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ORIGINAL ARTICLE

Investigation of IG-110 Nuclear Graphite Oxidation Behavior at High Temperature

Herlina[1], A. K. Rivai[2] and S. T. Wicaksono[3]

[1]Department of Mechanical Engineering, University of Southeast Sulawesi, Jl. Captain Piere Tendean No.109.A, Kendari, Indonesia
[2]Research Center for Radiation Detection and Nuclear Analysis Technology, Research Organization For Nuclear Energy, National Research and Innovation Agency- BRIN, Puspiptek B.J. Habibie Science and Technology Area, South Tangerang, Banten 15314, Indonesia
[3]Department of Materials and Metallurgical Engineering, Sepuluh Nopember Institute of Technology, Jalan Chemical Engineering, Keputih, Surabaya, East Java 60111, Indonesia

ABSTRACT – IG-110 is one of nuclear graphite types for high temperature gas cooled reactor. One of the issues of the graphite in the reactor system is the interaction with air or/and water which can reduce the integrity of the material. In this study, the sample of IG-110 has been tested at high temperature in an air environment. The oxidation test was done using a magnetic suspension balance to analyze the changes in weight with direct monitoring. The test was carried out at a temperature of 630°C. Morphological and microstructural analysis were observed and tested using scanning electron microscope (SEM) and X-ray diffractometer (XRD). The oxidation rate of the sample was relatively low. Rougher sheets shape, larger pores, and slight cracks were observed for the tested sample which indicate the traces of oxidation of the samples with no any critical damage occurred in the sample. Lattice parameters, density, crystal size, and d-space of the sample after oxidation test slightly change, which show the reversible characteristic of the sample from the temperature viewpoint.

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INTRODUCTION

One of the important requirements for structural materials in high temperature gas cooled reactors (HTGR) is excellent performance at high temperature. As one of the main materials in the nuclear reactor at high temperature, graphite needs to have high performance at high temperature [1]–[2]. Gaphite provides many advantages, particularly for its thermomechanical properties and chemical inertness in a non-oxidizing environment [3]. Graphite is used as a core material for HTGR, namely as a moderator, structural component, efficient heat storage medium, and fuel transport and fuel matrix [4]–[5]. Graphite plays a role in the reactor apart from being a mechanical support for fuel as well as facilitating the nuclear chain reaction by moderating high-energy neutrons [6].

Nuclear grade graphite made from petroleum coke or coal tar which is typically isotropically formed with pores in a wide range of dimensions formed during the manufacturing process in offgassing. Nuclear graphite has a high purity so it can avoid the absorption of low energy neutrons and the activation of impurities [7]. Nuclear graphite porosity plays an important role at high temperature [8]. Nuclear graphite will undergo macroscopic dimension shrinkage of 3–4%, then increase during high temperature irradiation [9]. However, graphite has low oxidation stability at high temperature (>450°C), causing a loss of integrity of the core components. Loss of integrity occurs due to a decrease in strength and elastic modulus with the formation and expansion of pores caused by oxidation [10]. Graphite oxidation will result in a decrease in the weight of the material and changes in the microstructure [11]. Oxidation occurs from several stages from low temperature to high temperature which affects the microstructure and pore size distribution of oxidized graphite [12].

The mechanism of graphite oxidation at high temperature in various gas environment conditions is very important to investigate the behavior of graphite. In the oxidation process, several stages of the reaction will occur, namely [13]:

Graphite oxidation reaction:

$$C + aO_2 \rightarrow bCO + cCO_2 \quad (1)$$

Boudouard reaction:

$$C + CO_2 \rightarrow 2CO \quad (2)$$

CO combustion reaction:

$$2CO + O_2 \rightarrow 2CO_2 \quad (3)$$

The oxidation rate equation is semi-empirically related to the classical Arrhenius temperature:

*CORRESPONDING AUTHOR | Herlina | ✉ linhaherlina21@google.com

$$\text{rates} = k_0 e^{\frac{E_A}{RT}} P_{O_2}^n \quad (4)$$

$$\text{rates} = k_0 e^{\frac{E_A}{RT}} [O_2]^n \quad (5)$$

From equation (1)–(5), k_0 is the pre-exponential factor, E_A is the activation energy, n is the reaction order, R is the universal gas constant, T is the temperature, P is the partial pressure of molecular oxygen gas and the concentration of molecular oxygen O_2.

The method of manufacture and purity of graphite is very influential because it will affect the mechanical properties of graphite [9]. Thus, the different shapes and dimensions of the sample can result in different oxidation kinetics [10]. The oxidation behavior of graphite is caused by high temperature so that pores open or formed and the strength gradually decreases with loss of sample mass [13]. Expansion of graphite with increasing temperature affects the graphite lattice parameters [14]. The irradiation behavior of the disordered filler structures and the initial crystallinity play an important role in the evolution of the microstructure [15]. In addition, physical and thermal changes will reduce the integrity of the graphite core [16]. In this study, the oxidation behavior of IG-110 nuclear graphite at high temperature in air environment has been investigated. IG-110 is one of the nuclear graphite materials used for HTGR reactors [8]–[11], [14]–[17]. IG-110 is a fine-grained isotropic graphite which exhibits high thermal strength and durability, making it very suitable for use in the nuclear industry. However, it was reported that IG-110 oxidizes faster with deeper oxidant penetration which is related to the needle-shaped filler structure of the petroleum coke as the source [18]. The characteristics of nuclear graphite are very important to note, such as its pores and cracks because it can accommodate unfavorable operational conditions [19]. Therefore, the purpose of this research is to simulate and analyze the oxidation behavior of graphite IG-110 when the entry of air into the reactor occurs at temperature of 630°C.

EXPERIMENTAL METHOD

Materials and Instruments

The graphite investigated in this study is IG-110 produced by Toyo Tanso Ltd, Japan with the properties as shown in Table 1 [20]. The microstructure of the original sample was characterized before oxidation experiment carried out using scanning electron microscope (SEM) of JEOL JSM-6510LA and x-ray diffractometer (XRD) of Phillips PANalytical Empyrean.

Table 1. Thermal and mechanical properties of graphite IG-110 [20]

Properties of materials	Score
Bulk density (g/cm^3)	1.75
Young's modulus (GPa)	9.6
Compressive strength(MPa)	70.5
Rockwell hardness(MPa)	74.2
Fracture toughness (MPa)	0.82
Thermal conductivity (W/mK)	116
Porosity (vol%)	21.6
Impurity (ppm)	<20

Method and Procedure

Equipment used in this study was Rubotherm magnetic suspension balance (MSB) produced by Präzisionsmess-technik GmBH. The oxidation test equipment works based on the change in mass when the sample is exposed to the setting temperature. The weighting method uses electromagnetic suspension technology, where the sample is weighted in a separate room from the balance. This balance is capable for measuring the changes in mass up to 0.05 mg. Data collection during the measurement process is carried out by the central processing unit which can display the process in situ [21]. Oxidation test was done at a temperature of 630°C which was heated up immediately from room temperature. Afterward, the material characterization was carried out using SEM and XRD.

RESULTS AND DISCUSSION

Weight Loss Analysis-MSB

The results of weight loss analysis of the sample test using magnetic suspension balance (MSB) apparatus at 630°C which was heated up immediately from room temperature is shown in Figure 1. The results show that there is a slightly increasing of weight loss rate during the testing. The weight loss occurred due to the interaction process between graphite and oxygen at high temperature which was then formed CO and CO_2 molecules as the results of the oxidation. However, the oxidation rate of the sample is relatively low at 630°C in air with the order of ~0.03 g/cm^3 which then reach the relatively constant value. The phenomenon occurred because at high temperature, >630°C up to 800°C, oxygen molecules are not able to infiltrate as deep as the graphite pore structure since the backflow of CO and

CO_2 leaving the internal porosity inhibits the oxygen molecules [22]–[23]. The results estimate that critical damage will not occur when IG-110 graphite is exposed to air at 630°C in the reactor due to air ingress, at least within that duration time.

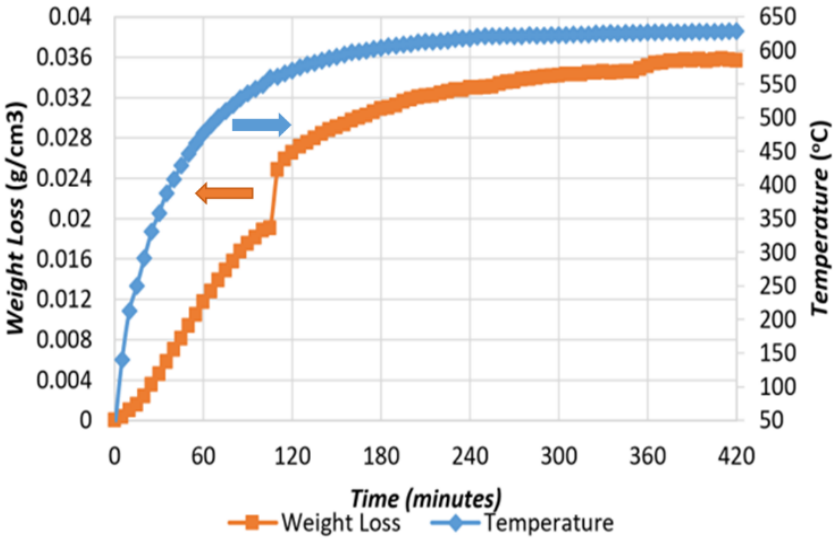

Figure 1. Measurement of weight loss with temperature and time correlation under air environment

Scanning Electron Microscope Analysis

The morphology and microstructure of the as received and tested at 630°C in air samples were analyzed using scanning electron microscope (SEM) to determine the changes in the surface structure of the graphite after testing. Figure 2 shows the results of SEM analyses of the samples for (a) as received and (b) after oxidation test. The results show that there are transformations in the surface structure of graphite. The sheets shape and pores profile of surface structure were observed for the as received sample. Then, rougher sheets shape, larger pores, and slight cracks were observed for the tested sample. The results show the traces of oxidation of the samples at high temperature. Oxidation which has occurred causes an increase in the porosity and microstructure of graphite [24]. Nevertheless, the transformation of the surface structure is superficial with no any critical damage in the sample.

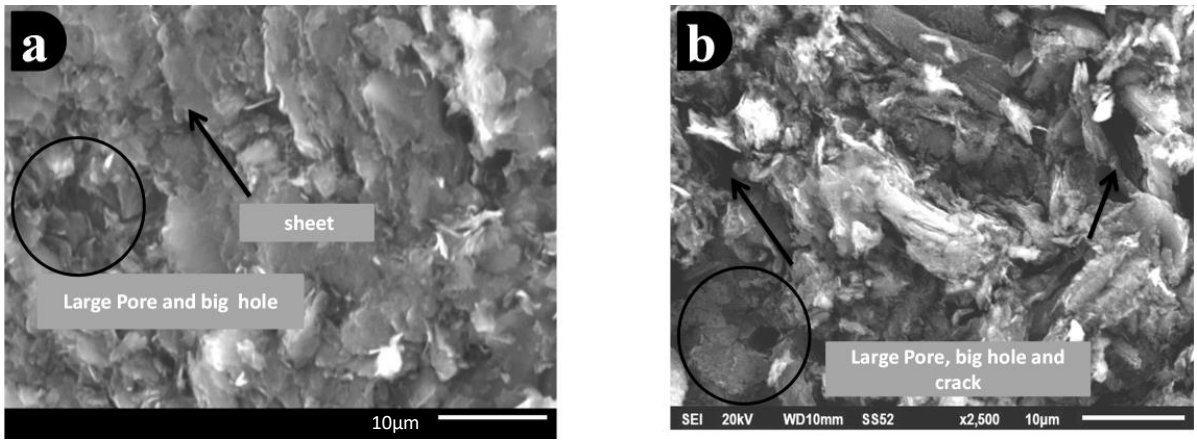

Figure 2. SEM characterization analysis for IG-110 samples (a) as received and (b) after oxidation at 630°C

X-Ray Diffraction Analysis

Figure 3 shows the X-ray diffraction (XRD) pattern of the as received and tested samples. The data of XRD were analyzed using Origin and Match softwares. The results show that the structure of the as received and tested samples were dominated by carbon with hexagonal structure. Therefore, there was no structure phase transformation during the oxidation. However, a decrease in intensity and a shift in the sample peak after oxidation was observed.

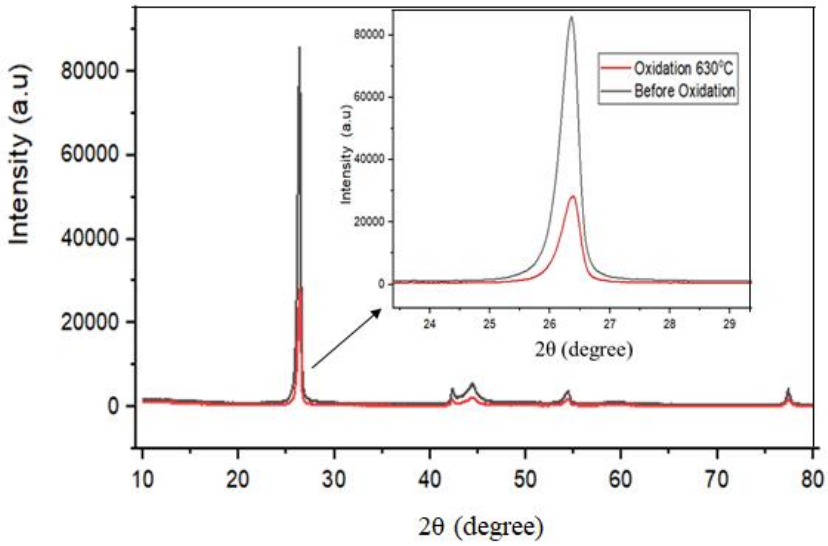

Figure 3. X-ray diffraction spectra for IG-110 as received and after oxidation at 630°C in air environment

Table 2 shows the values of the IG-110 graphite lattice parameters for the as received and tested samples. The results show that the lattice parameter values and the density of the graphite slightly change after the oxidation test. Table 3 shows the results of the crystal size and d-spacing for diffraction peaks of the IG-110 graphite as received and tested samples. The results showed that the crystal size and d-space values of the graphite were slightly change after the oxidation test. The reaction process of carbon with oxygen causes a shift in d-spacing during the oxidation process.

Table 2. IG-110 lattice parameters for as received and after oxidation at 630°C samples

IG-110 graphite	a (Å)	b (Å)	Density (g/cm^3)	Space group
As received	2.460	6.731	2.261	P63mc
After oxidation	2.459	6.726	2.264	P63mc

Table 3. Crystal size and d distance from IG-110 nuclear graphite

Graphite IG-110	As received	After oxidation
Crystal size (nm)	21.088	20.305
d-space (nm)	0.338	0.213

The slight changes of lattice parameters, density, crystal size, and d-space are also reported in other nuclear graphite at high temperature up to 800°C [14]. During the oxidation test, the IG-110 sample was expanded at high temperature and then shrink when returned to the room temperature. The current characterization for the tested sample was done at room temperature. A very small change in the lattice parameters, density, crystal size, and d-space indicate that the sample is reversible for that tested condition. This is eventuality caused by the characteristics of petroleum coke as the source for graphite IG 110 [19]. Then graphite also has high purity and fine grain [25]. For detail investigation, it is necessary to characterize the microstructure of the sample directly during high temperature oxidation test.

CONCLUSION

Oxidation test for IG-110 nuclear graphite at high temperature of 630°C in air environment has been done. The oxidation rate of the sample is relatively low which means critical damage might not occur when IG-110 graphite is exposed to air at 630°C in the reactor due to air ingress. Rougher sheets shape, larger pores, and slight cracks are observed for the tested sample which indicate the traces of oxidation of the samples with no any critical damage occurred in the sample. Lattice parameters, density, crystal size, and d-space change very small which indicate the reversible characteristic of the sample from the temperature viewpoint. As for next investigation, direct microstructure characterization of IG-110 during high temperature testing is necessity.

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