INFLUENCE OF AIR OXIDATION ON THERMAL SHOCK RESISTANCES OF NUCLEAR CARBON MATERIALS

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Abstract

The purpose of this study is to evaluate the influence of air oxidation at 500 °C on thermal shock resistances and thermal shock fracture toughnesses of a carbon fibre reinforced carbon composite (C/C composite) made from rayon carbon fibre felt and three fine-grain, isotropic, nuclear graphites. These thermal shock resistances and thermal shock fracture toughnesses for the four nuclear carbon materials were degraded slightly by oxidation. The extents of degradations of the thermal shock parameters were less than those of mechanical and fracture mechanics properties. However, the extent of degradation of thermal diffusivity was much less than those of the thermal shock parameters. In observations of the microstructures of the fracture surfaces, after oxidation of the graphite, the size and the number of pores were increased and the fracture surfaces were roughened by oxidation of boundaries of graphite particles. After oxidation of the C/C composite, there was preferential removal of the boundary layer between carbon fibre and pyrolytic carbon matrix and carbon fibre pull out. However, the more graphitized cores of pyrolytic carbon remained and the extents of degradations of the thermal shock parameters for the C/C composite were less than those of the graphites.

1. INTRODUCTION

Nuclear carbon materials have valuable properties such as low atomic number, high specific strength and stiffness, high heat resistance and high thermal shock parameters. As a result, they find applications in very severe conditions such as moderators and reflectors in gas cooled nuclear reactors and plasma facing components for fusion reactor devices.

The mechanical properties of carbon materials are generally known to be degraded by oxidation [1-4]. In some accident scenarios for nuclear reactors, carbon materials are exposed to air at high temperature. The purpose of this study is to evaluate the influence of air oxidation on thermal shock resistances and thermal shock fracture toughnesses for a carbon fibre reinforced carbon composite (C/C composite) made from rayon carbon fibre felt and three fine-grain isotropic graphites that are used as

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core constructional materials for the high temperature gas cooled test reactor (HTTR) of Japan Atomic Energy Research Institute (JAERI) and main materials of plasma facing components for a fusion reactor device (JT-60U) of JAERI. The C/C composite and the three graphites were oxidized at 500 ± 3 °C in air. The thermal shock resistance and the thermal shock fracture toughness were measured by an eccentric local heating method. The mechanical and fracture mechanics properties and the thermal diffusivity were also measured and then the microstructures of the fracture surfaces were examined using a scanning electron microscope (SEM).

2. MATERIALS

Table 1 shows properties of the C/C composite and three nuclear graphites that were all made by Toyo Tanso Co. Ltd. The CX-2002U composite is used as a divertor plate for the JT-60U of JAERI. The properties of the C/C composite are anisotropic, the bulk density is less than the graphites, and the compressive strength is about two thirds those of the graphites. The thermal conductivity of the C/C composite in the parallel direction is about three times those of the graphites and the coefficient of thermal expansion in the parallel direction is about a half those of the graphites. The thermal conductivity and the coefficient of thermal expansion of the perpendicular direction are a little larger than those of the graphites. The IG-110 graphite is used as a core constructional material for the HTTR of JAERI. The IG-110U graphite is used as a part of the first wall for a fusion reactor device (TEXTOR) at Jülich, Germany. The IG-430U graphite is used as a main material of plasma facing components for the JT-60U of JAERI. The IG-110U and IG-340U graphites and the CX-2002U composite are ultra high purity materials as a result of a special heat treatment.

Specimens in this study were in the form of disks of 20 mm in diameter and 2 mm in height for thermal shock tests and rectangular rods of 4x6x50 mm and 6x8x70 mm for mechanical and fracture mechanics tests. In the case of the C/C composite, the rectangular rods enabled properties to be measured in the parallel direction and the disks were used to measure properties of the perpendicular direction because thermal shock fracture occurs at the weakest point.

Table 1. Properties of a C/C composite (CX-2002U) and three graphites (IG-110, IG-110U, IG-430U).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>CX-2002U</th>
<th>IG-110</th>
<th>IG-110U</th>
<th>IG-430U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density $\gamma$ (g/cm$^3$)</td>
<td>1.67</td>
<td>1.77</td>
<td>1.78</td>
<td>1.84</td>
</tr>
<tr>
<td>Shore hardness $H_s$ (((/)/(_L)))</td>
<td>3.5 (3.0)</td>
<td>54</td>
<td>52</td>
<td>60</td>
</tr>
<tr>
<td>Specific resistance $\rho$ ($\mu$Ωcm)</td>
<td>3.23</td>
<td>1100</td>
<td>1040</td>
<td>930</td>
</tr>
<tr>
<td>Bending strength $\sigma_b$ (MPa) (((/)/(_L)))</td>
<td>41.0</td>
<td>39.2</td>
<td>41.2</td>
<td>56.8</td>
</tr>
<tr>
<td>Compressive strength $\sigma_c$ (MPa) (((/)/(_L)))</td>
<td>51.1</td>
<td>78.4</td>
<td>76.4</td>
<td>99.0</td>
</tr>
<tr>
<td>Young's modulus $E$ (GPa) (((/)/(_L)))</td>
<td>11.3</td>
<td>9.8</td>
<td>9.8</td>
<td>10.8</td>
</tr>
<tr>
<td>Thermal conductivity $k$ (W/mK) (((/)/(_L)))</td>
<td>33.1</td>
<td>116</td>
<td>116</td>
<td>140</td>
</tr>
<tr>
<td>Coefficient of thermal expansion $\alpha$ (x10$^{-6}$/K) (((/)/(_L)))</td>
<td>2.0 (5.9)</td>
<td>4.6 (4.5)</td>
<td>5.2 (5.2)</td>
<td></td>
</tr>
</tbody>
</table>

(*1) // and \_L indicate the parallel and the perpendicular directions.
(*2) Mean values at 350~450°C, (*3) Mean values at R.T.~1000°C.
3. AIR OXIDATION

Specimens were cleaned ultrasonically in distilled water and acetone. After drying, the specimens were uniformly oxidized in conditions of natural convection inside a cylindrical graphite tube of 40 mm in diameter and 400 mm in length arranged inside a siliconit electric furnace (SPSH-24). The temperature of the 80 mm hot zone in the centre inside the tube was 500 ± 3 °C. The temperature corresponds to that of the first wall as plasma facing components for the next fusion reactors (DEMO reactors) [5]. The range of temperature and oxidation rate in this study did not result in changes in the shapes of specimens, this indicates that oxidation was chemically controlled. The range of oxidation weight loss was up to about 10 % that is considered to be the range in which there is the most radical change in the properties of carbon materials [4].

4. EXPERIMENTAL

The burn-off, B, was calculated from:

\[ B = 100 \left( \frac{w_0 - w}{w_0} \right) \]  

where \( w_0 \) and \( w \) are the weights before and after oxidation, respectively.

The influences of burn-off on various properties were represented by the empirical relationship [1]:

\[ S = S_0 \exp(-nB) \]

where \( S \) and \( S_0 \) are the values of various properties after and before oxidation, respectively, and \( n \) is an empirical constant.

4.1. Thermal shock resistance and thermal shock fracture toughness

Figure 1 shows the specimens for (a) thermal shock resistance, \( \Delta \) [6], and (b) thermal shock fracture toughness, \( \nabla \) [7], measurements which were made using an eccentric local heating method [8]. Thermal shock resistance and thermal shock fracture toughness were evaluated by measuring the critical values fractured by an electric heating power, \( W \), that heats transiently and quickly an eccentric local area, as follows:

\[ \Delta = \frac{\sigma_t k/E \alpha}{S \beta W / \pi h (a/R)^2} \]  

\[ \nabla = \frac{K_{IC} \beta}{F_{te} (\pi c)^{1/2}} \frac{\pi h W / \pi h (a/R)^2}{W_{mm}^{1/2}} \]

where \( \sigma_t \), \( K_{IC} \), \( k \), \( E \), and \( \alpha \) are the tensile strength, the mode I fracture toughness, the thermal conductivity, the Young’s modulus and the coefficient of thermal expansion of the tested material, respectively. \( S \) is the non-dimensional specific thermal stress (= 0.01371 in this study). \( F_{te} \) is the non-dimensional stress intensity factor (= 0.01790 in this study). \( \beta \) is the heat efficiency values of which for the CX-2002U composite, the IG-110, IG-110U and IG-430U graphites before oxidation are about 0.49, 0.47, 0.49 and 0.48 in this study, respectively. Those of the oxidized materials are nearly equal to the values before oxidation. \( a \), \( c \), \( h \) and \( R \) are the radius of the heating area, the side slit length, the height and the radius of the disk specimen, respectively.

The measurements of thermal shock resistance and thermal shock fracture toughness by the eccentric local heating method simulate the rapid heating and cooling of core structures of gas cooled nuclear reactors and the irregular heat load and attack on plasma facing components of fusion reactor devices by electrically charge particles at plasma disruption.

5. EXPERIMENTAL RESULTS AND DISCUSSIONS

5.1. Thermal shock resistance and thermal shock fracture toughness

Figure 2 shows the relation between logarithm of the ratio of thermal shock resistances after and before oxidation, \( \ln(\Delta/\Delta_0) \), and burn-off for the CX-2002U(\perp) composite. The white and black symbols in this figure indicate the samples that "did not fracture" and that "did fracture" by thermal shock test, respectively. Thermal shock resistance, \( \Delta \), before oxidation was calculated from the range between maximum data of "did not fracture" and minimum data of "did fracture" by thermal shock test.
Fig.1. Specimens for (a) thermal shock resistance and (b) thermal shock fracture toughness measurements.

Fig.2. Relation between thermal shock resistance ratio, \( \ln(\Delta/\Delta_0) \), and burn-off of the CX-2002U(\perp) composite.

The critical value of the thermal shock resistance of the CX-2002U(\perp) composite decreases slightly with increasing of burn-off, as follows:

\[
\Delta = 60.5 \exp(-0.027B) \quad (W/mm) \quad (5).
\]

Table 2 shows the parameters of the empirical relationship, \( S = S_0 \exp(-nB) \), for thermal shock resistances, thermal shock fracture toughnesses and thermal diffusivities of nuclear carbon materials. The \( S_0 \) values of thermal shock resistances for the CX-2002U(\perp) composite and the IG-430U graphite are almost equal and larger than those of the IG-110 and IG-110U graphites. The \( n \) value of thermal shock resistance decreases in the following order: IG-110U graphite, IG-430U graphite, IG-110 graphite and CX-2002U(\perp) composite. The extent of degradation of thermal shock resistance for the CX-2002U(\perp) composite is the smallest because of reinforcement by carbon fibre felt. In this study, the \( n \) value of the IG-430U graphite is larger than that of the IG-110 graphite and it is nearly equal to those of the IG-110 and TS-1621 graphites oxidized at 600°C [1].

Figure 3 shows the relation between logarithm of the ratio of thermal shock fracture toughnesses after and before oxidation, \( \ln(V/V_0) \), and burn-off for the CX-2002U(\perp) composite. The critical value of the thermal shock fracture toughness decreases slightly with increasing burn-off as does thermal shock resistance. The parameters in Table 2 show that the \( S_0 \) value of thermal shock fracture toughness increases in the following order: IG-110 graphite, IG-110U graphite, IG-430U graphite and CX-2002U(\perp) composite. The \( n \) values of thermal shock fracture toughnesses for the CX-2002U(\perp) composite and the IG-430U graphite are less than those of other graphites. As with thermal shock resistance, the extent of degradation of thermal shock fracture toughness for the CX-2002U(\perp)
Table 2. Parameters of the empirical relationship, $S = S_0 \exp(-nB)$, for thermal shock resistances, thermal shock fracture toughnesses and thermal diffusivities of nuclear carbon materials.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>CX-2002U (-L)</th>
<th>IG-110</th>
<th>IG-110U</th>
<th>IG-430U</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>60.5</td>
<td>39.9</td>
<td>45.0</td>
<td>60.2</td>
</tr>
<tr>
<td>$n$</td>
<td>0.027</td>
<td>0.036</td>
<td>0.072</td>
<td>0.066</td>
</tr>
<tr>
<td>$S_0$</td>
<td>94.8</td>
<td>59.7</td>
<td>69.0</td>
<td>73.8</td>
</tr>
<tr>
<td>$\n$</td>
<td>0.026</td>
<td>0.031</td>
<td>0.036</td>
<td>0.027</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>78.5</td>
<td>64.0</td>
<td>63.8</td>
<td>65.0</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.007</td>
<td>0.014</td>
<td>0.018</td>
<td>0.013</td>
</tr>
</tbody>
</table>

The composite is the smallest because of reinforcement by carbon fibre felt. In this study, the $n$ value of the IG-110U graphite is a little larger than that of the IG-110 graphite and it is about a half of the $n$ value for the thermal shock resistance. The $n$ values of three graphites are less than those of the IG-110 and TS-1621 graphites oxidized at 600°C [1].

The thermal shock resistance and the thermal shock fracture toughness in the parallel direction of the CX-2002U composite are very large [9] so that they are determined by properties in the perpendicular direction.

5.2. Other properties

Table 3 shows the parameters of $S_0$ and $n$ for Young's modulus, bending strength, Rockwell hardness and the mode I fracture toughness of nuclear carbon materials. In general, the extents of degradations of mechanical and fracture mechanics properties of the CX-2002U composite are less than those of the IG-430U graphite that, in turn, are less than those of the IG-110 and IG-110U graphites whose degradations are similar to each other. Exceptions are the $n$ values of Rockwell hardness of the CX-2002U composite and the mode I fracture toughness of the IG-430U graphite. The extents of degradations of mechanical and fracture mechanics properties are larger than those of the thermal shock parameters, and much larger than that of thermal diffusivity in table 2.

6. MICROSTRUCTURES OF THE FRACTURE SURFACES

Photograph 1 shows typical fracture appearances in (a) thermal shock resistance and (b) thermal shock fracture toughness tests for the CX-2002U(-L) composite. The thermal cracks extend from the outside edge or the tip of the side slit to the centre of the heating area. Photograph 2 shows typical cracks from the tip of the side slit in thermal shock fracture toughness test for (a) the CX-2002U(-L) composite and (b) the IG-430U graphite before oxidation. The thermal cracks extend through pores along the boundaries of the carbon fibres or graphite particles. The thermal cracks after oxidation are similar to those before oxidation.

Photograph 3 shows the microstructures of the fracture surfaces of (a) the CX-2002U(-L) composite and (b) the IG-430U graphite in thermal shock fracture toughness test by SEM. After oxidation of the C/C composite, there are preferential removal of the boundary layer between carbon fibre and pyrolitic carbon matrix, and pull out of carbon fibres about 7 μm in diameter. However, the more graphitized cores of pyrolitic carbon remain and the extents of degradations of the thermal shock parameters and thermal diffusivity of the C/C composite were less than those of the graphites. After oxidation of the graphite, the size and the number of pores increase and the fracture surfaces roughen by oxidation of boundaries of graphite particles. Consequently, the mechanical and fracture mechanics properties and the thermal shock parameters of the graphite degraded by the increasing porosity and the weakening of bonding between graphite particles. However, the more graphitized graphite particles remain and the extent of degradation of the thermal diffusivity was very small. The microstructures of the fracture surfaces for other oxidized graphites are similar.

219
Fig. 3. Relation between thermal shock fracture toughness ratio, \( \ln(V/V_0) \), and burn-off of the CX-2002U(L) composite.

Table 3. Parameters of the empirical relationship, \( S = S_0 \exp(-nB) \), for mechanical and fracture mechanics properties of nuclear carbon materials.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>CX-2002U (L)</th>
<th>IG-110</th>
<th>IG-110U</th>
<th>IG-430U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus E (GPa)</td>
<td>12.3</td>
<td>0.039</td>
<td>9.7</td>
<td>0.109</td>
</tr>
<tr>
<td>Bending strength ( \sigma_b ) (MPa)</td>
<td>41.9</td>
<td>0.045</td>
<td>37.0</td>
<td>0.104</td>
</tr>
<tr>
<td>Rockwell hardness ( H_{R,15x} )</td>
<td>44.3</td>
<td>0.101</td>
<td>73.2</td>
<td>0.084</td>
</tr>
<tr>
<td>Mode I fracture toughness ( K_{IC} ) (MPa.m(^{1/2}))</td>
<td>1.19</td>
<td>0.040</td>
<td>0.85</td>
<td>0.087</td>
</tr>
</tbody>
</table>

Photo 1. Typical fracture appearances in (a) thermal shock resistance and (b) thermal shock fracture toughness tests for the CX-2002U(L) composite.
Photo 2. Typical cracks from the tip of the side slit in thermal shock fracture toughness test for (a) the CX-2002U(±) composite and (b) the IG-430U graphite before oxidation.

Photo 3. Microstructures of the fracture surfaces of (a) the CX-2002U(±) composite and (b) the IG-430U graphite in thermal shock fracture toughness test by SEM.
7. EVALUATION OF THE LIFE LIMIT FOR CARBON MATERIALS

In the safety design of the HTTR, the standard strength of Su for carbon and graphite is established as the strength corresponding to 99% probability of non-destruction and 95% reliability [10]. The average of the standard strengths in tension and compression for the IG-110 graphite is 78% of the mean strength. If the above design standard were applied to the case of the C/C composite and graphites for fusion reactor devices, when the strength degraded to the value of 78% of the mean strength, these members ought to be exchanged or repaired because of the life limit. The parameters B and D that are the slopes in loading and unloading curves in dynamic hardness tests [11,12] were correlating to bending strength, \( \sigma_b \), and Young's modulus, E, respectively. By using the results of dynamic hardness tests, we can evaluate the extents of degradations and can decide the life limit and the exchanging period of structural carbon materials.

The residual pressure in the vacuum vessel is only about 10<sup>-8</sup> Torr [13] so that plasma facing components for fusion reactor devices do not need to be exchanged as a result of air oxidation. However, properties of carbon materials are more likely to be degraded further in an accident, by plasma disruption and by neutron irradiation. So studies of these problems are necessary in the future.

![Fig.4. Calculated temperature dependences of (a) thermal shock resistance and (b) thermal shock fracture toughness for the IG-110 graphite.](image)

8. DEDUCED THERMAL SHOCK RESISTANCES

The deduced thermal shock resistance, \( \Delta' \), and the deduced thermal shock fracture toughness, \( \tau' \), were calculated by using the properties in table 3 and substituting the value of 70% of bending strength for tensile strength, thermal conductivity deduced from thermal diffusivity, and assuming a constant coefficient of thermal expansion. However, properties of the CX-2002U composite in table 3 are the values in the parallel direction to the felt surface, therefore, the deduced values of the CX-2002U composite in this chapter are the reference values. Table 4 shows the parameters of \( S_0 \) and \( n \) for the deduced thermal conductivity, the deduced thermal shock resistance and the deduced thermal shock fracture toughness of nuclear carbon materials. The \( S_0 \) values of the deduced thermal shock resistances for the IG-110 and IG-110U graphites are larger than those of the CX-2002U composite and the IG-430U graphite and they are larger than the experimental values of thermal shock resistances in table 2. The deduced values are, therefore, too optimistic for use in the safety design of these carbon materials. The \( n \) values of the deduced thermal shock resistance and the deduced thermal shock fracture toughness are less than the experimental values, excepting the thermal shock fracture toughness of the IG-430U graphite. Thus, the deduced values are also too optimistic for the safety design of these materials. Therefore, it is necessary to evaluate directly thermal shock resistances and thermal shock fracture toughnesses of carbon materials by experimental methods as in this study.
Table 4. Parameters of the empirical relationship, $S = S_0 \exp(-nB)$, for the deduced properties of nuclear carbon materials.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>CX-2002U</th>
<th>IG-110</th>
<th>IG-110U</th>
<th>IG-430U</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>99.6</td>
<td>81.6</td>
<td>81.8</td>
<td>86.1</td>
</tr>
<tr>
<td>$n$</td>
<td>0.017</td>
<td>0.024</td>
<td>0.028</td>
<td>0.023</td>
</tr>
</tbody>
</table>

9. TEMPERATURE DEPENDENCES OF THERMAL SHOCK RESISTANCES

Temperature dependences of thermal conductivity, $k$, Young’s modulus, $E$, and coefficient of thermal expansion, $\alpha$, for the IG-110 graphite were experimentally obtained by JAERI [10] and those of tensile strength, $\sigma_t$, and the mode I fracture toughness, $K_{JC}$, for the IG-11 graphite were also measured [14]. Tensile strength and the mode I fracture toughness of the IG-110 graphite are considered to be nearly equal to those of the IG-11 graphite because the IG-110 graphite was obtained by heat treatment of IG-11 graphite for the high purity. The temperature dependences of thermal shock resistance and thermal shock fracture toughness for the IG-110 graphite can be estimated by using the above data. Figure 4 shows the calculated temperature dependences of (a) thermal shock resistance and (b) thermal shock fracture toughness for the IG-110 graphite. These thermal shock parameters decrease rapidly with increasing temperature from room temperature to 1500°C, and then they increase gradually with increasing temperature over 1500°C. The experimental values of thermal shock resistance and thermal shock fracture toughness of the IG-110 graphite correspond to the calculated values at 800°C and 400°C, respectively. The calculated values estimated from room temperature properties are larger than the experimental values of thermal shock parameters. They are, therefore, too optimistic for the safety design of these carbon materials.

10. CONCLUSION

Four nuclear carbon materials, a C/C composite made from rayon carbon fibre felt and three fine-grain isotropic graphites, were oxidized at 500 ± 3 °C in air. These thermal shock resistances, thermal shock fracture toughnesses and various other properties were measured and the microstructures of the fracture surfaces were also examined. The results are summarized as follows:

(1) Thermal shock resistances and thermal shock fracture toughnesses of the CX-2002U(±) composite and the IG-430U graphite are larger than those of other graphites. Thermal shock resistances and thermal shock fracture toughnesses are degraded slightly by oxidation. In general, the extents of degradations of the CX-2002U(±) composite are the smallest and those of the IG-430U graphite are less than those of the other graphites. The extents of degradations of thermal shock resistance and thermal shock fracture toughness are less than those of mechanical and fracture mechanics properties, however, they are larger than that of thermal diffusivity.

(2) In the C/C composite, the boundary layers between carbon fibres and pyrolitic carbon matrix are preferentially oxidized and pull out of carbon fibres occur. However, the more graphitized cores of pyrolitic carbon remain. In the graphites, the size and the number of pores increase and the fracture surfaces roughen by oxidation of boundaries of graphite particles.

(3) Structural members ought to be exchanged or repaired when the strength degraded to the value of 78 % of the mean strength. This can be evaluated by dynamic hardness test.

(4) The deduced thermal shock resistance and the deduced thermal shock fracture toughness were calculated from the relevant parameters and temperature dependences of thermal shock resistance and thermal shock fracture toughness of the IG-110 graphite were also calculated. However, those values...
do not agree with the experimental data and they are too optimistic to use in the safety design of these carbon materials. Therefore, thermal shock resistances and thermal shock fracture toughnnesses of nuclear carbon materials should be evaluated directly by experimental methods as in this study.

REFERENCES