OXIDATION EFFECTS ON THE STRENGTH AND FRACTURE TOUGHNESS OF THE SELECTED NUCLEAR GRAPHITE GRADES AT 600 °C.

Byung Jun Kim, Daejong Kim, Changheui Jang, Dept. of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon, 305-701, Republic of Korea
Se-Hwan Chi, Nuclear Hydrogen Development and Demonstration Team, Korea Atomic Energy Research Institute, Daejeon, 305-353, Republic of Korea

Abstract

The nuclear grade graphite is the proposed materials for the in-core components of the very high temperature gas-cooled reactor (VHTR) currently being developed. Understanding and evaluating the strength and fracture toughness of various graphite grades at operating conditions are critical in the design and operation of the reactor. In the current nuclear graphite database available for the design of VHTR, however, most of the strength and the fracture toughness data are of oxidized specimens tested at room temperature. Thus, limited data are available on the changes in the strength and fracture toughness at high temperature due to oxidation. Furthermore, no data are yet available to examine the possible decrease in the fracture toughness due to the increase in the strength with temperature after oxidation. In this study, we performed the bending tests for the selected nuclear graphite grades oxidized by 0 to 15 %. Specimens were oxidized and tested at 600 °C which is in the chemical oxidation regime and corresponds to helium coolant inlet temperature near the core support structure. The strengths and fracture toughness values were measured by 3-point bending test at the room temperature and at 600°C in nitrogen environment for the oxidized specimens. Test results were discussed in view of the differences in the test temperature, oxidation, pore microstructure and the type of the coke.

Introduction

Understanding the effects of oxidation on the strength of nuclear graphite are important for the safety analysis and design of the very high temperature gas-cooled reactor (VHTR), because the graphite may suffer from structural degradation via oxidation during normal reaction operation or accident. Until recently, several researchers (Thrower et. al, 1982; Eto and Growcock et. al, 1983; Wood et. al, 1980) have investigated the effect of oxidation on the structure and strength of nuclear graphite. For example, a 50% tensile strength reduction by about 10% weight loss was reported. Although the relationship between strength and oxidation has been studied by a number of investigators [Beavan et. al, 1979; Yoda and Eto et. Al, 1985; Fuller et. al, 1997], no data are yet available for examination of the possible change in the fracture toughness due to the increase in the strength with temperature after oxidation. In the present study, we tested and estimated the fracture toughness of nuclear graphite in various temperature (20^{o}C~700^{o}C) after uniform oxidation by 0 to 15%. In addition, the crack growth behaviors and toughening mechanism of nuclear graphite are investigated through the microstructural observation.

Experimental

In this study, two different materials were investigated; an petroleum coke graphite, IG-110, isostatically molded and purified by Toyo Tanso Co, Ltd and pitch coke graphite, NBG-18, vibrationally molded purified by SGL Carbon Co, Ltd. Single edge notched beam (SENB) specimens were machined from graphite blocks. Physical properties of IG-110, NBG-18 are summarized in Table 1.

The strengths and fracture toughness values were measured by 3-point bending test at the room temperature, 600^{o}C and 700°C in nitrogen environment for the oxidized specimens. The dimension of the SENB specimen was 100 mm in length (L), 80 mm in the distance between support spans (S), 4 mm in initial crack length (a_0), 10 mm in width (W). We decided to purge nitrogen gas to achieve no-oxidation environment in a furnace over 600^{o}C. When nitrogen gas was flowed at 10L/min, we could rise the furnace temperature up to 700^{o}C causing only slight oxidation specimen below 0.03%.

Table 1. Typical physical properties of IG-110 and NBG-18 graphite

	Density (Mg/m^3)	Electrical resistivity (μΩ)	Flexural strength (MPa)	Compressive strength (MPa)	Grain size (μm)	CTE (10^{-6}/^{o}C)
IG-110	1.77	11.0	39.2	78.4	10	4.5
NBG-18	1.85	9.7	29.7	80.6	300	4.49

For fracture toughness for three-point flexure, K_{IC} is obtained by the following equation [Draft].

$$K_{Ic} = g\left[\frac{P_{\max} S_o 10_{-6}}{BW^{3/2}}\right]\left[\frac{3[a/W]^{1/2}}{2[1-a/W]^{3/2}}\right] \tag{1}$$

$$g = g(a/W) = A_o + A_1(a/W) + A_2(a/W)^2 + A_3(a/W)^3 + A_4(a/W)^4 + A_5(a/W)^5$$

where:

K_{IC}= fracture toughness (MPa√m),

P_{max} = maximum force (N),

S_o = outer span (m)

B= side to side dimension of the test specimen perpendicular to the notch depth (m),

W= top to bottom dimension of the test specimen parallel to the notch depth (m), and

a= notch depth (m)

Coefficients for above equation are summarized in table 2.

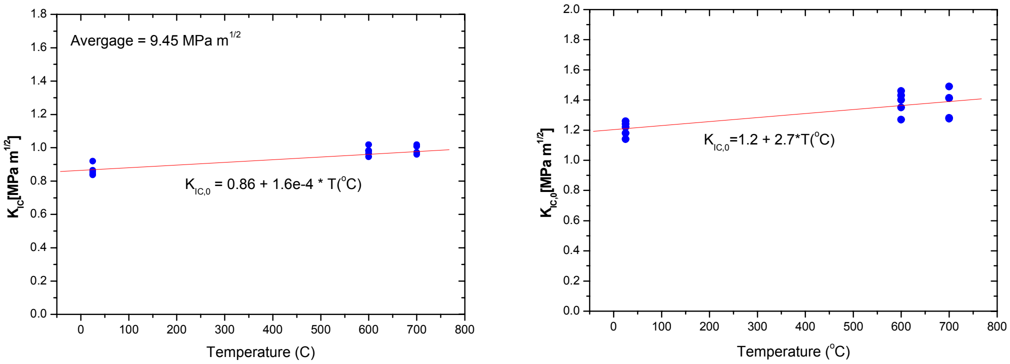
Table 2. Coefficients for the Polynomial g(a/W) for Three-point Flexure

	S_o/W				
	5	6	7	8	10
A_o	1.9109	1.9230	1.9322	1.9381	1.9472
A_1	-5.1552	-5.1389	-5.1007	-5.0947	-5.0247
A_2	12.6880	12.6194	12.3621	12.3861	11.8954
A_3	-19.5736	-19.5510	-19.0071	-19.2142	-18.0635
A_4	15.9377	15.9841	15.4677	15.7747	14.5986
A_5	-5.1454	-5.1736	-4.9913	-5.1270	-4.6896

Results and discussion

Fracture toughness at high temperature

Accordingly, the mechanical properties of nuclear graphite such as fracture toughness and strength [Morton et. al, 1964] are reported to be strengthened at high temperature. Figure 1 shows the fracture toughness vs. temperature curves for two materials. These results show that fracture toughness of IG-110 is about 14% higher at 600°C than at room temperature. Trend of fracture toughness at 600°C is similar to that of at more high temperature (700°C). These show good accord with the data of NBG-18 graphite experiments. However, comparing to IG-110 graphite, the value of NBG-18 graphite has higher standard deviation.



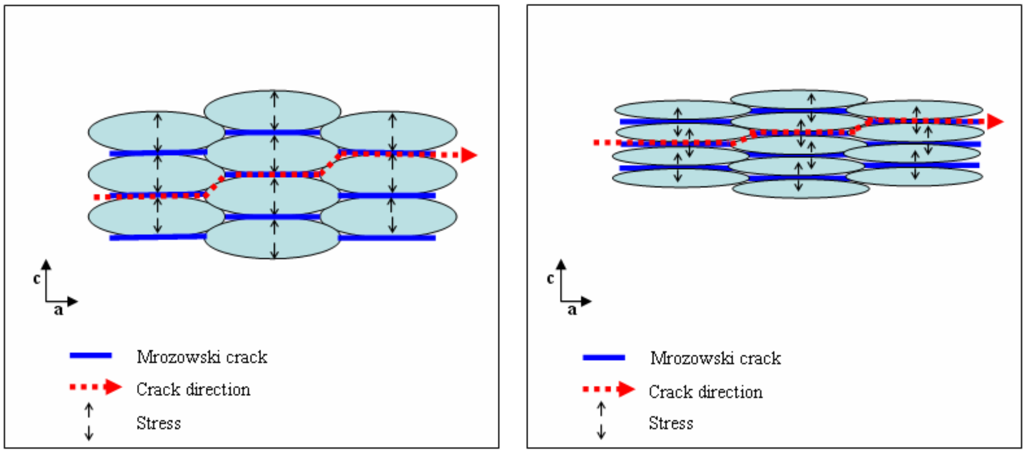
(a) (b)

Figure 1. Fracture toughness of (a) IG-110 and (b) NBG-18 with temperature

Mrozowski crack is formed as intercrystalline voids during cooling from the graphitization temperature (2000-3000°C) [Mrozowski. et. al, 1956]. As the thermal expansion coefficient of graphite is greater in c-axis than a-axis, the Mrozowski crack is subjected to tensile residual stresses along c-direction (Fig-2(b)) at low temperature.

Mrozowski cracks act as sources of crack opening, and then primary crack progresses easily with interface of the Mrozowski crack due to residual tensile stress. However, as graphite has high thermal expansion of c-direction at high temperature, residual tensile stress changes to compressive stress (Fig-2(a)). While the Mrozowski crack is under compressive stress, the porosity of graphite is macroscopically decreased. Because they act as significant obstacles for crack extension, fracture toughness of graphite is increased. And Martens et al. [Martens et al, 1960] propose a strengthening effect at high temperature, resulting from a plasticity increase which permits permanent deformation to reduce stress concentrations at the notches represented by defects in the graphite structure. Through the examination of fracture test, we found that fracture toughness of nuclear graphite is increased at high temperature.

The microstructure of crack behavior was observed by SEM, and the main mechanisms for fracture toughness enhanced of IG-110 graphite were considered to be crack bridging, deflection and microcracking (Fig-3(a-b)). In case of NBG-18, fracture toughness mechanism of crack bridging wasn't observed. However, when crack tip meets pore in matrix, crack direction is deflected by its direction and shape (Fig-3(c-d)).



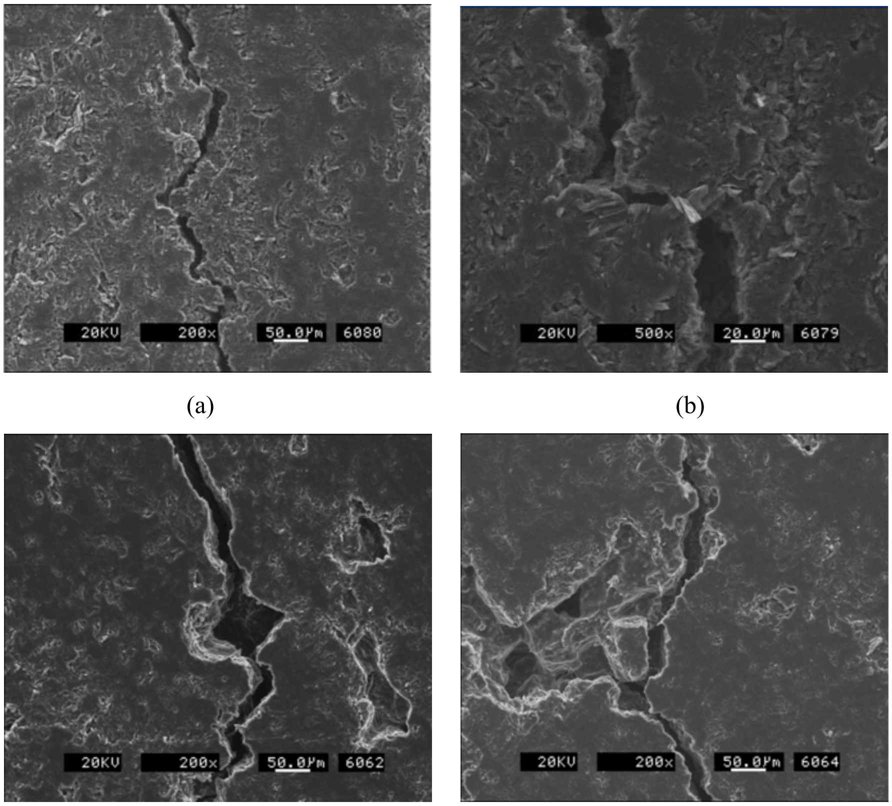
(a) (b)

Figure 2. Schematic description of residual stress at (a) high temperature and (b) room temperature

Fracture test of oxidized graphite

Generally, the graphite strength is known to be exponentially decreased by porosity [Lange et. al, 1970]. As nuclear graphite is oxidized, the porosity of graphite is increased. Fracture toughness of IG-110 and NBG-18 graphite is exponentially decreased due to oxidation. The fracture toughness of the specimens of IG-110 and NBG-18 graphite oxidized in air is plotted in figure 4.

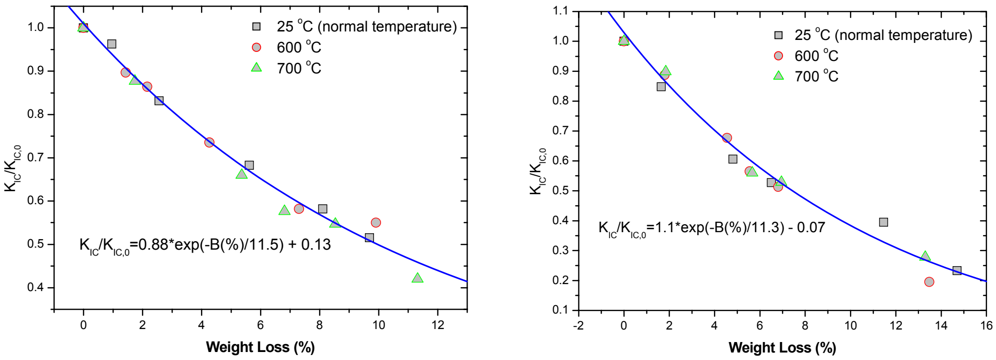
It can be seen in figure 4 that, in the case of IG-110 graphite, the decrease in fracture toughness is slightly smaller than NBG-18 graphite. Grain size and strength of coke particle shall affect the fracture toughness of nuclear graphite. The IG-110 graphite has average grain size of 10μm. On the other hand NBG-18 graphite has average grain size of 200μm. The grain size of two materials is shown in figure 5. Board and Squires [Board and Squires. et. al, 1966], examining PGA graphite, found that cracks propagate predominantly in the binder. Preferential oxidation and weakening of the binder phase was noted. Binder phase act as significant support to combine with coke particle. If the binder is some degree of oxidation at IG-110 graphite, coke particle can be supported by them due to fine coke particles. However, in the case of NBG-18 graphite, they can't support the bigger coke particle. Decrease in the fracture toughness of the oxidized NBG-18 graphite is faster than IG-110.



(a) (b)

(c) (d)

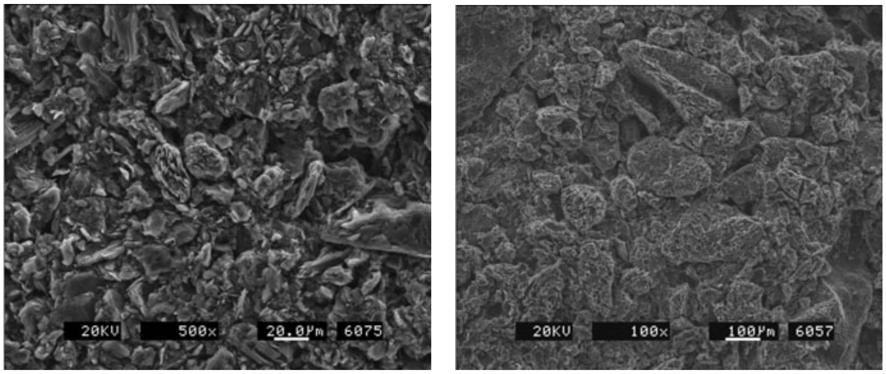
Figure 3. Toughening mechanisms; (a),(b) crack bridging and deflection at IG-110 (c),(d) deflection induced by pore at NBG-18



(a) (b)

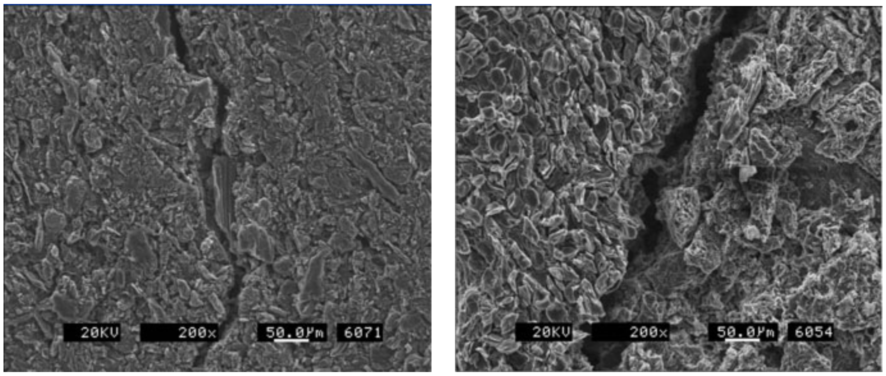
Figure 4. Effect of weight loss on fracture toughness (a) IG-110, (b) NBG-18

Crack behavior of microstructure was observed in Figure 6. Cracks of IG-110 graphite propagate into the weakening of the binder phase due to oxidation. Fracture toughness mechanisms such as crack deflection and microcracking were observed similarly to non-oxidized specimen. Fracture surface of IG-110 graphite is tough. However, fracture surface of NBG-18 graphite is smooth, and then cracks propagate straight without any obstacle (fig-6(b)).



(a) (b)

Figure 5. Grain size of (a) IG-110 and (b) NBG-18



(a) (b)

Figure 6. Microstructure of crack behavior oxidized (a) IG-110 and (b) NBG-18

Quantitative study of the fracture toughness on the oxidized graphite

In the previous section, we described the effect of temperature and weight loss on the graphite fracture toughness and the mechanisms. In this section, the effects of temperature and weight loss on the graphite fracture toughness were quantitatively investigated and the correlations were developed for prediction. Especially, the prediction of the fracture toughness of the oxidized graphite is important for the analysis of reactor structural integrity of VHTR.

Figure 1-(a) shows the variation of fracture toughness with temperature on IG-110 graphite. As shown in this figure, the fracture toughness is slightly strengthened by temperature. The trend of data is seen to be linear, so we assumed that the fracture toughness of IG-110 linearly increase with temperature and developed the correlation by data regression. The correlation can be expressed as follows,

$$K_{IC,0} = 0.86 + 1.6\times10^{-4} T(^{o}C) \qquad \text{(for IG-110)} \qquad (2)$$

where $K_{IC,0}$ is the fracture toughness of original graphite (without weight loss), and T is the temperature of the material. This empirical correlation is applicable for the temperature range between 25 and 700 °C. The values calculated by this correlation become the reference values to predict the fracture toughness for oxidized graphite, IG-110 introduced below.

Figure 4-(a) shows the variation of fracture toughness with weight loss. To normalize the data for temperature, the measured fracture toughness values (K_{IC}) were divided by the original fracture toughness ($K_{IC,0}$), which can be predicted by Eq. (2). The physical meaning of the normalized fracture toughness ($K_{IC,0}$) is the decrease ratio of the fracture toughness by weight loss. In this figure, the normalized fracture toughness is not dependent on the temperature variation. It means that the normalized fracture toughness is a function of only weight loss. Since the graphite strength is known to be exponentially decreased by porosity, the correlation for the normalized fracture toughness can be expressed by exponential function as follows,

$$K_{IC} / K_{IC,0} = 0.88\exp(-B(\%)/11.5) + 0.13 \qquad \text{(for IG-110)} \qquad (3)$$

where B is the percent of weight loss. This empirical correlation is applicable for the range between 25 and 700 °C.

Figure 1-(b) and figure 4-(b) show the effect of temperature and weight loss on the fracture toughness of NBG-18 graphite. By the same methods as performed for IG-110, the following correlations were obtained.

$$K_{IC,0} = 1.2 + 2.7\,T(^{o}C) \qquad \text{(for NBG-18)} \qquad (4)$$

$$K_{IC} / K_{IC,0} = 1.1\exp(-B(\%)/11.3) - 0.07 \qquad \text{(for NBG-18)} \qquad (5)$$

Both of the correlations are applicable for the same temperature ranges as the one of IG-110.

In order to see the dependency of materials on the fracture toughness, all of data are plotted and compared on the same graph. Figure 7 shows it. According to this figure, it seems that the normalized fracture toughness does not depend on the type of graphite (IG-110, NBG-18). Based on this graph, the following correlation was obtained.

$$K_{IC} / K_{IC,0} = 1.3\exp(-B(\%)/17.3) - 0.3 \qquad (6)$$

This correlation can be used for both of IG-110 and NBG-18. But applicability of this correlation to other types of graphite needs to be investigated with more experimental data.

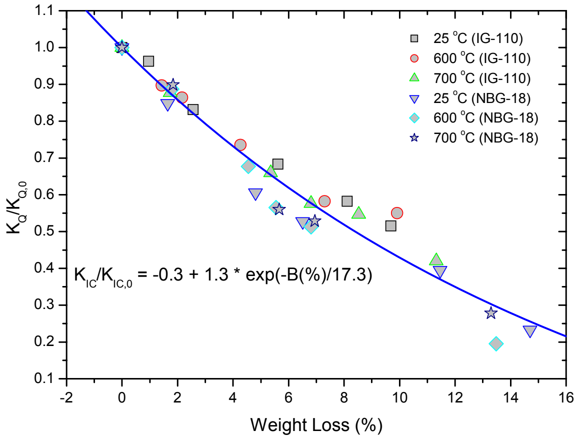


Figure 7. Effect of weight loss on fracture toughness

Conclusions

The fracture toughness and crack growth behavior of nuclear grade graphite were investigated through the 3-point bending test and microstructure observations. Fracture toughness of IG-110 was about 14% higher at 600°C and 700°C than at room temperature. Similar results were observed in NBG-18 graphite experiments. The increase in fracture toughness at high temperature was caused by the change in residual stress of Mrozowski crack from tensile to compressive, thus act as significant obstacles for crack extension.

Fracture toughness of IG-110 and NBG-18 graphite was exponentially decreased due to oxidation. The decrease in fracture toughness at IG-110 graphite was slightly smaller than NBG-18 graphite. However, the normalized fracture toughness was not affected by the type of graphite (IG-110, NBG-18). Based on the experimental data, the following correlation was obtained.

$$K_{IC} / K_{IC,0} = 1.3 \exp(-B(\%) / 17.3) - 0.3$$

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