Oxidation Protection Coatings for Carbon Materials by Interfacial Control
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Porous carbon substrates have been sealed completely with a molten silicate glass, where the wettability of the carbon to the molten glass was improved by infiltration and pyrolysis of perhydropolysilazane. The interfacial structure between the carbon and glass depended on the N₂ partial pressures during sealing. Coating of the glass at a higher N₂ partial pressure was not followed by formation of cristobalite due to oxidation of the products pyrolyzed on the carbon substrate. The molten glass easily infiltrated into the substrate. Under lower N₂ partial pressures such as in Ar, the glass covered only the carbon substrate and seldom penetrated into the substrate. In this case, cristobalite was produced at the interface, with many pores also forming at the interface. The pores are due to the large amount of SiO produced by oxidation of the pyrolyzed species, leading to suppression of molten glass infiltration into the carbon. The structural changes occurring as a result of variation in N₂ partial pressures are described in terms of thermodynamic calculations.
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1. Introduction
Superheated steam drying has received considerable attention for various industrial applications such as drying of paper and pulp, spray drying, food processing and sterilization, because superheated steam does not contain O₂ or CO₂, and its exhaust gas can be easily recycled by condensation. Furthermore, the drying velocity of superheated steam is faster than that of air drying above certain temperatures. However, in order to develop advanced applications such as waste disposal and hydrogen generators in addition to improving their work efficiencies, the operating temperatures of heaters, which are the key components of superheated steam systems, should be increased to above 1000 K. Although conventional heaters are made of metallic materials, their upper temperature limit is about 800 K because of their poor thermal stability and steam oxidation resistance.
Carbon materials are promising candidates for use in heaters since they have excellent thermal stability, are lightweight and relatively cheap. It is well known, however, that their oxidation resistance is significantly inferior to that of metals. Various investigations have been carried out to improve oxidation protection coatings applied to carbon, e.g., multilayered coatings consisting of carbon/Si–SiO₂/mullite, or carbon/SiC/YSi₃/Y₂SiO₅. Unfortunately, the oxides acting as the protective layers are not fully densified, so that it is difficult to achieve sufficient durability in high temperature superheated steam for long periods.
Coatings of molten glass on carbon substrates can act as densified oxidation protective layers. However, the wettability of the carbon to the molten glass on its own is too low to be perfectly covered with the glass. Hence, the carbon is usually coated with the glass after its wettability has been improved by deposition of Si or SiC layers on the carbon. It is well known, however, that cristobalite is produced at the interface between a glass and Si or SiC. This cristobalite is probably produced by oxidation of the Si-species. Since the transformation of cristobalite from β- to α-types at about 540 K during cooling is accompanied by a large volume shrinkage (3.9%), microcracks are initiated at the interface and/or in the cristobalite layer either during cooling after coating with the glass or during thermal cycling when in use. This can result in failure or separation of the glass layer from the carbon substrate.
In this study, porous carbon substrates have been sealed completely with a molten silicate glass. The wettability of the carbon to the molten glass was improved by infiltration and pyrolysis of an Si–N precursor. Control of the N₂ partial pressures during coating of the molten glass inhibits production of cristobalite with the atmosphere conditions during coating estimated by thermodynamic calculations. The N₂ partial pressure dependence of the interfacial structures is compared with prediction from the thermodynamic calculations.

2. Experimental procedure
Carbon plates (ETU-10, 28 mm x 38 mm x 3 mm) from Carbonics Co., Japan were used for substrates. Their open porosity was 15 vol%. The carbon substrates were soaked in a precursor solution of perhydropolysilazane (N–N110, Clarient Japan, xylene solvent), drying by evaporation of the solvent in vacuo, and treated at 873 K for 1 hour in N₂ under atmospheric pressure. Soaking and pyrolysis of the substrates was repeated three times. Each surface modified carbon substrate was set in a carbon mold and Y-Al–Si–O glass, which was prepared beforehand by melting a mixture of 33 wt% Y₂O₃, 21 wt% Al₂O₃ and 46 wt% SiO₂ at 1660 K, was filled around the substrates. The glass of this composition has the same thermal expansion coefficient as the carbon substrates and a glass transition temperature of about 1150 K. The carbon substrates were coated with the molten glass at 1773 K, using a carbon heater, for 1 hour in N₂ or Ar (total pressure of 10⁶ Pa).
Cross sections of the specimens were observed using a scanning electron microscope (SEM). The interfaces between the glass layer and carbon substrate of the specimens were examined using a transmission electron microscope (TEM) with energy-dispersive X-ray spectroscopy (EDS) and electron diffraction (ED). Crystalline phases of the pyrolyzed products of the precursor, which was dried and heat-treated under the same conditions as the coatings of the molten glass, were identified by X-ray diffraction (XRD). The chemical compositions of the products were calculated from the total amount of C, N and O in the products.
Fig. 1. Chemical potential diagram of the Si–C–N–O system at 1773 K.

3. Thermodynamic stability

Thermodynamic analysis was performed for the Si–C–N–O system, assuming a simplified glassy matrix of SiO₂. Figure 1 shows the chemical potential diagram of the Si–C–N–O system at 1773 K. Since Si₃N₄ may form by reaction between SiO₂ and Si₃N₄, which is one of the pyrolyzed products, it was added to the stable condensed phases for the calculations. As seen in Fig. 1, Si₃N₄, Si₃N₄O and SiO₂ consequently become the most stable phase as the O₂ partial pressure is increased when N₂ partial pressures are above 3 × 10⁵ Pa. The partial pressure of O₂ in the furnace depends on that of CO, which is produced by reaction of the carbon mold with oxygen derived from the glass, as it is being coated. Although the CO partial pressure around the samples was expected to increase during coating, it shouldn’t have exceeded the total pressure of 10⁶ Pa. Consequently, when a surface modified layer of Si₃N₄ is coated onto the carbon substrates, followed by coating of the molten glass under an N₂ partial pressure greater than 3 × 10⁵ Pa, the Si₃N₄ is oxidized to form Si₃N₄O. In other words, oxidation of Si₃N₄ does not produce SiO₂. Under an N₂ partial pressure less than 4 Pa, the stability of phases such as Si, SiC and SiO₂ depends on both the O₂ partial pressure and carbon activity. The stability region of SiO₂ extends to lower O₂ partial pressures than that for higher N₂ partial pressures. If Si and/or SiC are coated onto the carbon substrates, they act as a strong driving force for oxidation and formation of SiO₂ (cristobalite).

Figures 2 and 3 show equilibrium partial pressures of SiO in the Si–C–N–O system at 1773 K under N₂ partial pressures above 3 × 10⁵ Pa and below 4 Pa, respectively. In O₂ partial pressures where Si₃N₄O is the most stable phase under N₂ partial pressures greater than 3 × 10⁵ Pa, the corresponding partial pressure of SiO is much lower than for the same O₂ pressure under N₂ pressures below 4 Pa. The coating of molten glass under the higher N₂ pressure is expected to suppress formation of bubbles in the glass due to the production of a large amount of SiO as well as inhibition of cristobalite formation, resulting in a dense glass layer strongly adhered to the carbon substrate.

Fig. 2. Equilibrium partial pressure of SiO in the Si–C–N–O system at 1773 K under N₂ partial pressures above 3 × 10⁵ Pa.

Fig. 3. Equilibrium partial pressure of SiO in the Si–C–N–O system at 1773 K under N₂ partial pressures below 4 Pa.

4. Results and discussion

Figure 4 shows XRD patterns of the products of the precursor pyrolyzed under the same conditions as the molten glass coating. The pattern of the pyrolysis products under N₂ can be attributed to a mixture of Si₃N₄ and a slight amount of Si as shown in Fig. 4(a). The pattern for Ar exhibits peaks that can be assigned to SiC in addition to Si₃N₄ and Si (Fig. 4(b)). The intensity of peaks corresponding to Si for the pyrolysis product under Ar is much larger than that for N₂.

Table 1 lists the compositions of the products of precursor pyrolyzation. It is assumed that the summed fractions of C, N, O subtracted from total amount (100 wt%) leaves the Si content. Assuming that there is no free carbon because Si was also present, the compositions of compounds such as Si₃N₄, SiO₂, SiC and Si were determined from the elemental compositions listed in Table I. Pyrolysis of the precursor in Ar increases the amounts of both Si and SiC compared with that in N₂. This is in good agreement with our calculations showing that Si and SiC are thermodynamically stable under lower N₂ partial pressures as shown in Fig. 1. The surface modified layers formed on the carbon substrates are probably the same compounds as
Table 1. Compositions of Products of Precursor Pyrolyzation at 1773 K Under a Total Pressure of 10^4 Pa

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Elemental composition, wt%</th>
<th>Calculated composition, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>N</td>
</tr>
<tr>
<td>N$_2$</td>
<td>61.4</td>
<td>38.1</td>
</tr>
<tr>
<td>Ar</td>
<td>65.5</td>
<td>32.6</td>
</tr>
</tbody>
</table>

Fig. 4. XRD patterns of products of precursor pyrolyzation (a) in N$_2$ and (b) in Ar.

Fig. 5. SEM micrographs and EDS line profiles of cross sections of the interface between the glass layer and carbon substrate for the specimen fabricated in N$_2$: (a) low magnification and (b) high magnification.

Fig. 6. SEM micrographs and EDS line profiles of cross sections of the interface between the glass layer and carbon substrate for the specimen fabricated in Ar: (a) low magnification and (b) high magnification.

but it also infiltrated into the interior as shown in Fig. 5(a). The excellent wettability of the carbon to the molten glass has therefore been confirmed experimentally. There are no deteriorated regions or pores at the interface between the glass layer and the carbon substrate. Examination of the interface using TEM with EDS and ED did not reveal a Si$_3$N$_4$ layer, even though it should have been formed by pyrolysis of the precursor soaked on the carbon substrate, as the glass was in direct contact with the carbon. We therefore think that the Si$_3$N$_4$ dissolved into the molten glass. The inhibiting of cristobalite formation at higher N$_2$ pressures is consistent with the thermodynamic diagrams given in Figs. 1 and 2.

Figure 6 shows SEM micrographs and EDS line profiles of cross sections of the interface for the specimen fabricated in Ar. The glass sealed only the surface of the carbon substrate and scarcely percolated into the substrate (Fig. 6(a)). A degenerate layer (a few microns thickness) was formed at the interface (Fig. 6(b)). TEM analysis indicated that this layer consists of cristobalite. Moreover, there were many pores at the interface, as can be seen in Fig. 7. Cristobalite is thought to be produced by oxidation of surface modified species such as Si and SiC on the carbon substrate during glass coating in Ar as predicted from Figs. 1–3. The pores formed as a result
of the large formation amount of SiO produced by oxidation, and suppress infiltration of the molten glass into the carbon.

5. Conclusions
The wettability of porous carbon substrates to molten silica glass was improved by infiltration and pyrolysis of perhydropolysilazane. The glass fully covered and infiltrated into the surface modified carbon substrates for the higher N\textsubscript{2} pressure without formation of cristobalite due to oxidation of the pyrolyzed products. In contrast, cristobalite formed at the interface when coated in Ar. Many pores also formed at the interface. The pores were probably a result of the large amount of gaseous SiO produced by oxidation. The N\textsubscript{2} partial pressure dependence of the interfacial structures is in agreement with thermodynamic calculations.

References