

## Effect of a Thermal Oxidation on the Compressive Strengths of Selected Nuclear Graphites

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### 1. Introduction

In a very high temperature gas-cooled reactor (VHTR), graphite structures may be exposed to oxidative impurities contained in the helium coolant gas during a normal operation and/or air that ingress into the coolant in the event of a depressurization. In both cases, they are believed to be oxidized at various temperatures corresponding to their locations, i.e. core, core support, moderator and reflector, in the reactor [1]. The degradation of a compressive strength of nuclear graphite caused by a thermal oxidation is one of the most serious problems for the safety analysis and design of the VHTR. The effects of an oxidation on the compressive strength have been extensively studied, however the results were dependent on not only the oxidation conditions but also on the structures of the graphite so more studies are needed to thoroughly understand the subject [2-6].

In this study, we examined the change of the compressive strengths of five candidate nuclear graphites for the VHTR.

### 2. Experiments

Five nuclear graphites, i.e. IG-110, IG-430, NBG-17, NBG-25 and PCEA were used for this study. Typical properties of the graphites are summarized in Table 1. The samples with the size of  $\phi 15 \times 107 \text{mm}^3$  were thermally oxidized at  $600^\circ\text{C}$  in dry air with a flow rate of  $2 \text{mL/min}$  using a 3 zone controlled tube furnace up to 12% burn-off. The temperature was chosen to oxidize the samples uniformly in the chemical reaction controlled regime [1]. The oxidized samples were machined to compression specimen ( $\phi 10 \times 20 \text{mm}^3$ ). Compression tests were performed at room temperature at the loading rate of  $0.5 \text{mm/min}$ . The changes in the open pore size and distribution after the oxidation were examined by a mercury porosimetry measurement.

Table 1 Samples used in the present study

Material	Coke	Forming	Manufacturer	Density	Coke particle size ( $\mu\text{m}$ )
IG-110	Petrol.	Isostatic mold	Toyo Tanso	1.77	10.
IG-430	Pitch	Isostatic mold	Toyo Tanso	1.82	10
NBG-17	Pitch	Vibrational--mold	SGL		Max. 800
NBG-25	Petrol.	Isostatic mold	SGL	1.81	Max. 60
PCEA	Petrol.	Extrusion	GrafTech	1.83	360

### 3. Results and Discussion

#### 3.1 Compressive Strength

Fig. 1 shows the changes in the fractional compressive strength as a function of the decrease in the bulk density (weight loss) after the oxidation. A reduction of the compressive strength was observed with a decrease of the bulk density due to an oxidation for the five graphites.

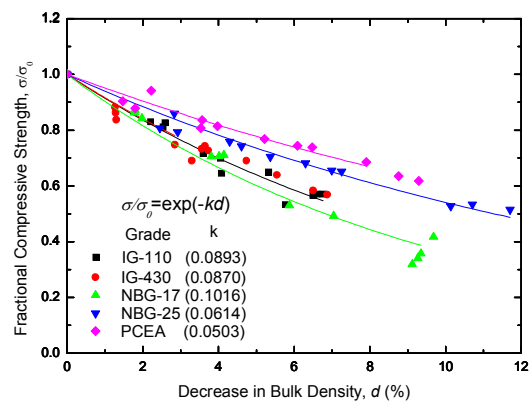


Figure 1. Changes in the fractional compressive strength,  $\sigma/\sigma_0$  as a function of the decrease in bulk density,  $d$  after the thermal oxidation.

The dependency of the compressive strength with increasing oxidation of the graphite can be described by the Knudsen relation in the form [2]

$$\sigma / \sigma_0 = \exp(-kd) \quad (1)$$

where  $\sigma_0$  is the compressive strength of the unoxidized graphite and  $k$  is an exponent and  $d$  is the decrease in the bulk density. A higher value  $k$  indicates a greater effect of the thermal oxidation on the compressive strength. The values of  $k$  for the five graphites are also given in Fig. 1. It was found that the value of  $k$  for NBG-17 is the highest and that of PCEA is the lowest.

#### 3.2 Porosity and Pore Size Distribution

Table 2 Compressive strengths, coke particle sizes and porosities of the unoxidized graphites

Material	IG-110	IG-430	NBG-17	NBG-25	PCEA
Compressive strength (MPa)	80.3	89.9	74.7	103.9	58.25
Coke particle size ( $\mu\text{m}$ )	10	10	Max. 800	Max. 60	360
Porosity (%)	18.4	18.0	15.3	17.4	18.3

The compressive strengths of the unoxidized samples are summarized in Table 2 with their coke particle sizes

and porosities. It is well known that the smaller the coke particle size and porosity are, the higher the compressive strength of nuclear graphite is. However, the compressive strengths of the unoxidized graphites do not correlate well with the porosities and the particle sizes. Thus it is considered that the compressive strengths are dependent on the pore distribution in addition to the porosity [3, 5].

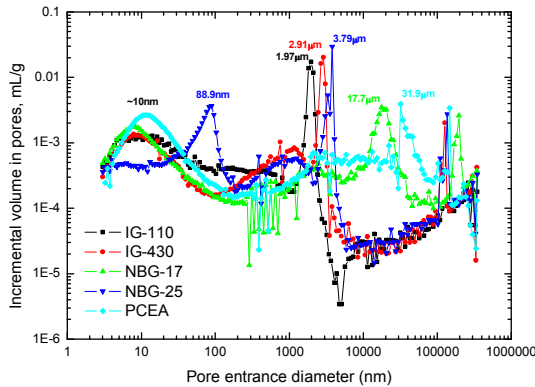


Figure 2. Pore entrance diameters vs. incremental volume in pores for the unoxidized graphites.

Fig. 3 shows the pore distribution of the unoxidized graphites. The range of the pore entrance diameter can be divided into four regions, i.e. (1) region I: 10~100nm (0.001~0.003mL/g), (2) region II: 2~4µm (0.017~0.03mL/g), (3) region III: 10~100µm (0.004~0.004mL/g) and (4) region IV: 127~200µm (~0.002mL/g). The pore size of fine-grained graphites (IG-110, IG-430 and NBG-25) is concentrated in the region II. The pore distribution of the coarse-grained graphites (NBG-17 and PCEA) is relatively broad and concentrated in region III which is considered to be related with their low compressive strengths.

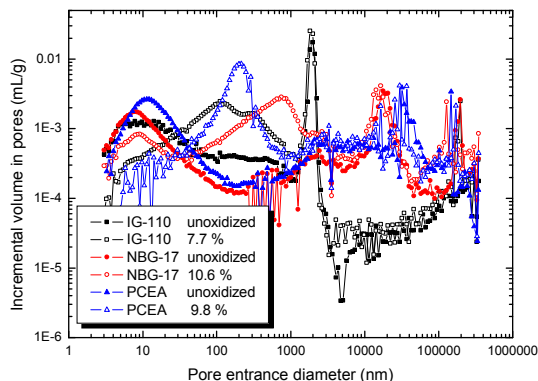


Figure 3. Changes in the distribution of pore entrance diameter after the oxidation.

Fig. 3 shows the changes in the pore distribution after the oxidation. The pores of about 10nm in diameter are considered to be enlarged to pores of about 100~200nm

in diameter for IG-110 and PCEA, and about 1µm for NBG-17 after the oxidation. Furthermore, an increase in the incremental volumes of the pores of about 20~100µm in diameter was observed in NBG-17.

From the results, it is considered that the pore distribution has a significant effect on the change in the compressive strength, especially in the case where the open porosity increases owing to an oxidation.

#### 4. Summary

The changes of the compressive strengths of five candidate nuclear graphites after the oxidation at 600°C up to 12% burn-off were studied, which are summarized as follows.

1. The compressive strength decreased due to the oxidation and the changes varied depending on the graphite used.
2. The changes of the compressive strength due to the oxidation were significantly affected by the pore size distribution in addition to the porosity.

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