Oxidation Effects on Thermal Emissivity of Selected Nuclear Graphite

Se-Hwan Chi[1*], Seung-Kuk Seo[2], Jae-Seung Roh[2], Min-Hwan Kim[1]

[1] *Nuclear Hydrogen Development and Demonstration Project, KAERI, Dae Duk Science Town, Yuseong, Daejeon 305-353 Rep. of Korea*
[2] *School of Advanced Materials and Systems Engineering, Kumoh National Institute of Technology, Gumi, Gyeoungbuk 730-701, Rep. of Korea*

[*] *Corresponding author: shchi@kaeri.re.kr*

1. Introduction

The thermal emissivity (TE) of graphite core components is an important thermal property that controls the transfer of heat out of core to the final heat sink during an off-normal event in a graphite-moderated high temperature reactor (HTGR) **[1]**. This requires heat transport via thermal radiation across the gas gap (1~3 mm) between the graphite core and the steel core barrel.

Thermal emissivity, which is defined as the ratio of energy radiated by a material to that radiated by a theoretical black body (emissivity = 1) at the same temperature and under the same conditions, is known to show little variance for carbon or graphite typically ranging between 0.60 and 0.95 **[2]**. However, since graphite is nearly the perfect black body material, it is expected that the emissivity of given graphite will largely depend upon the component surface conditions (roughness, pore structure, crystallographic orientation, crystallinity) and environment (temperature, radiant media) [**1, 3, 4, 5**].

During operation, the surface of graphite core components is expected to be greatly affected owing to chronic exposure to oxidation resulting from impurities in the helium environment [**1**]. Thus, if new grades of advanced microstructures for core components of HTGR are developed, since oxidation is microstructure dependent, studies on the TE of the grades are needed to provide information necessary for the safety evaluation of core concerning the transfer of heat out of core to the final heat sink during an off-normal event.

In the present study, the TE of selected nuclear grades developed for HTGR core components have been determined both in as received and oxidized condition, in air (100 - 500℃, wave length: 5 – 20 ㎛) and the changes in TE owing to oxidation were evaluated based on the surface condition (roughness, crystallinity, porosity) and environment (temperature).

2. Experimental

2.1 Materials, Oxidation and Thermal Emissivity Measurement.

Materials employed in the present study are shown in **Table 1**.

Table. 1. Nuclear graphite grades employed in the study. (Coke size: ㎛, Elec. Resistance: Ω.㎛, Density: g/cm^3)

	IG-11	IG-110	IG-430	PCEA	NBG-18
Form. Method	Iso	Iso	Iso	Ext.	Vib.
Coke Type	Pet	Pet	Pit.	Pet.	Pit.
Ave. coke size	10	10	10	360	300
Elec. Resis.					10.2, 10.3
Density	1.76	1.77	1.82	1.83	1.85

Specimens (40 x 40 x 3 mm^3) were prepared to the surface roughness condition (Ra) of 0.5 for TE measurement (**Fig. 1**) at 100 ~ 500℃ in as-received (weight loss: 0 %) and two oxidized conditions (weight loss: 5%, 10 %), where oxidation were performed in a tube furnace at 600℃ in air (air flow rate: 5 litter /min). Humidity and temperature were kept at 35% and 25℃ during TE measurements.

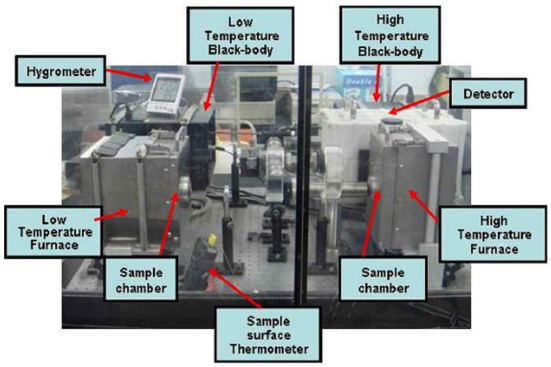

Fig. 1 Infra-red spectrum measurement system (FT-IR, MIDAC M2400-C, 4000-400 cm^{-1}, Resolution: 0.5 cm^{-1}, 5-20㎛,100-500℃).

The emissivity of black-body furnace (Infrared Systems Dev. Corp, Model 563, Hyperion R, Copper, Thermal stability: ±0.1 ℃) is 0.995 at 30 – 550℃.

2.2 Surface Roughness (SEM, Confocal Laser Scanning Microscopy) and Crystallinity (Raman Spectroscopy) Measurements

Specimens after TE measurements were subjected to

scanning electron microscopy (SEM), confocal laser scanning microscopy(CLSM), and Raman spectroscopy (Reinshaw, Ar, 514.5 nm, beam size: 1nm, Resolution: 0.4cm±1~2cm^{-1} at x 200) for surface roughness and crystallinity measurements, respectively.

2.3 Evaluation of Effects of Pore on TE by Artificial Pore Simulation Method (APSM)

Effects of pore on TE were evaluated at 100 and 500℃ from TE measurements on surfaces with 0, 32, 64, and 128 artificial holes (dia: 500 ㎛, depth: 250㎛) introduce- by drilling .

3. Results and Discussion

3.1 Oxidation and Temperature Effects on TE

Figure 1 show the oxidation effects and temperature dependencies of TE of, for example, IG-110 (b) and PCEA (c). TE appeared to increase with oxidation (5%, 10%) irrespective of grades at 100-500℃. The increases in TE owing to the increase in oxidation from 5% to 10%, however, were not so large as the one from the as-received (0% oxidation) to 5% oxidation. Detailed comparison of the temperature dependencies of TE appeared to show a difference between the IG-grades and PCEA or NBG-18. While IG grades show a rather temperature independency of TE, Non-IG were not. Large similarities in the change of TE owing to oxidation were observed from a comparison made between PCEA (wave length: 5 to 20 ㎛) and AUC graphite (wave length: 0.2 to 10 ㎛) [**6**] of similar manufacturing processes (extrusion) and ingredients (petroleum coke, filler particle size). Thus, at 500℃, while the former showed an increase in TE from 0.596 (polished) to 0.696 (oxidized), the latter were 0.554 (polished) to 0.772 (oxidized), respectively. These increase in TE after oxidation may be attributed to the changes in surface condition (roughness, porosity) and crystallinity owing to the selective oxidation of binder [**7**]. The differences in the temperature dependencies have also been related to the anisotropic optical properties, which in turn are related to the electrical anisotropy, of graphite [**7**].

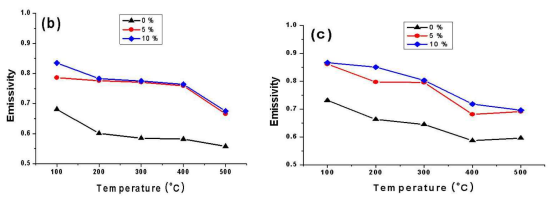

Fig. 2 Oxidation effects and temperature depend- encies of TE for IG-110 (b) and PCEA (c).

3.2. Surface Roughness and Crystallinity Effects on TE

Large increases in TE were observed owing to an increase in oxidation from 5% to 10%. For this increase in oxidation, the changes in surface roughness were negligible though some apparent increases in roughness were observed for specimens oxidized to 5% weight loss. Observed increases in TE were attributed to the increase in crystallinity in oxidized surfaces owing to the selective oxidation of binder phase during oxidation (**Fig. 3**).

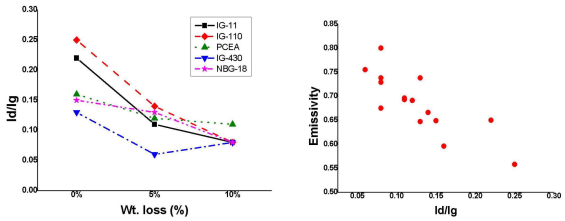

Fig. 3 Raman results (Id/Ig - Weight Loss) and Emissivity-Id/Ig relationship for 5 grades examined.

In addition to crystallinity, the crystal orientation and porosity are known to affect the emissivity. The higher emissivity observed in polycrystalline graphite to pyrolytic graphite has been attributed to higher porosity in poly-crystalline graphite [4]. The effects of pore on TE were examined by APSM. Result obtained from APSM showed a positive role of porosity for the increase in TE.

4. Conclusion

Preliminary study on the effects of oxidation on the emissivity of nuclear graphite for HTGR shows that various surface condition (roughness, crystallinity, porosity) affect TE. An increase in the crystallinity, surface roughness, and porosity owing to oxidation appears to increase the TE of nuclear graphite for HTGR.

Acknowledgement

This study was supported by Nuclear Research & Development program of the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP). (Grant code: NRF-2012M2A8A2025682).

REFERENCES

[1]. Graphite Technology Development Plan, PLN-2497, 10/04/10, INL (Project No. 23747) 2010

[2] Handbook of Carbon, Graphite, Diamond and Fullerenes, edited by Hugh O. Pierson, Noyes Pub., New Jersey, USA (1993). P. 108-109.

[3] ibid. P. 108 (1993).

[4] G. W. Autio and E. Scala, Carbon 4(1966) 11-28

[5] David M. Haaland, Carbon 12 (1974) 633-638

[6] B. E. Baker, Nuclear Engineering and Design 14 (1970) 413-444.

[7] J. D. Plunkett and W. D. Kingery, Proceedings of 4th Conference on Carbon held in Buffalo, New York (Pergamon Press, New York, 1960)pp. 457-472.