Transactions of the Korean Nuclear Society Spring Meeting
Chuncheon, Korea, May 25-26 2006

Mrozowski Cracks and Oxidation Behavior of IG-110 and IG-430 Nuclear Graphites

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1. Introduction

In very high temperature gas-cooled reactor (VHTR), graphite acts as a moderator and reflector as well as a major structural component that may provide channels for the fuel and coolant gas, channels for control and shut down, and thermal and neutron shielding. During operation, however, many of the physical properties of graphite are significantly modified as a result of temperature, environment, and irradiation. One example is the mechanical, physical and thermal property changes due to oxidation. It is known that oxidation of graphite will result in loss of structural integrity, change the thermal conductivity, reduce the fracture toughness and strength of the components [1].

The purpose of present study is to understand and evaluate the differences in the oxidation behavior of two nuclear graphite grades of different fillers in view of graphite selection for nuclear hydrogen development and demonstration (NHDD) project.

2. Experimental

2.1 Materials and oxidation experiment.

The materials used in the present study are IG-110 and IG-430 isotropic nuclear graphites manufactured by Toyo Tanso. IG-11, unpurified version of IG-110, was included to compare with IG-110, not with the IG-430, during the oxidation experiments. Specimens with a size of 6 x 6 x 6 (mm3) were prepared from graphite blocks (300 x 300 x 200 mm) of IG-11, IG-110 (petroleum coke) and IG-430 (pitch coke) for oxidation experiments. The temperature dependency of the oxidation rate was determined for 400 ~ 1,300 ^{0}C in the He-2.5% air environment by using a thermogravimetry (TG) (flow rate: 40 CC/min). The differences in the oxidation characteristics as appeared in the oxidized surfaces between the un-irradiated and irradiated IG-110 and IG-430 specimens were investigated by an optical microscopy and scanning electron microscopy (SEM).

Table 1 compares some of the physical and mechanical properties of the grades reported in the manufacturer's materials test sheet.

2.2 OM and TEM Microscopy

A polarized light was used for optical microscopy. For the TEM microscopy, after preparing 3mm∅ disks (thickness ≈ 0.5 mm) by using an ultrasonic disk cutter and a polishing

up to No. 2000 SiC paper, all the specimens were dimpled (t ≤ 10 ㎛) using a 30 g load and 1 ㎛ paste, and ion-milled (Ar, 3 KeV-14μA)

Table 1. Comparison of Some of the Physical and Mechanical Properties of Nuclear Graphites (IG-110, IG-430) and IG-11 Non-Nuclear Graphite (manufacturer data sheet).

Grade	IG-110	IG-430	IG-11
Coke	Petro.	coal-tar	Petro
Grain Size, mm	0.02	0.01	0.02
Appar. density, g/cm^3	1.77	1.82	1.77
Anisotropy ratio	1.10	1.09	-
Ash content, ppm	<10	<10	479
Impurity, ppm	~ 0.1	~ 0.1	-
E, GPa	9.7	10.6	9.04
Tensile Strength, MPa	27.2	37.8	25.4
Compre. Str., MPa	79	96	86
Ther. Cond., W/mK	129-140	138-147	122

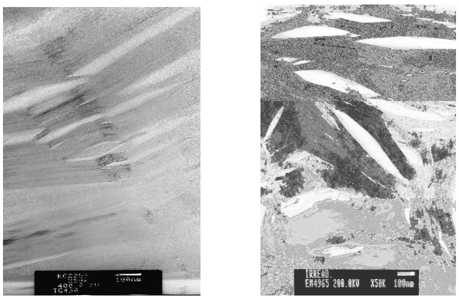
3. Results and discussion

3.1 Comparison of the as-received microstructure

Optical microscopy of IG-110 and IG-430 nuclear graphites has shown that the size and total area of the pores in IG-430 appeared somewhat smaller than those of IG-110 [2]. Both graphites showed that the size of the pores was about the size of the coke particles. In the case of IG-110, based on the reported total porosity, 21 %, the ratio between the open pore to the closed pore was estimated to be about 2 : 1. This observation may be attributed to the difference in the density and grain size between the grades,

Figure 1 compares the TEM microstructure of the two grades by focusing on the Mrozowski cracks. In Fig. 1, it is worth noting the large differences in the width and length of the Mrozowski cracks between the two graphites.

Table 2 compares both the width and length of the Mrozowski cracks as they appeared in Fig. 1. Even with a limited number of measurements, Table 2 clearly shows that a few larger sized Mrozowski cracks both in width and length are observed in IG-110, and the average size of the cracks would be far larger in the IG-110 than the IG-430.



(1) IG-110 (2) IG-430

Figure 1. TEM Microstructure of (1) IG-110 and (2) IG-430 graphites.

Table 2. Comparison of the width and length of Mrozowski cracks (unit:nm).

IG-110 width	IG-110 length	IG-430 width	IG-430 length
57.8	450.0	62.1	363.6
60.9	562.5	62.1	515.1
71.8	312.5	69.7	484.8
73.4	593.7	56.0	727.2
78.13	875.0	-	-
57.81	450.0	-	-
176.87	1491.9	-	-
199.9	2307.0		

3.2 Comparison of the oxidation behavior.

Figure 2 shows the temperature dependency of the oxidation rate of the as-received, un-irradiated IG-11, IG-110 and IG-430. It is worth noting that the observed three temperature ranges based on the oxidation rate are nearly the same to the reported classification based on the oxidation mechanism [3]: 400 ~ 600℃ (chemical reaction regime), 600 ~ 850℃(in-pore diffusion regime), and over 850℃ (mass transfer regime). In addition, Figure 2 shows that the oxidation rate of the IG-11 is far higher than the other two nuclear grades, IG-110 and IG-430, possibly due to its high impurities and ash content. Fig. 2 also shows that the oxidation rate of the IG-110 appeared higher than the IG-430. To understand this observation, the fundamental differences between the grades on the factors that could have a strong influence on the obtained results needs to be compared.

In this regards, some relevant information may be found from the TEM microscopy on the grades, Fig. 1 and Table 2. The large differences in the size and density of the Mrozowski cracks between the grades in Fig. 1 and Table 2, which are believed to be originated from the difference in the thermal conductivity between the grades, can be considered as one of the key factors for the present observations. It is believed that, since the Mrozowski cracks are attributed to the differential thermal strain on a cooling from the final heat-treatment temperature [4], the IG-110 of a low thermal conductivity will have a larger number of large cracks than the IG-430 of a high thermal conductivity due to its higher thermal stress during cooling from the calcination temperature (~ 1,000 ℃) or graphitization temperature (~ 3,000 ℃).

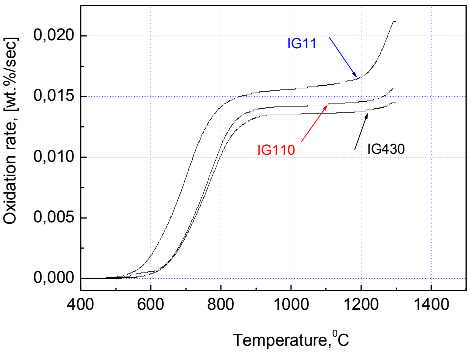


Figure 2. The temperature dependency of the oxidation rate of the as-received, un-irradiated IG-11, IG-110 and IG-430.

It is easy to understand that a microstructure with a high density of large Mrozowski cracks will have more reaction sites for an oxidation.

V. Conclusion

The higher oxidation rate of the IG-110 of petroleum coke than the IG-430 of pitch cokes may be attributed to the differences in the density and size of Mrozowski cracks. These differences in the Mrozowski cracks between the grades are believed to be originated from the difference in the thermal conductivity of the grades. When the limited conditions of the present study are considered, further investigations are required.

Acknowledgement

This work has been carried out as a part of Nuclear Hydrogen Development and Demonstration project in Korea Atomic Energy Research Institute (KAERI) under the Nuclear R & D Program by Ministry of Science and Technology (MOST), Korea.

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