

Effect of Gas Pressurization on Oxidation Behavior of Nuclear Graphite

Eung-Seon Kim*, Ji-Yong Sung, Min-Hwan Kim, Yong-Wan Kim

Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 305-353

*Corresponding author: kimes@kaeri.re.kr

1. Introduction

In a high temperature gas-cooled reactor (HTGR), nuclear graphite has been widely used as a fuel element, moderator, or reflector block and core support structures owing to its excellent moderating power, mechanical properties, and machinability. These graphite components may be oxidized due to impurities from a graphite outgassing and He coolant, and a leakage in a heat exchanger [1]. The mechanical properties of graphite are severely degraded by oxidation, a reduction of 50 % in its compression strength at a burn-off of 10 % for example [2]. Therefore, the oxidation of graphite has been widely studied to analyze the safety of the HTGR and assess the operational life of the core structures [3-6].

Unfortunately, historical nuclear grades no longer exist that new grades must be characterized to demonstrate the current grades of graphite exhibit acceptable properties upon which the thermo-mechanical design of the structural graphite in the HTGR is based. Although the coolant He gas pressure is around 5~7 MPa, in most cases, the former oxidation researches were performed under atmospheric pressure. In this study, the change in oxidation behavior of nuclear graphite after gas pressurization was investigated.

2. Experiments

2.1 Materials and Optical Microscopy

Two grades of nuclear graphites, IG-110 produced by Toyo Tanso Co. Ltd, Japan and NBG-17 produced by SGL Carbon Group, Germany were used for this study. Based on the ASTM D7219-08, the IG-110 is classified as fine-grained graphite, and the NBG-17 is classified as medium-grained graphite, respectively. The microstructural properties of the two grades are summarized in Table 1.

Table 1: Properties of two grades of nuclear graphites

Grade	IG-110	NBG-17
Coke	Petroleum	Coal tar
Forming method	Iso-static	Vibro-mold
Density (g/cm ³)	1.78	1.84
Average grain size (μm)	20	Max. 800
Pycnometric density (g/cm ³)	2.046	2.012
Total porosity (%)	21.82	18.87
Open porosity (%)	13.41	8.63

Samples were mounted using a vacuum-impregnation apparatus (Struers, EpoVac) to fill most accessible pores with epoxy resin and thus maintain the original structure of the graphite. The sample mounts were ground up to P4200 grit SiC paper and finally polished on a high napped cloth using 0.05 μm alumina powder. The optical pore structures were examined using an optical microscope (Olympus GX51).

2.2 Thermal Oxidation Test

The specimen for the oxidation test was a cylinder with a 6 mm diameter and 6.0 mm length. The specimens were pressurized up to 10 MPa using Ar gas. The specimens were then dried for 2 hours at 110 °C. The thermal oxidation tests were performed at 550 and 750 °C using a thermogravimeter (Setaram Instrumentation, Model SETSYS Evolution-1750). The oxidant was dry air with a flow rate of 60 ml/min.

3. Results and Discussion

The thermal oxidation test results are shown in Fig.1. The oxidation rates of IG-110 were higher than those of NBG-17 both at 550 and 750°C. However, as the temperature increased the difference was reduced. In the chemical reaction controlled regime (550°C), the chemical reaction rates are slow that the reaction are occurs throughout the bulk of the graphite, depending on the porosity of the sample. The higher oxidation rate of IG-110 is related with the higher open porosity, as summarized in Table 1. However, in the diffusion rate-controlled regime (750°C), the chemical reaction rates are so fast that the reactions are controlled by diffusion of the gaseous reactants that the difference in the oxidation rate was reduced.

After the gas pressurization, the oxidation rate significantly increased. The gas pressurization effect was remarkable in the fine-grained graphite, IG-110 at 550°C. Normally, the reaction rate of graphite oxidation can be expressed as follows;

$$R = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) p_{O_2}^n A$$

where A is a pre-exponent factor, E_a is an activation energy, R is a gas constant, T is the temperature, P_{O_2} is the partial pressure of the oxygen, n is the order of the reaction, and A is the reaction surface area. Considering that all test conditions were the same, the higher

oxidation rate after the gas pressurization can be attributed to an increase in the reaction surface area.

3. Conclusions

The thermal oxidation rates were increased after the gas pressurization, especially in the fine-grained graphite, IG-110 with a lot of thin closed pore wall. It is considered that the newly formed reaction surface under the gas pressure increased the oxidation rate.

Acknowledgement

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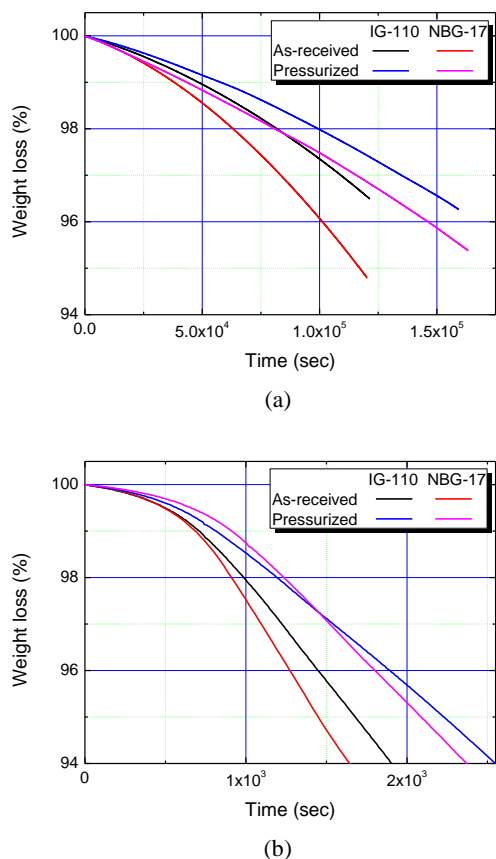


Fig. 1. Changes in the weight loss after gas pressurization, (a) 550°C and (b) 750°C.

Fig. 2 shows the optical pore structures of the nuclear graphites. Two types of open pores were identified within the binder phases. One was gas entrapment pores formed during the mixing and baking stage of the manufacturing. The other was narrow, slit-shaped pores formed as a result of either volumetric shrinkage on the baking or of anisotropic contraction on cooling from the graphitization temperatures. They were often found at domain/mosaic boundaries in the binder phase and frequently connected to the gas entrapment pores. Normally, finer entrapment pores are formed in the fine-grained graphites. Some of the initially closed pores may become open due to the breakage of a thin pore wall under gas pressure, and consequently, the reaction surface area increased.

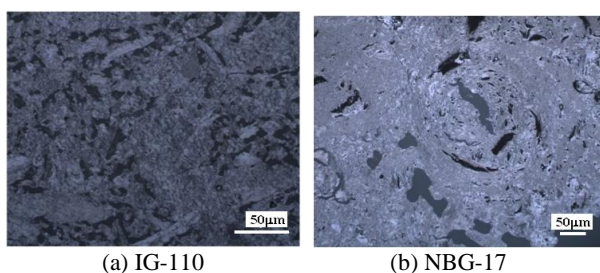


Fig. 2. Optical pore structures of the nuclear graphites