gaining the advantages of each coating while limiting their drawbacks[7].

In this chapter, the multi-coating of LaB₆-Si/polycarbosilane/SiO₂ was introduced. It was discussed the oxidation behaviors of the C/C composite with LaB₆-Si coating, with LaB₆-Si coating impregnated by polycarbosilane (PCS) and with LaB₆-Si/PCS coating combined with SiO₂ coating by sol-gel technique. The additives of LaB₆-Si play a role of diffusion barriers to lower the oxidation rates of the composite at temperatures below 900°C. The impregnation of PCS improved the compatibility of the coating layer on the composite and the oxidation resistance below the transition temperature. The SiO₂ coatings by sol-gel technique sealed cracks in the applied protective layer. The effective oxidation resistance of the C/C composite with the multi-coating was shown up to 1400°C.

5.2. Fabrication of the Multi-coating on C/C composite

The 2-D C/C composite used in the present work were CCM-290C (Nippon Carbon Co.), as described in chapter 2. The temperature of final treatment was 2200°C. The specimens used in coating and oxidation testing were made into sheets with the size about 4 × 5 × 0.7 mm. Figure 5.1 showed the process chart of multi-coating on the C/C
Fig. 5.1. Process chart of the multi-coating on the C/C composite
composite. The sheets of C/C composite were dipped in the lanthanum borate (LaB₆) slurry that was made from LaB₆ powder (<10 μm in size) and polyethylene (as a binder) with the mixing in volume ratio of 1:10. After drying at 800°C for 2 hours in nitrogen, 2000°C treatment had been carried out for one hour in argon. Then, they were dipped in the silicon slurry that was made from silicon power (<50 μm in size) and polyethylene and dried at 800°C for 2 hours in nitrogen.

Considering the wettability on the carbon materials, PCS was chosen for impregnating on the C/C composite coated with LaB₆-Si. PCS has an excellent solubility in various non-polar organic solvents, like n-hexane, toluene and xylene, at ambient temperatures. In the present experiment, the PCS was dissolved by toluene with the volume ratio of 1:10. The impregnation of PCS was carried out for the LaB₆-Si-coated composite by dipping in the PCS solution and sintering at 1000°C for one hour in nitrogen.

Figure 5.2 showed the TG analysis of PCS in flowing argon (30 cm³/min). When being fired in an inert atmosphere, PCS starts to decompose at about 500°C. At about 800°C, it transforms into a black amorphous inorganic polymer with loss of organic groups.
Then, SiO₂ coating was prepared on the PCS-coated composites with sol-gel technique, as the same as the way introduced in chapter 4. The precursor solution was prepared by mixing of silicon tetraethoxide (Si(OEt)₄), ethanol (EtOH) in molar ratio of 1:20. H₂O as a catalyst, containing 6.3 wt% HNO₃, was added to the solution in mol ratio of H₂O/Si(OEt)₄ of 1:5. The solution was stirred at 60°C for 45 min for partial hydrolysis. After the solution was cooled to room temperature, the composites with LaB₆-Si/PCS coating were dipped in the precursor solution and then treated at 800°C for 0.5 hr in nitrogen. Four cycles of the dip-coating process were carried out in the present experiment.

Measurements of the oxidation behavior of the C/C composite with and without coatings were carried out in the TG instrument between room temperature and 1400°C in flowing air (flow rate 30 cm³/min) as described in previous chapters. Specimens were allowed to cool in air and characterized by XRD and SEM.

### 5.3. Oxidation of the C/C Composites with LaB₆-Si Coating

Figure 5.3 showed Arrhenius plots of the oxidation rates for both uncoated C/C composite and LaB₆-Si-coated one at temperatures up to 1100°C. For both specimens, two steps of oxidation rates were shown with transition temperature about 900°C. A

![Fig. 5.3. Arrhenius plots of the oxidation rate for the uncoated C/C composite and LaB₆-Si coated C/C composite](image-url)
significant increase in oxidation rate was shown below 900°C. While, above 900°C this increase was notably reduced, with the curves relatively flatten out. From the Arrhenius plots, the values of apparent activation energy were about 110 kJ/mol at lower temperature and 15 kJ/mol at higher temperature for the uncoated C/C composite. As discussed in previous chapter, for the oxidation of uncoated C/C composite in air, the low-temperature rate-limiting step was likely to be the chemical reaction on the composite surface, to give oxidation products and leave defects in the carbon network. At the higher temperatures the rate was then controlled by oxygen diffusion into pore and adsorption at active sites. This results in a lowering of the apparent activation energy as the temperature increased[8-9].

In the present study, LaB₆ and Si were coated on the C/C composite and then treated at 2000°C in argon and 800°C in nitrogen respectively. Boron carbide and Lanthanum carbide were not found after adding LaB₆ and 2000°C treatment. After coating Si and 800°C treatment, due to a few mounts of oxygen in the binder (polyethylene) or in the furnace tube that would be reacted with LaB₆-Si powders, the low-molten point phase of B₂O₃-SiO₂ was detected by XRD analysis, as shown in Fig. 5.4. This result agreed with the SiO₂-B₂O₃ phase diagram[10]. Figure 5.5 showed the surfaces of the composites after adding LaB₆. LaB₆ powder dispersed on the surface of the composite, but the whole area of the composite surface could not be covered.

After coating Si and 800°C treatment, the loosen powder layer was located on the surface of composites, as shown in Fig. 5.6 (a). The larger pore with the width of about 60 mm were found in the powder layer. The existing of the larger pores was likely due to the particle size used in the present works. Figure 5.6 (b) showed that the additives of LaB₆-Si were filled into the open pore of the C/C composite. At the lower temperatures, the oxidation rate was still controlled by the surface reaction. The additives of LaB₆-Si powders decreased the oxidation rates of the composite due to the decreasing of the exposed surface areas, as shown in Fig. 5.3. However, the effects of these additives were dependent on the compatibility of additives and the composite. The increase of reaction rates, caused by processes such as pitting, surface etching, and channel formation, would degrade the combination between additives and the composite and lower the protective effect of the additives. The Arrhenius plot of the LaB₆-Si-coated composite in Fig. 5.3 indicate that these additives gave the lower oxidation rates of the composite at lower temperatures. Below 900°C, the increase of the oxidation rates for the coated composite was accelerated by four orders of magnitude at 700°C and the apparent activation energy was shown to be about 190 kJ/mol. At the higher temperatures, where the oxidation rate was controlled by gaseous diffusion, the effect of the additives was
Figure 5.4. The X-ray profiles of the C/C composites with different coatings: a) with LaB$_6$; b) with LaB$_6$-Si; c) with LaB$_6$-Si/PCS; d) with LaB$_6$-Si/PCS/SiO$_2$. CuK$_\alpha$, Ni filter, C.P.S. 400, 1°-0.15 mm-1°, scanning speed 2°/min
Fig. 5.5. Surface of the LaB$_6$-coated C/C composite

Fig. 5.6. Surface (a) and section (b) of the LaB$_6$-Si coated C/C composites
insignificant and the apparent activation energy was shown to be about 21 kJ/mol. In spite of the presence of B-Si-O system oxide, it did not form a complete layer to protect the composite from the diffusion of oxygen because of the pores around the LaB₆-Si particles. Comparing the results in chapter 3, the Si powder had scare effect on improvement of the oxidation resistance of LaB₆ coated C/C composite, except lowering the effective surface of the C/C composite for oxidation that gave a lower oxidation rate at lower temperature range. The reason was that the coating was made of the powder materials and too many pores and cracks existed in this powder coating. The formation of the oxides of boron, silicon and lanthanum could not sealed the pores before a serious attack of oxygen to C/C composite. Like other diffusion barriers[11], the LaB₆-Si coating on the composite gave an effective oxidation resistance in lower temperature range.

5.4. Oxidation of the C/C Composites with LaB₆-Si/Polycarbosilane

The solution of PCS-toluene was impregnated into the pores around LaB₆-Si particles, as shown in Fig. 5.7 (a), and PCS was coated on the composite after 1000°C treatment in the present work. Because of the remarkable shrinkage of PCS solution when toluene was vaporized, the cracks formed in the PCS coating on the composite, as shown in Fig. 5.7 (b). The release of organic groups results in the oxidation of a part of LaB₆-Si powder. The oxides of lanthanum, boron and silicon were found by XRD analysis, as shown in Fig. 3 (c). Also, it was most likely showed the appearance of LaC₂ in the composite with this XRD pattern. The formation of lanthanum carbide on the surface of the composite would give an improvement of compatibility between the composite and the coating layer and decreased the active sites in the carbon network.

Figure 5.8 showed the Arrhenius plots for the C/C composites with and without PCS coating. Below 950°C, due to the additives of LaB₆-Si, the increase of the oxidation rates for the PCS-coated C/C composite was shown almost the same as the increase for the C/C composite without PCS coating. The apparent activation energy of the oxidation rate for the PCS-coated C/C composite was shown to be about 200 kJ/mol that was similar to the values for the C/C composite without PCS coating. While below 950°C, relative to the oxidation rate of the composite without PCS, the oxidation rate of the composite with PCS was decreased by one order of magnitude. The shift of transition temperature from the surface reaction to the gaseous diffusion indicated the change of effective surface area for the oxidation reaction. The smaller the effective surface area is, the higher the transition temperature is. In the present work, the decrease of the effective surface area was likely to be the impregnation of PCS. However, the shrinkage of the PCS during the vaporization of the toluene solvent gave the serious cracks in the PCS
Fig. 5.7. Section (a) and Surface (b) of the LaB$_6$-Si/PCS coated C/C composites

Fig. 5.8. Arrhenius plots of the oxidation rate for the LaB$_6$-Si coated C/C composite and LaB$_6$-Si/PCS coated C/C composite
coating. These cracks made the coating unsuccessfully to protect the composite from the diffusion of oxygen at higher temperatures. The high-temperature oxidation rate was still controlled by gaseous diffusion and the apparent activation energy was shown to be about 33 kJ/mol.

5.5. Modification of the LaB$_6$-Si/Polycarbosilane Coating by SiO$_2$ Sol-gel Coating

For the problem of microcracking occurring in any protective layer, boron, boron compounds and silicon compounds are often included in the composite to form borate or B-Si-O system glasses which can flow to give crack sealing$^{[6,13]}$. At the present work, the B-Si-O oxide was formed after adding LaB$_6$-Si, but it was not successful to seal the serious cracks in the PCS coating. Sol-gel technique was employed to make a SiO$_2$ coating on the composite. From XRD analysis shown in Fig. 5.3, the forming of new phases was not found in the coated C/C composite after SiO$_2$ coating. Figure 5.9 showed the SiO$_2$ coating sealed into the cracks of the PCS coating. No open cracks that crossed the coating layer were observed in the PCS-SiO$_2$ coating layer, as shown in Fig. 5.9 (a), although microcracks were found on the surface of the SiO$_2$ coating, as shown in Fig. 5.9 (b).

Figure 5.10 showed the results of isothermal oxidation at 1100°C for the coated C/C composites. The oxidation for the SiO$_2$ coated composite was not shown at 1100°C over 5 hours. After the isothermal oxidation, the composites with and without SiO$_2$ coating were characterized using scanning electron microscopy, as shown in Fig. 5.11. The oxidation of the PCS without SiO$_2$ coating appeared at specific active sites, as shown in Fig. 5.11(a), but did not appear in the PCS with SiO$_2$ coating, as shown in Fig. 5.11(b). Comparing to the composite without SiO$_2$ coating, the cracks of PCS coating were sealed completely by SiO$_2$. This sealing did not fill into the interfaces between the coating layer and the C/C composite, as shown in Fig. 5.11(c). It was suggested that the wetting of SiO$_2$ on the PCS coating has been improved in oxidized circumstance, and a continuous coating layer was formed at the exterior of the coating. The continuous coating of PCS-SiO$_2$ protected the C/C composite from the corrosion of oxygen over 1100°C.

Figure 5.12 showed the weight loss of the C/C composites with different coatings as a function of temperatures. A little weight loss less than 2 wt% was found for the SiO$_2$ coated composite at the temperature up to 1400°C. It is known that boron oxide is appreciably volatile at high temperature. Greene and Margrave$^{[16]}$ calculated the values for the vapor pressures of various boron oxide species from thermodynamic data. The results of their works suggested that the vapor pressure of HBO$_2$ was over 1 mmHg (at P$_{He}$ = 1...
Fig. 5.9. Section (a) and Surface (b) of the LaB$_6$-Si/PCS/SiO$_2$ coated C/C composites

Fig. 5.10. Weight loss with time of the C/C composites with different coatings, in flowing air (30 cm$^3$/min), at 1100°C

- Uncoated C/C composite
- LaB$_6$-Si coated C/C composite
- LaB$_6$-Si/PCS coated C/C composite
- LaB$_6$-Si/PCS/SiO$_2$ coated C/C composite
Fig. 5.11. Morphology of the C/C composites with different coatings after oxidation at 1100°C.
(a) Surface of LaB$_6$-Si/PCS coated C/C composite.
(b) Surface of LaB$_6$-Si/PCS/SiO$_2$ coated C/C composite.
(c) Section of LaB$_6$-Si/PCS/SiO$_2$ coated C/C composite.
Fig. 5.12. Weight loss with temperature of the C/C composite with different coatings at flowing air (30 cm³/min)

- Uncoated C/C composite
- LaB₆-Si coated C/C composite
- LaB₆-Si/PCS coated C/C composite
- LaB₆-Si/PCS/SiO₂ coated C/C composite

Fig. 5.13. Section (a) and Surface (b) of the LaB₆-Si/PCS/SiO₂ coated C/C composites after oxidation at 1400°C
atm) at 900°C; the vapor pressure of B$_2$O$_3$ was about 10$^{-2}$ mmHg at 1000°C and 1 mmHg at 1400°C. In the present work, it is expected that H$_2$O and EtOH released from precursor solution resided and formed the boron hydroxide in the composites. The vaporization of hydroxide resulted in the weight loss at the temperatures of 800°C-1000°C, as shown in Fig. 5.12. When the temperature was over 1300°C, the vaporization of B$_2$O$_3$ became notable with increase of temperatures. On the other hand, the oxidation of PCS at specific active sites and the vaporization of SiO$_2$ were found on the surface of PCS coating, as shown in Fig. 5.13 (a). Carbon oxides and SiO$_2$ would be produced by the oxidation of PCS coating. Figure 5.13 (b) showed the section of the composite after the oxidation at 1400°C. A glass layer enclosing Si powders was formed on the surface of C/C composite. Figure 5.14 showed the results of the isothermal oxidation for the coated composites at different temperatures. The coating gave a better protection at the temperature up to 1300°C, while the weight loss of the composite was increased gradually at 1400°C. It is suggested that the coatings were degraded by the vaporization of B$_2$O$_3$ and SiO$_2$ and could not protect the composite from the diffusion of oxygen at 1400°C.

![Fig. 5.14. Weight loss with time of LaB$_6$-Si/PCS/SiO$_2$ coated C/C composite at different temperatures](image)

Fig. 5.14. Weight loss with time of LaB$_6$-Si/PCS/SiO$_2$ coated C/C composite at different temperatures
5.6. Conclusion

A multi-coating including LaB$_6$ powder, Si powder, polycarbosilane and SiO$_2$ was fabricated on the C/C composite. The considerable improvement of oxidation resistance was obtained by this multi-coating.

In the case of LaB$_6$-Si coated and LaB$_6$-Si/PCS-coated composites, the oxidation rates were controlled by oxygen diffusion at the temperatures over 900°C and 950°C under the experimental conditions. Below the temperature of 900°C, the additives of LaB$_6$-Si could lower the oxidation rates of the composite as diffusion barriers by over two orders of magnitude in the present experiments. The apparent activation energy for LaB$_6$-Si coated C/C composite was calculated to be about 21 kJ/mol at higher temperature and about 190 kJ/mol at lower temperature.

The coating of PCS sealed the larger pores around the LaB$_6$-Si particles and improved the compatibility between the coating layer and the C/C composite. This gave a decrease of the effective surface for oxidation and further retarding the diffusion of oxidizing gases. Below 950°C, the oxidation rate of the PCS-coated composite was decreased by one order of magnitude, comparing to that of the composite without PCS. The apparent activation energy for LaB$_6$-Si/PCS coated C/C composite was calculated to be about 33 kJ/mol at higher temperature and about 200 kJ/mol at lower temperature.

A continuous protective layer that sealed smaller pores and cracks was formed after SiO$_2$ coating by sol-gel technique. The wetting of SiO$_2$ on PCS was improved in oxidation circumstance. The continuous coating layer was formed by SiO$_2$-PCS at the exterior of the coating and protected the C/C composite over 1100°C. With increase of temperature, the glass layer enclosing Si powders formed on the surface of the C/C composite. For the C/C composite with LaB$_6$-Si/PCS/SiO$_2$ coatings, a remarkable resistance for the onset of oxidation was shown at the temperatures up to 1300°C.

The results in this study demonstrated that the multi-coating of LaB$_6$-Si/PCS/SiO$_2$ offered an excellent oxidation resistance for C/C composite at a wide temperature range.
References

Chapter 6. ESTABLISHMENT OF A MODEL FOR MULTI-COATING SYSTEM OF LaB$_6$-Si/PCS/SiO$_2$

6.1. Introduction

The oxidation resistance of C/C composite was improved gradually by the improvement of the protective coating. An excellent oxidation resistance was shown in the C/C composite with the multi-coating of LaB$_6$-Si/PCS/SiO$_2$. In a wide temperature range, this multi-coating protected the C/C composite from the oxidation onset by the diffusion of oxidizing gases from open pores and cracks, that was used to degrading other single coatings and multi-coatings\(^{[1-3]}\).

Generally, if the pores or cracks exist in the protective layer or C/C composites are exposed to oxidizing environments, oxidation rate would be controlled by the diffusion of oxidizing gases at enhanced temperature\(^{[4]}\). Oxidation would occur very rapidly because oxygen can diffuse rapidly to carbon through the cracks by the diffusion and oxidation products, CO/CO$_2$, can diffuse rapidly away from it. The best oxidation protection of C/C composites would occur when the composites are crack-free with no open porosity, and C/C composites are not directly exposed to the oxidizing environments. This means that the C/C composites are buried deep within the protective materials. There had been no successful coating or protective layer to separate the C/C composite from oxidizing environment.

In this chapter, the thermodynamic and kinetic of the oxidation of carbon was discussed. The effect of the diffusion of oxidizing gases was also discussed as an important factor on the oxidation behavior of coated C/C composites. A model was then presented to explain the mechanism of the oxidation behavior of the C/C composite with the multi-coating of LaB$_6$-Si/PCS/SiO$_2$.

6.2. Requirements of Multi-coating System and Their Components

The factors which must be considered when designing an oxidation resistance system are shown in Fig. 6.1. The primary function of an oxidation resistance system is to isolate the C/C composite from the oxidizing environment. To achieve this, the system must have a number of functions. At least one component of the system must form an effective barrier to the entrance of oxygen that lowers the oxygen permeability. In addition, it is also important to minimize the diffusion of carbon outwards from the C/C composite.
Because of the difference of coefficient of thermal expansion of C/C composite and coating, microcracks was possibly formed by mismatch on cooling down from the coating deposition temperature. For the system to protect against oxidation, it must possesses a self-healing capability. One of the internal layers must be either a glass or a glass-forming compound which can flow into and seal any cracks which develop in the process of coating forming and possibly develop in oxidation period.

![Diagram of coating system](image)

**Fig. 6.1. Considerations for designing an oxidation resistance system of multi-coating**

It is necessary to establish a good adherence between C/C composite and the coating. This requires good wettability and use of the proper process route. A suitable bond layer may provide the necessary resistance to the outward diffusion of carbon as well as forming a strong bond at the surface of C/C composite. The compatibility must be ensured between the coating system and C/C composite and between the various layers of the system. The coefficient of thermal expansion of layers in contact with each other should be matched as closely as possible to avoid the generation of large stresses during heating and cooling.

The combination of properties can not be met by any single material. It is necessary to develop multi-coating where each layer performs a specific function and allows the coating to be effective in oxidation resistance at a wide temperature range.
6.3. Model for the Multi-coating System of LaB$_6$-Si/PCS/SiO$_2$

A multi-coating system was schematically illustrated in Fig. 6.2. LaB$_6$ and silicon were chosen as the primary oxygen barriers. The introduction of boron was done by the LaB$_6$ coating and 2000°C heat-treatment. As described in chapter 3, boron and lanthanum diffused into the C/C composite after 2000°C heat-treatment. The diffusion not only improved the effects of oxidation barrier but also improved the graphitization of C/C composite that benefited for the decrease of active sites for oxidation in the C/C composite. Considering that the boron oxide was unstable over 1000°C, silicon that begin to be oxidized and form SiO$_2$ at 800°C was coated over the diffusion layer of lanthanum and boron [5-7]. In addition, oxides of silicon and boron in the coating will flow into and seal the cracks that generated in the coating.

![Diagram of multi-coating system](image)

Fig. 6.2. Multi-coating system of LaB$_6$-Si/PCS/SiO$_2$ on C/C composite

PCS was impregnated and covered the powder layer as the material for bond layer that have a good wettability on carbon materials. The PCS coating, that was formed in amorphous material of Si-C, have a good stability in oxidizing environment under 1100°C, as described in chapter 5. With further oxidation, PCS coating will be oxidized to SiO$_2$ that have excellent compatibility with B$_2$O$_3$-SiO$_2$ glass formed from the oxidation of silicon and boron. With the sol-gel technique, SiO$_2$ coating was used to seal and covered the cracks in the PCS coating. By the SEM analysis, the cracks and pores were found in the coating, but no crack was found that crossed the multi-coating of LaB$_6$-Si/PCS/SiO$_2$. 

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In the discussion of this chapter, it was considered that the invisible microcracks still existed in the multi-coating, as shown in Fig. 6.2.

The multi-coating was formed with amorphous and powder materials. Compared with the coating of ceramic materials, like SiC and Si$_3$N$_4$, it was believed that the multi-coating of LaB$_6$-Si/PCS/SiO$_2$ had a good thermal compatibility between the coating and C/C composite and between the various materials in the coating.

6.4. Effects of the Multi-coating on Oxidation

6.4.1. Oxidation of Carbon

For the C-O system, there are several gas phases existed in higher temperature, like C, C$_2$, C$_3$, C$_4$, C$_5$, C$_2$O, C$_3$O$_2$, CO, CO$_2$, O and O$_2$. Whereas, considering with the thermodynamic data from JANAF table, there are only C$_3$O$_2$, CO and CO$_2$ that were possibly produced under the standard conditions because only these oxides of carbon have the negative free energy ($\Delta G^\circ$) in the temperatures concerned generally in investigations, as shown in Fig. 6.3.

For the following chemical reactions,

\[
\begin{align*}
3C(s) + O_2(g) &= C_3O_2(g) \\
C(s) + \frac{1}{2}O_2(g) &= CO(g) \\
C(s) + O_2(g) &= CO_2(g)
\end{align*}
\]

the relation between the partial pressure of oxides and oxygen can be established as following,

\[
\begin{align*}
\log Kp_{C_3O_2} &= \log PC_3O_2 - \log PO_2 \\
\log Kp_{CO} &= \log PCO - \frac{1}{2}\log PO_2 \\
\log Kp_{CO_2} &= \log PCO_2 - \log PO_2
\end{align*}
\]

Where $K_p$ is the equilibrium constant of chemical reaction and depended on the temperature that the chemical reaction is done. The values of $K_p$ with different temperature can be calculated with the thermodynamic data from JANAF Table. At a
Fig. 6.3. Standard free energy of the gases possibly produced in C-O system

Fig. 6.4. Relationship among $P_{CO_2}$, $P_{CO}$ and $P_{CO_2}$ at different temperatures

- $CO_2$ at 800°C
- $CO$ at 800°C
- $C_3O_2$ at 800°C
- $CO_2$ at 1400°C
- $CO$ at 1400°C
- $C_3O_2$ at 1400°C
certain temperature, the relationship among the partial pressure of oxygen and the partial pressures of $\text{C}_3\text{O}_2$, CO and CO$_2$ can be estimated, as shown in Fig. 6.4. The chemical reactions between carbon and oxygen will happen even in very low partial pressure of oxygen. It is easy to find that principle products of the oxidation of carbon are CO(g) and CO$_2$(g) in the presented temperature range. In fact, the measurement of oxidation rate in TG experiment becomes effective at about 500°C. The thermodynamic discussion about the oxidation of carbon would be really effective above this temperature. Thus, in the investigations on the oxidation of carbon, CO(g) and CO$_2$(g) have been considered as the products of the oxidation of carbon.

6.4.2. Effects of B$_2$O$_3$ Formation in the Multi-coating

With the model described above, the beginning of oxidation was due to the oxygen resided under the coating and the oxygen diffusion through the invisible microcracks. Because of the pores and cracks in the coating, theoretically, oxidation would co-occur for all components of the coating. With the TG experimental results as described previously, the oxidation was firstly influenced by the oxidation of boron that diffused into the C/C composite and LaB$_6$ before 500°C. The following reaction was considered,

$$2\text{B(s)} + \frac{3}{2}\text{O}_2(\text{g}) = \text{B}_2\text{O}_3(\text{l})$$  \hspace{1cm} (6-7)

$$2\text{LaB}_6(\text{s}) + \frac{21}{2}\text{O}_2(\text{g}) = \text{La}_2\text{O}_3(\text{s}) + 6\text{B}_2\text{O}_3(\text{l})$$  \hspace{1cm} (6-8)

Direct effect of this reaction was the decrease of the partial pressure of oxygen on the surface of C/C composite and the effective surface of carbon for oxidation. With enhanced temperature, these effects would be enlarged by the oxidation of lanthanum and the accelerated oxidation of LaB$_6$.

Considering the oxidation system of B-O in the low partial pressure of oxygen, the formation of volatile sub-oxides must also be considered. A number of volatile sub-oxides (BO, BO$_2$, B$_2$O$_2$ and B$_2$O) have been observed. Of these, only B$_2$O$_2$ would be considered, because B$_2$O$_2$ has the largest negative free energy of formation and has been observed to be the major gaseous species. In this study, the reactions

$$2\text{B(s)} + 2\text{B}_2\text{O}_3(\text{l}) = 3\text{B}_2\text{O}_2(\text{g})$$  \hspace{1cm} (6-9)
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\[ \text{B}_2\text{O}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{B}_2\text{O}_3(\text{l}) \]  \hspace{1cm} (6-10)

were considered. The reactions of \((6-9)\) and \((6-10)\) were shown in Fig. 6.5. Obviously, the formation of the nonprotective gaseous sub-oxide of \(\text{B}_2\text{O}_2\) would degrade the formation of \(\text{B}_2\text{O}_3\) in low partial pressure of oxygen (\(P_0_2\)). If the partial pressure of \(\text{B}_2\text{O}_2\) (\(P_{\text{B}_2\text{O}_2}\)) remained below the equilibrium value, \(P_{\text{B}_2\text{O}_2(\text{equil})}\), \(\text{B}_2\text{O}_3\) would not be really formed. This process of the reaction is generally called active oxidation. The \(\text{B}_2\text{O}_2\) gas vaporized from \(\text{B}_2\text{O}_3\) would meet the oxygen and oxidized to be \(\text{B}_2\text{O}_3\) if the \(P_0_2\) was enough high. This process of reaction is generally called as passive oxidation.

![Fig. 6.5. Simulation of the oxidation of boron under the multi-coating](image)

Considering the steady state, \(P_{\text{B}_2\text{O}_2} = P_{\text{B}_2\text{O}_2(\text{equil})}\), there is a partial pressure of oxygen, \(P_{0_2(\text{trans})}\), that responds to \(P_{\text{B}_2\text{O}_2(\text{equil})}\). When \(P_0_2 > P_{0_2(\text{trans})}\), the formation of \(\text{B}_2\text{O}_3\) would be stable by the process of passive oxidation; when \(P_0_2 < P_{0_2(\text{trans})}\), \(\text{B}_2\text{O}_3\) would not be formed because of active oxidation. The diffusion of oxygen to the surface of \(\text{B}_2\text{O}_3\) is equal to that of \(\text{B}_2\text{O}_2\) away from this surface. Assuming that the diffusions are controlled by the diffusion of gaseous phase, the relationship between \(P_{0_2(\text{trans})}\) and \(P_{\text{B}_2\text{O}_2(\text{equil})}\) can be expressed as the following,

\[ \left( \frac{P_{0_2(\text{trans})}}{RT} \right) \left( \frac{D_{0_2}}{\delta_{0_2}} \right) = \left( \frac{P_{\text{B}_2\text{O}_2(\text{equil})}}{RT} \right) \left( \frac{D_{\text{B}_2\text{O}_2}}{\delta_{\text{B}_2\text{O}_2}} \right) \]  \hspace{1cm} (6-11)
where \( R \) is the gas constant, \( T \) absolute temperature, \( D_{O_2} \) and \( D_{B_2O_3} \) the diffusion coefficients of the oxygen and \( B_2O_2 \), \( \delta_{O_2} \) and \( \delta_{B_2O_3} \) the distance of the diffusion of oxygen and \( B_2O_2 \). The relationship between distance \( (\delta) \) of diffusion and diffusion coefficient can be expressed as the equation (6-12),

\[
\delta = \sqrt{2D\tau}
\]  

(6-12)

where \( \tau \) is the time of the diffusion of molecular. Simplified with \( \tau_{O_2} = \tau_{B_2O_3} \), the approximation was obtained as following,

\[
\frac{\delta_{O_2}}{\delta_{B_2O_3}} = \left( \frac{D_{O_2}}{D_{B_2O_3}} \right)^{1/2}
\]  

(6-13)

Thus, the equation (6-11) was simplified as the following,

\[
P_{O_2}(\text{trans}) = P_{B_2O_3}(\text{equil}) \left( \frac{D_{B_2O_3}}{D_{O_2}} \right)^{1/2}
\]  

(6-14)

Based on the Chapman-Enskog expression, the diffusion coefficient has a relationship as the following,

\[
D \propto \frac{1}{M^{1/2}d}
\]  

(6-15)

where \( M \) is the molecular weight of the particular species and \( d \) the molecular diameter. The molecular weight and diameter of oxygen are 32 and 2.98 Å, respectively. The molecular weight of \( B_2O_2 \) is 53.6, and its molecular diameter was estimated from the bond distance to be 4.94 Å\(^{11-12}\). Substituting these values in equation (6-15) and (6-14), the ratio of the diffusion coefficients was obtained,

\[
\frac{D_{B_2O_3}}{D_{O_2}} = 0.466
\]  

(6-16)
and the relationship of $P_{O_2}(\text{trans})$ and $P_{B_2O_3}(\text{equil})$ was shown as the following,

$$P_{O_2}(\text{trans}) = 0.683 P_{B_2O_3}(\text{equil}) \quad (6-17)$$

With the thermodynamic data from JANAF tables, the relationship between $P_{O_2}(\text{trans})$ and temperature was established, as shown in Fig. 6.6.

Where the partial pressure of oxygen is lower than $P_{O_2}(\text{trans})$, the $B_2O_3$ would not be formed on the surface of carbon by the forming of $B_2O_2(g)$, which will move away until it reaches a region that the partial pressure of oxygen is larger than $P_{O_2}(\text{trans})$. In the multi-coating of $LaB_6$-Si/PCS/SiO$_2$ as shown in Fig. 6.2, the region with higher partial pressure of oxygen would be in the invisible microcracks in the PCS/SiO$_2$ layer that was the most important channel for the diffusion-in of oxygen. Thus, the $B_2O_2(g)$ that diffused into the microcracks would be oxidized to form $B_2O_3(l)$ and sealed these microcracks. So far, the coating made a complete separation between the C/C composite and the oxidizing environment. Considering that an equilibrium system would be established under the coating, the partial pressure of oxygen would become further lower.
than that before the microcracks had been completely sealed. The location of B$_2$O$_3$ glass would prefer to the area near the PCS/SiO$_2$ layer rather than that on the surface of C/C composite.

The possible weight loss in this period would be depended on the diffusion of oxygen into the coating and the gaseous oxides of carbon, boron and silicon out of the coating. Before the microcracks were sealed, the diffusion was principally done through the microcracks; after the microcracks were sealed, the diffusion was then done only through the condense phase that was formed by PCS and SiO$_2$ and B$_2$O$_3$.

### 6.4.3. Effects of SiO$_2$ Formation in the Multi-coating from Si Powder

Similar with the formation B$_2$O$_3$, the SiO$_2$ formation from Si powder was considered at a low P$_{O_2}$. With the thermodynamic data from JANAF table, the Si-SiO-SiO$_2$ system was recognized as the important system for the transition of active-passive oxidation. In this analysis, the following reaction was considered.

$$\text{Si(s) + SiO}_2(\text{s}) = 2\text{SiO(g)} \quad (6-18)$$

As long as the partial pressure of SiO (P$_{\text{SiO}}$) remains below the equilibrium value at the considering temperature, P$_{\text{SiO}}$ (equil), SiO$_2$ will not be formed. Assuming that the diffusion of oxygen to the surface of SiO$_2$ is equal to that of SiO away from the surface in steady state, the following relationship can be obtained.

$$P_{O_2}(\text{trans}) = P_{\text{SiO}}(\text{equil}) \left( \frac{D_{\text{SiO}}}{D_{O_2}} \right)^{1/2} \quad (6-19)$$

The molecular weight of SiO is 44 and its molecular diameter was estimated from the bond distance to be 3.66 Å. With the relationship in Chapman-Enskog equation, the transition of active-passive oxidation of Si can be approximately predicted by

$$P_{O_2}(\text{trans}) = 0.833 P_{\text{SiO}}(\text{equil}) \quad (6-20)$$

Using the thermodynamic data from the JANAF table, the relationship between P$_{O_2}$(trans) and temperature was established for Si-SiO-SiO$_2$ system, as shown in Fig. 6.7. It was indicated that the dispersed Si powder would be oxidized by forming SiO(g) at
low partial pressure of oxygen. As the case of $B_2O_2$, $SiO(g)$ would move away from the surface of $Si$ until it reached the location of substantially high $PO_2$ and $SiO_2$ would be condensed. This location was most possibly applied at the surface beneath the PCS-$SiO_2$-$B_2O_3$ layer described above, at which the oxygen from oxidizing environment diffused across the PCS-$SiO_2$-$B_2O_3$ layer to enter the cracks or pores in the multi-coating. This effect supported the PCS-$SiO_2$-$B_2O_3$ layer to separate the $C/C$ composite from the oxidizing environment.

Comparing Fig. 6.7 with Fig. 6.6, the $PO_2(\text{trans})$ for $SiO-SiO_2$ was shown to be larger than the $PO_2(\text{trans})$ for $B_2O_2-B_2O_3$. It was indicated that the $SiO_2$ was more stable than $B_2O_3$ at the same partial pressure of oxygen. The contribution of $SiO_2$ for the sealing the microcracks was less than that of $B_2O_3$ before the effect of $B_2O_3$ was degraded by the evaporation of $B_2O_3$ with enhanced temperature. The importance of the $SiO_2$ formation from $Si$ powder was that it would sealed the microcracks and still kept the $C/C$ composite away from the oxidized environment while and after the degradation of $B_2O_3$ with the increased temperature.
6.4.4. Effects of the PCS in the Multi-coating

As the previous description, PCS coating impregnated and covered the powder layer as the bond layer that was consisted in amorphous form of Si-C. The formation of SiO$_2$ from PCS coating was considered similar to that from Si powder. With the experimental results in chapter 5, the PCS coating was stable in the oxidizing environment of the present experimental condition under 1100°C, the contribution of the formation of SiO$_2$ from the PCS coating for the sealing microcracks in the multi-coating was neglected. The important point for the oxidation resistance of the PCS coating was the formation of SiO$_2$ on the surface of the multi-coating which the oxidizing environment connected with. Different from the case of the formation of SiO$_2$ from Si powder in a low partial pressure of oxygen, the location with the enough high partial pressure of oxygen was supplied by the oxidizing environment near to the boundary between the SiO$_2$ formed by PCS coating and the oxidizing environment. Thus, the SiO$_2$ would formed on the surface of the PCS coating. The SiO$_2$ formed from the PCS coating would retarded the oxidation of PCS coating if the SiO$_2$ was enough to cover the PCS blocks. For this process, the weight loss would be induced by the evaporation of the oxides of carbon because of the oxidation of PCS coating. While, this was improved by the SiO$_2$ coating by sol-gel technique, as shown in chapter 5.

6.4.5. Effects of the SiO$_2$ Coating by Sol-gel in the Multi-coating

The most important effect for the SiO$_2$ coating by sol-gel technique was the sealing of the large cracks remained in the PCS coating. Only the invisible microcracks that existed in the multi-coating could implied the channel for the diffusion of oxygen and the gaseous products of oxidation. This point was regarded as the most important point for the multi-coating successfully to protect the C/C composite from the oxidation at the conditions of this study. Considering the case the cracks or pores were too large to be sealed by B$_2$O$_3$ and SiO$_2$, the coating would be not successful to protect the C/C composite from the oxidation, no matter that the components of the coating material were diffused into the C/C composite or dispersed on the surface of the C/C composite.

In addition, the B-rich B$_2$O$_3$-SiO$_2$ would be created in the microcracks by the combination of the SiO$_2$ from sol-gel coating and the B$_2$O$_3$ from the vapor of B$_2$O$_3$. Comparing with the case of pure B$_2$O$_3$ at the same temperature, the B$_2$O$_3$-SiO$_2$ was improved in two aspects for the oxidation resistance of the multi-coating. One was that the viscosity of B$_2$O$_3$ was increased by the combining with SiO$_2$ that would decrease the diffusion rate of the oxygen across the coating; another was that the vaporizing rate of
B₂O₃ was decreased by the lowering the equilibrium pressure of gaseous B₂O₃ on the surface of B₂O₃-SiO₂ that would extend the effect of the sealing microcrack by B₂O₃ with enhanced temperature. With further increase of temperature, the B-rich B₂O₃-SiO₂ would change into the Si-rich B₂O₃-SiO₂ by the evaporation of B₂O₃ from the microcracks near the surface of the multi-coating. The weight loss was reasonably induced by this evaporation, as shown in Fig. 6.8. When the temperature was increased up to the point that the evaporation of SiO₂ should be considered, generally over 1200°C[6,13], the SiO₂ layer would shift to and finally locate on the surface of C/C composite.

![Graph showing weight loss with temperature](image)

**Fig. 6.8.** Weight loss with temperature of the C/C composite with the multicoating of LaB₆-Si/PCS/SiO₂

### 6.5. Conclusion

With the thermodynamic and kinetic analysis, a model for the multi-coating of LaB₆-Si/PCS/SiO₂ was established. With this model, the effects of every individual layer were discussed systematically in the formation and oxidation resistance of the multi-coating.

In the formation of the multi-coating, LaB₆ and silicon were chosen as the primary oxygen barriers. The introduction of boron was done by the LaB₆ coating and 2000°C heat-treatment and silicon powder was dispersed with LaB₆ on the surface of the C/C
composite. The impregnated PCS as the bond layer was covered the powder layer of LaB$_6$-Si that have a good wetting ability on carbon materials. The SiO$_2$ coating by sol-gel technique was used to seal and covered the large cracks in the PCS coating. The multi-coating of LaB$_6$-Si/PCS/SiO$_2$ was formed with amorphous and powder materials that supplied a good thermal compatibility between the coating and C/C composite and between the various materials in the coating.

In the oxidation resistance of the multi-coating, it was demonstrated that the invisible microcracks were sealed by the formation of B$_2$O$_3$-SiO$_2$ due to the oxidation of boron, LaB$_6$ and Si at low partial pressure of oxygen in the multi-coating. With the calculation in thermodynamics and kinetics, it was also predicted that the complete coating firstly formed around the boundary of the multi-coating and the oxidizing environment, instead of the surface of C/C composite. Then, the B$_2$O$_3$-SiO$_2$ would shift to and finally locate on the surface of C/C composite with the increase of temperature. It was suggested that the SiO$_2$ coating by sol-gel played as the most role in the multi-coating for the oxidation resistance. All the results derived from the model in this chapter were supported by the experimental results obtained.


APPENDIX

(1) Binary Diffusion Coefficient $D_M$ of Chapman-Enskog

For gas mixtures at low pressures, e.g., below 10 atm, the diffusion coefficient $D_M$ is expressed in Chapman-Enskog kinetic theory as the following,

$$D_M = 0.0018583 \sqrt{\frac{2T^3/M}{P \sigma_M \Omega_M}}$$

where $P$ is the pressure, $T$ the absolute temperature, $M$ the molecular weight, $\sigma_M$ is the effective size of molecular, $\Omega_M$ is the collision integral (that was tabulated by R. B. Bird and J. O. Hirschfelder et al.).

2) Mean Diffusion Distance $\delta$

Considering $\delta$ is the diffusion distance of a molecular in a period of $\tau$, the relationship in Fick’s Second Law is expressed as following,

$$\frac{dc}{d\tau} = D \frac{d^2c}{d^2\delta}$$

(1)

where $c$ is the concentration of diffusion molecular in unit of molecular number per distance. From equation (1), the relationship of the concentration $(c)$, time $(\tau)$ and diffusion distance $(\delta)$ can be established,

$$c = \beta \tau^{-1/2} e^{-\frac{\delta^2}{4Dr}}$$

(2)

where $\beta$ is a constant which can be obtained from the condition that all diffusion molecular is contained between $\delta = -\infty$ and $\delta = +\infty$. Thus,

$$N = \int_{-\delta}^{\delta} \int_{-\infty}^{\infty} \tau^{-1/2} e^{-\frac{\delta^2}{4Dr}} d\delta = 2\beta(\pi D)^{1/2}$$

(3)
or \[ \beta = \frac{N}{2(\pi D)^{1/2}} \] (4)

Bring equation (4) into equation (2), the concentration (c) can be expressed as the following.

\[ c = \frac{N}{2(\pi D \tau)^{1/2}} e^{-\delta^2 / 4D \tau} \] (5)

where \( N \) is the molecular number when \( \delta = 0 \) and \( \tau = 0 \). The probability \( P \) that molecular occur between \( \delta \) and \( \delta + d\delta \) by diffusion can be expressed as the following equation.

\[ P = f(\delta) d\delta = \frac{c(\delta) d\delta}{N} = \frac{1}{2(\pi D \tau)^{1/2}} e^{-\delta^2 / 4D \tau} d\delta \] (6)

Considering the diffusion is happening in both negative and positive directions, the mean square distance by diffusion molecular in a time \( \tau \) is expressed as

\[ \langle \delta^2 \rangle = \int_{-\infty}^{\infty} \delta^2 f(\delta) d\delta = \int_{-\infty}^{\infty} \delta^2 \frac{1}{2(\pi D \tau)^{1/2}} e^{-\delta^2 / 4D \tau} d\delta = 2D \tau \] (7)
References

Chapter 7. Summary

C/C composite material has received an increasing amount of attention in recent years. Much of the attention has been focused on developing this material for use as high-temperature structural components in advanced gas-turbine engines. The driving force for this research is the desire to increase the efficiency of these engines which requires that they must operate at higher temperature. However, a major problem arises when the C/C composite is exposed to an oxidizing environment. Once the temperature is over 500°C, the carbon reacts considerably with oxygen and is rapidly burnt away. Although the development of an effectively protective system for carbon has been in progress for more than 50 years and many different materials have been tried, yet, the most concerned problem is to find the most promising system which is formed to react with oxygen which penetrates through cracks in the protective layer and to form a glass which flows and seals these cracks. In addition, this system is required to have a good compatibility with C/C composite.

For this aim, several attempts were made to find a suitable coating on the C/C composite in the present study. The principal approaches include in three parts of works: the oxidation behaviors of the C/C composite without any coating (Chapter 2), the oxidation resistance of the C/C composite with the single-coating (Chapter 3 and Chapter 4) and the oxidation resistance of the C/C composite with the multi-coating (Chapter 5 and Chapter 6).

Chapter 1 summarizes the development history and important findings in the field of the oxidation of carbon materials and C/C composites. Backgrounds and purpose of the present study are also introduced in this chapter.

In chapter 2, the effect of heat-treatment temperature on the oxidation behaviors of two kinds of C/C composites was discussed. With improvement of graphitization by increasing of heat-treatment temperature, contradiction effects on oxidation behaviors of C/C composites were generated. The ordering of structure with the improvement of graphitization was benefit to lowering active sites; otherwise, the increase of cracks and the generation of stress increased the concentration of active sites around cracks. With this contradictory effects, anomalous oxidation behaviors with the increase of heat-treatment temperature were shown in the present study. Generally, the C/C composites heat-treated at 2200°C and 2700°C were shown the best oxidation resistance and the one heat-treated at 2000°C was the worst.

With theories of Griffith and Jenkins and the data from measurement by B.E.T. method, the effects of stress were analyzed on the oxidation behaviors at lower
temperature. It was suggested that the oxidation behavior of C/C composites at lower temperature were considerably influenced by the repeatedly change of stress with increasing of heat-treatment temperature. Although it was difficult to establish a simple relationship between oxidation and the change of strain-stress, a qualitative analysis was applied to explain this relationship in this experiment.

In chapter 3, the oxidation behaviors of C/C composites with LaB$_6$ coating were discussed in two cases. In the case of C/C composite coated with LaB$_6$ at 500°C, LaB$_6$ showed effective resistance to oxidation below 900°C, due to the boron oxide blocking the active sites on the carbon surface. This effects extended above 1000°C with the formation of the oxide film of lanthanum and boron. Under the present experimental conditions, the apparent activation energies were calculated to be 160 kJ/mol at lower temperatures and about 75 kJ/mol at higher temperatures. In the case of the C/C composites coated with LaB$_6$ at 2000°C, it was suggested that the diffusion of lanthanum and boron was benefit for the structural ordering of carbon and removed the active sites in the C/C composites. Comparing with the case of the C/C composites coated with LaB$_6$ at 500°C, a further improvement of oxidation resistance was shown with the apparent activation energies of 210 kJ/mol at lower temperatures and 80 kJ/mol at higher temperatures. The effective resistance of LaB$_6$ retarded the oxidation of C/C composites, but did not protect the C/C composites from the onset of oxidation.

In chapter 4, the formation of SiO$_2$ coating on the carbon material and the C/C composite coated with SiO$_2$ by sol-gel technique and its effects on the oxidation behavior were discussed. Trying with a series of SiO$_2$ precursor solutions by adjusting the ratio of Si(OEt)$_4$/EtOH, the optimum molar ratio of Si(OEt)$_4$/EtOH was decided to be 1:20. For all the samples, the cracks were formed in the coatings when the pyrolyzing process. It was not successful to seal these cracks by coating cycles because the polarized solution had a bad wettability on carbon materials and the very rough surfaces of samples made the coating not to be uniformed. It was suggested that the improvement of SiO$_2$ coating on carbon material or C/C composite was depended not only on the decrease of the ratio of Si(OEt)$_4$/EtOH, but also on the flowing of the precursor solution into the cracks, pores and pits in the carbon material or C/C composite. Comparing the carbon sample and C/C composite, it was also found that the coating on C/C composites was more difficult than that on carbon samples, especially on the carbon fibers.

In spite of the existence of serious cracks, the effects of SiO$_2$ coating on the oxidation resistance was shown. Responding to the formation of SiO$_2$ coating, for both carbon samples and C/C composites, the best of oxidation resistance was observed in the samples by dip-coating in the precursor solution of Si(OEt)$_4$/EtOH being 1:20. It was suggested that the oxidation resistance by the SiO$_2$ coating was due to the decrease of
effective surface of carbon for oxidation and the barrier of the diffusion of oxidation gases by the cracks at higher temperatures. However, it was not successful to protect C/C composites from the onset of oxidation. Further improvement of coatings would need to be carried out for enhancing the oxidation resistance of C/C composite.

In chapter 5, improvement of the oxidation resistance of the C/C composite with the multi-coating of LaB₆-Si/polycarbosilane/SiO₂ was carried out based on the previous study. A considerable enhancement of oxidation resistance was obtained by this multi-coating.

In the case of LaB₆-Si coated and LaB₆-Si/PCS-coated composites under the present experimental conditions, the oxidation rates were controlled by oxygen diffusion at the temperatures over 900°C and 950°C, respectively. Below the temperature of 900°C, the additives of LaB₆-Si played the role of diffusion barriers and lowered the oxidation rates of the composite by over two orders of magnitude. The apparent activation energy for LaB₆-Si coated C/C composite was calculated to be about 21 kJ/mol at higher temperature and about 190 kJ/mol at lower temperature. It was found that the impregnation of PCS sealed the larger pores around the LaB₆-Si particles and improved the compatibility between the coating layer and the C/C composite. This gave a decrease of the effective surface for oxidation and further retarding the diffusion of oxidizing gases. Below 950°C, the oxidation rate of the PCS-coated composite was decreased by one order of magnitude, comparing to that of the composite without PCS. The apparent activation energy for LaB₆-Si/PCS coated C/C composite was calculated to be about 33 kJ/mol over 950°C and about 200 kJ/mol below 950°C.

A continuous protective layer that sealed smaller pores and cracks was formed after SiO₂ coating by sol-gel technique. It was found that the wetting of SiO₂ on PCS was improved in oxidation circumstance and the continuous coating layer was formed by SiO₂-PCS at the exterior of the coating and protected the C/C composite over 1100°C. With the increase of temperature, the glass layer enclosing Si powders formed on the surface of the C/C composite. A remarkable resistance of the C/C composite with LaB₆-Si/PCS/SiO₂ coating was shown at the temperatures up to 1300°C.

In chapter 6, a model for the multi-coating of LaB₆-Si/PCS/SiO₂ was established with the thermodynamic and kinetic analysis. With this model, the effects of every individual layer were discussed systematically in the formation and oxidation resistance of the multi-coating.

In the formation of the multi-coating in the model, LaB₆ and silicon played a role as the primary oxygen barriers. Boron was introduced by the LaB₆ coating and 2000°C heat-treatment, silicon powder was dispersed with LaB₆ powder on the surface of the C/C composite. The PCS impregnated as the bond layer covered the powder layer of LaB₆-Si.
The SiO₂ coating by sol-gel technique sealed the cracks in the PCS coating. Because of the formation of the multi-coating of LaB₆-Si/PCS/SiO₂ with amorphous and powder materials, a good thermal compatibility was obtained between the coating and C/C composite and between the various materials in the coating.

In the oxidation resistance of the multi-coating in the model, it was demonstrated that the invisible microcracks were sealed by the formation of B₂O₃-SiO₂ due to the oxidation of boron, LaB₆ and Si at low partial pressure of oxygen in the multi-coating. With the calculation in thermodynamics and kinetics, it was also predicted that the complete coating firstly formed around the boundary of the multi-coating and the oxidizing environment, instead of the surface of C/C composite. Then, the B₂O₃-SiO₂ would shift to and finally locate on the surface of C/C composite with the increase of temperature. It was suggested that the SiO₂ coating by sol-gel played as the most role in the multi-coating for the oxidation resistance. All the results derived from the model in this chapter were supported by the experimental results obtained.

For all the experimental results and discussion in this study, it is confirmed that effective oxidation protection can only be achieved if the coating system has a self-healing ability. A functional layer containing boron and silicon phases is necessary to seal cracks during oxidation. Sol-gel technique can become an important method to form the glass phase that seals the cracks in the functional layer.
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After I was graduated from Qinghua University, Beijing at 1985, I was engaged in the researches of ceramic materials at Shanghai Institute of Ceramics, Chinese Academy of Science. During this period, the researches were concerned with mechanic, electric, dielectric, ferroelectric and other physical properties of ceramics. For further understanding and widen the view of material science, the eagerness to strengthen the research background was supported by our institute. At 1992, I was introduced to Professor Kazuo Kobayashi who is one of the most energetic members in the field of carbon materials and C/C composite in Japan. I expressed my strong willingness to become a student in his laboratory. With his kind commendation, I was accepted by Nagasaki University, Japan as a recipient of a Japanese Government Scholarship from Jan. 1993. In April of the next year, I was admitted to the doctoral degree program of the Graduate School of Marine Science and Engineering, thus I was able to study and understand the oxidation behavior of C/C composites that was the new research field for me.

This thesis research was accomplished at the Advance Materials Laboratory in the Faculty of Engineering, Nagasaki University under the direction of Professor Kazuo Kobayashi. It is base on the primary research and the suggestion of Professor Kobayashi that improves the oxidation resistance by removing and protecting the active sites in carbon surface from oxidation environments with additives of boron, silicon and their compounds. Because of his abundant knowledge of material science and deep understanding of chemical and physical properties of carbon materials, my research progressed steadily. Therefore I wish to express my greatest admiration to Professor Kazuo Kabayashi for his enlightening and sympathetic guidance during this research.

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