MATERIALS RESEARCH COMMUNICATIONS
Vol. 2, No. 1 (2001) (6 pages)
@ Pusat Publikasi Ilmiah ITS

OXIDATION BEHAVIOR AND MICRO STRUCTURE ANALYSIS OF NUCLEAR GRAPHITE IG-110 AT 520℃ UNDER AIR ENVIRONMENT

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Received 14 July 2021; **Published** 30 November 2021

Abstract –Graphite IG-110 is a nuclear graphite structural and moderator material that has been used for high temperature gas cooled reactors (HTGR). Under normal operating conditions or accidental entry of air or water (air ingress or water ingress), a nuclear graphite. Therefore, the aim of this study is to investigate the oxidation resistant and microstructure change behavior of graphite IG-110 at high temperature under air environment. The sample of IG-110 was tested using Magnetic Suspension Balance (MSB) to analyze the weight change by in-situ for 420 minutes at a temperature of 520ºC. Morphological and microstructure analysis was carried out by optical microscope, SEM-EDS (Scanning Electron Microscope –Energy Dispersive X-ray Sprectroscope) and XRD (X-Ray Diffractometer). The results showed that Graphite IG-110 has a change in surface structure caused by the reaction of the material with oxygen in air at high temperatures. Furthermore, the crystal size of the material structure was slightly change. However, in general, the corrosion rate of graphite IG-110 at a temperature of 520℃ under the air environment is relatively low. So that if graphite IG-110 is exposed to air at a temperature of 520℃ for several hundred minutes in a nuclear reactor estimated does not suffer serious damage.

Keywords: Graphite, IG-110, Oxidation, Microstructure, Air

1. Introduction

Nuclear grade graphite is commonly manufactured from a filler coke and pitch binder. It manufactured from isotropic cokes (petroleum or coal-tar derived) and are specially formed to make them near-isotropic or isotropic materials from a highly isotropic (Windes et al., 2007). The porosity with approximately 20% and varying dimensions is formed during manufacturing for gas escaping. The macroscopic dimensions of nuclear graphite undergo 3-4% shrinkage and will increase during high temperature irradiation (Kurpaska et al., 2020). At high-temperature and under neutron irradiation environment porosity of nuclear graphite plays a very important role (Huang et al., 2019).

A nuclear graphite has excellent irradiation performance and adequate mechanical properties at high temperatures therefore it has been used extensively for moderators, reflectors, and structural materials for high-temperature gas-cooled reactors (HTGRs) (Zhu et al, 2017). Even graphite itself is non-flammable due to the lack of volatile species, when it is exposed to an oxygenated environment at high temperatures (>450ºC) thermal oxidation will occur (Katie dkk, 2018). One of the critical issues of the graphite in HTGRs is its low oxidation stability at high temperatures, and influence to integrity loss for nuclear components. Because of decreasing the strength and modulus of elasticity with the formation and expansion of pores. It was found that oxidation in a graphite material causes changes in the microstructure (Yi Je Cho dan Kathy Lu, 2020). Furthermore, oxidation of graphite fuel elements in HTGR leading to exposure of fuel particles to oxygen and then potentially followed by release of fission products (Joshua et al, 2017)

Initial reaction during graphite oxidation is affected by the opening of the pores. Then the surface area increases which causes gases diffuse and enter inside the graphite (Guiqiu et al, 2013).

Graphite is very easy to react with oxygen while oxidized graphite is a compound consisting of the element carbon (C) and lead produce carbon monoxide gas as following reaction:

$$2C + O_2 \rightarrow 2\,CO \quad (1)$$

According to Langmuir Hinshelwood formulation, the reaction rate of oxidization graphite is determined by the partial pressure of oxygen, temperature, and the activation energy of graphite (Sumijanto, 2014), as follows:

$$L = K.\ \exp(-E/RT)\ PO_2 \quad (2)$$

with:

L = Mass fraction rate of reacted graphite per second
K = reaction rate constant
E = Activation energy
R = Universal gas constant
T = surface temperature of graphite and coolant = Kelvin
PO_2 = partial pressure of oxygen

Forming process from coke source and filler grain size of a nuclear grapahite which influence to the microstructure and pore network play important role of oxidation behavior (Lee at el, 2018). Increasing material porosity lead to increasing of graphite oxidation that will produces material weight loss then cause of loss of graphite stiffness and strength. The integrity of graphite because of oxidation will affect directly to the integrity of the reactor (Olasov dkk, 2018). The overall oxidation damage effect including depth and gradient will affect to the mechanical, physical, and thermal properties of graphite(Joshua et al, 2018).

IG-110 is one of the nuclear graphite that has been used for structural and component of HTGR. Oxidation rate and behavior of IG-is influenced by the fine coke microstructure. The oxidation rate of IG-110 increases linearly with temperature and depth of oxygen penetration (Lee et al., 2014). Based on Ximing et al (2016), the kinetic regime temperature of graphite oxidation is divided by three regimes i.e. the regime I at 400–550°C which has lower apparent activation energies the regime II at 600–900°C, the regime III above 900°C. In this research work IG-110 oxidation behavior and the influence to its microstructure at a temperature of 520ºC under air environment was investigated. The aim of the study is to simulate and analyze the performance of IG-110 graphite if air ingress occur in the reactor at that temperature.

2. Experimental

2.1. Materials

A nuclear graphite IG-110 produced by Toyo Tanso Ltd, Japan) is used as an oxidation test material under air environment with temperature of 520ºC. The IG-110 graphite is made by pressing made from coke sources, and the main properties are shown in **Table 1**. Previous oxidation testing, the samples were characterized, then compared with after oxidation testing to analyze the microstructurechange because of the temperature and air. Furthermore, the oxidation rate and weight change testing was carried out.

Table 1. Main properties of nuclear graphite IG110

Property	Density [g/cm3]	Elastic modulus [Gpa]	Compression strength [Mpa]	Thermal conductivity[W/(m·K)]	Impurity rate [ppm]	Porosity [%]
IG-110	10,62	88,29	4,73	0,98	<20	21,2%

2.2 Graphite Oxidation Testing and Charactirization Equipment

MSB Rubotherm equipment produced by Präzisionsmess-technik GmBH, was used in this study. It is a corrosion test equipment that works based on changes in mass when the sample is exposed to an increase in the surrounding temperature. Weighing method uses electromagnetic suspension technology, where the sample is weighed in a separate room from the scales. The sample is connected to a permanent magnet in the chamber which interacts with an electromagnetic field outside which is connected to the scale. So that the sample does not experience direct contact with the scales (Salam et al, 2013).

Changes in sample mass are measured based on changes in the magnetic field caused by changes in the sample position during the heating process. The main part of the MSB is the sample chamber which consists of a sealed ceramic tube. In this ceramic chamber there is a sample to be heated. Various types of gas and air can be introduced into it during the measurement process, such as Argon (Ar), nitrogen (N2), water vapor and others.

Another component is a scale (micro balance) that works based on changes in the magnetic field that occur in the measurement room. This scale is capable of measuring changes in mass up to 0.05 mg. Data retrieval during the measurement process is carried out by a CPU that can display the process in-situ (Salam et al, 2013).

For microstructure analysis optical microscope of Olympus BX51, SEM-EDS (Scanning Electron Microscope – Energy Dispersive X-ray Spectroscope) of JEOL JSM-6510LA and XRD of Phillips Panalytical Empyrean were occupied. All the experiment, testing and characterization was carried out at Advanced Materials Science laboratory in the Center For Science and Technology of Advanced Materials – National Nuclear Energy Agency BATAN.

3. Results and Discussion

The profile of oxidation testing of IG-110 graphite is shown in **Fig. 1** The graphic shows the relationship between weight change with temperature and exposure time. The results showed that weight loss behavior occurred. In general the corrosian rate of the sample was $7x10^{-5}$mg/cm^2/minute. It means that the corrosion rate of IG-110 at temperature of 520ºC under air environment was relatively small. Therefore, if IG-110 graphite is exposured by air at temperature of 520ºC in the reactor because of air ingress up to hundred minutes then the material will not have seriously damage.

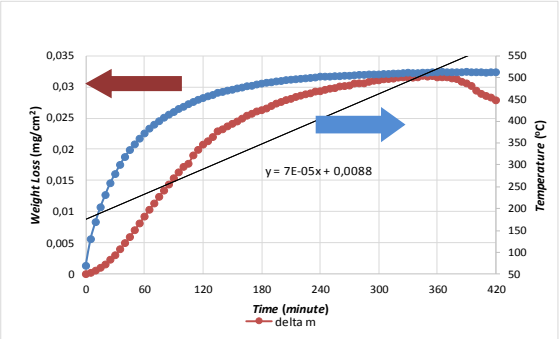

Fig. 1. The Relationship Between Mass Loss To Temperature and Time

3.1 Optical Microscope and SEM-EDS Observation Analysis of IG-110 Graphite Oxidation

In order to analyze the morphological changes in the surface structure of IG-110 graphite after testing, an Optical Microscope (OM) characterization and Scanning Electron Microscope (SEM) were carried out. Then Energy Dispersive X-ray Spectroscope (EDS) which is coupled with SEM was used to determine the elements formed in graphite before and after oxidation testing. **Figs. 2** show an optical microscope on graphite IG-110. This observation provides information that there has been a change in the surface structure as a result of the oxidation process. **Fig 2a** is the result of observations before oxidation has a rough and porous surface structure. Meanwhile, after oxidation at a temperature of 520℃, a smooth surface structure and small pores have been formed. Then SEM analysis was carried out to get more detail observation. **Figs. 3** shows the SEM results of the IG-110 graphite. **Fig.3a** shows a micrograph before oxidation that the surface structure with small and large pores was observed. Fig.3b shows a micrograph after oxidation testing that the surface structure with distribution of large pores and some small flakes was observed.

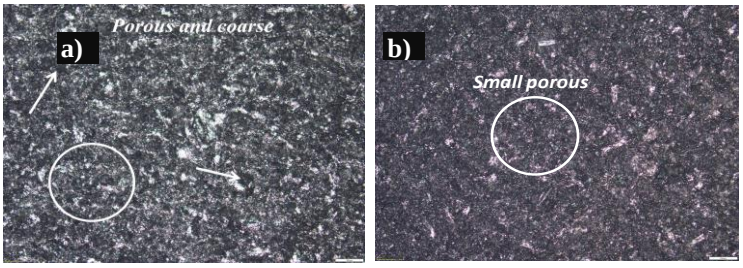

Fig. 2. Results of Optical Microscope Characterization Analysis, a) Before Oxidation, b) After Oxidation at 520ºC Temperature

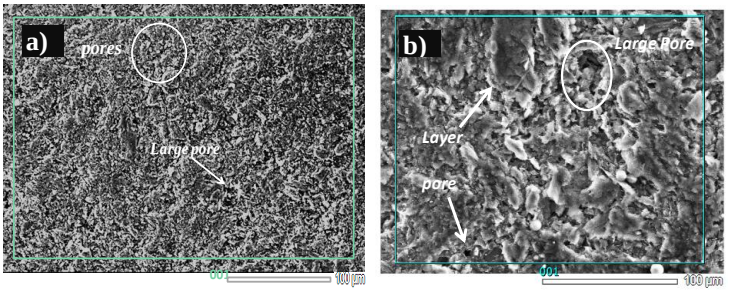

Fig. 3. Results of SEM Characterization Analysis, a) Before Oxidation, b) After Oxidation at 520ºC Temperature

Fig. 4 shows the results of the EDS analysis of graphite IG-110 before oxidation testing. The results showed that all the material was dominated by the element C of 100%. Meanwhile, on the graphite that has been oxidized (**Fig. 5**) at a temperature of 520℃ the C and O elements were observed with dominated by C element. Oxygen element was detected possibly because of trace of burning process of graphite during oxidation testing that produce carbon monoxide and/or carbon dioxide.

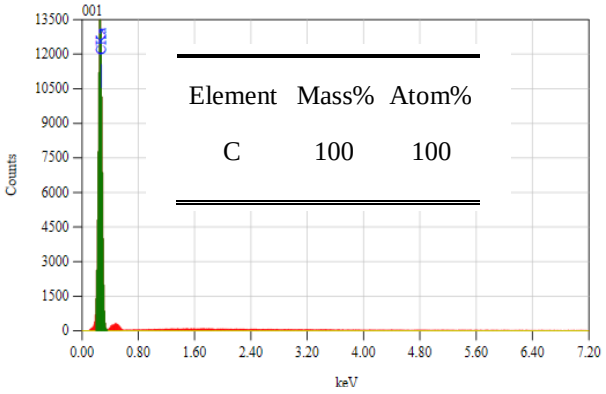

Fig. 4. Results of EDS Characterization Analysis before Oxidation

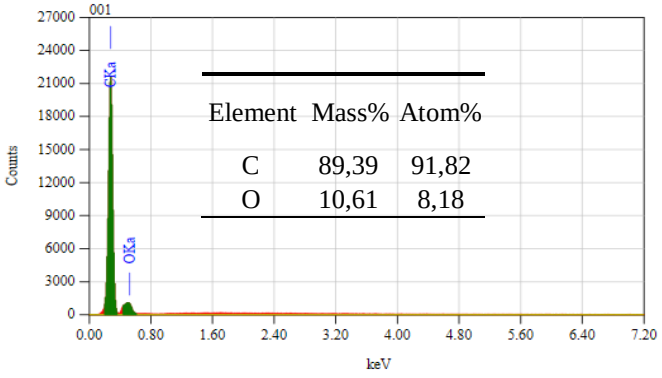

Fig. 5. Results of EDS Characterization Analysis after Oxidation

3.2 X-Ray Diffraction Analysis of Oxidation Graphite IG-110

XRD analysis was used to identify the surface structure of graphite before and after oxidation. Data processing analysis was done using Match and origin software. **Fig.6.** shows the XRD graph of the sample before and after oxidation testing. It can be seen that the diffraction pattern formed is almost the same, totally dominated by

carbon. The difference lies in the decrease in intensity and peak shift. In order to analyze the phenomenon, crystal size of the samples before and after oxidation testing were investigated and compared.

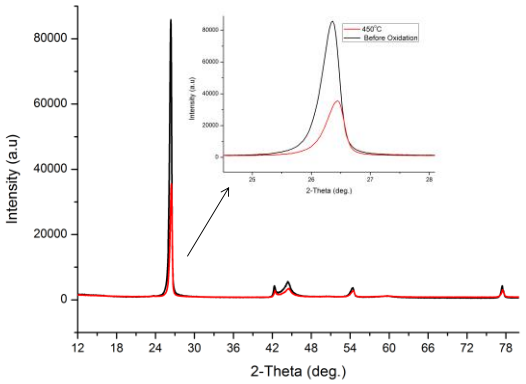

Fig. 6. X-Ray Diffraction Pattern Comparison between before and after Oxidation at 520ºC of Temperature under Air Environment

By selecting the diffraction peak curve of each crystal at the 2θ position, it can be determined the value of the diffraction half-peak curve widening (FWHM), then these values are entered into the Scherrer equation to determine the size of the graphite crystal. The Scherrer equation is as follows

$$D = \frac{k\,\lambda}{\beta.\cos\theta} \qquad (3)$$

Where k is the Scherrer constant (k = 0.9), λ is the X-ray wavelength used (λ = 0.15405 nm), β is FWHM (Full Width at Half Maximum). The diffraction peaks with the highest intensity were selected. The estimated crystal size value was calculated by averaging the crystal size value for each selected crystal plane.

Table 2. Results of Calculation of Crystal Size at the Diffraction Peak of Graphite IG-110

	Before oxidation℃	Oxidation 520℃
Crystal Size (nm)	21.08885642	20.45443
	17.54662364	18.62904
	5.064980798	5.263581
	13.34937784	13.21114
	24.76066795	22.35215
Average	16.36210133	15.98207022

Table 2 shows the results of the calculation of the crystal size at the diffraction peaks of graphite IG-110. It was calculated from the five crystal planes. The results showed that the crystal size values before and after oxidation was different. The calculation results showed that of the average crystal size of graphite material before oxidation was 16.36 nm while the crystal size after oxidation testing at a temperature of 520℃ under air environment was 15.98 nm. It can be seen that the crystal size after oxidation testing was smaller than before testing. The change of the crystal size occurred because the FWHM of the sample after oxidation was larger which contributed to the crystal structure.

4. Conclusions

Oxidation behavior and micro structure analysis of nuclear graphite IG-110 at 520℃ of temperature under air environment has been investigated with in-situ observation using MSB and micrograph observations. The results showed that Graphite IG-110 has a change in surface structure caused by the reaction of the material with oxygen in air at high temperatures. Furthermore, the crystal size of the material structure was slightly change. However, in general, the corrosion rate of graphite IG-110 at a temperature of 520℃ under the air environment is relatively low. So that if graphite IG-110 is exposed to air at a temperature of 520℃ for several hundred minutes in a nuclear reactor estimated does not suffer serious damage.

Acknowledgments

The authors express their gratitude to PSTBM Center For Science and Technology of Advanced Materials – BATAN National Nuclear Energy Agency for the permission and facilities to do this research at Advanced Materials Science Laboratory, to Drs. Bambang Sugeng for XRD operation and Mr. Agus Sudjatno, A.Md. for SEM-EDS operation, and Diene Noor Haerani, A.Md.Si. for Optical Microscopy operation.

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