A study of cesium impregnation behavior in IG-110 graphite matrix by using Laser Ablation ICP-MS (LA-ICP-MS)

Je-Kyun Baek [a], Sunghwan Yeo [b], Young Woo Lee [b], Sun-Ho Han [c], Ho Jin Ryu [a*]
[a] *Department of Nuclear and Quantum Engineering, KAIST, Daehak-ro 291, Yuseoug-gu, Daejeon, 34141, Korea*
[b] *Next Generation Fuel Division, KAERI, Daedeok-daero 989-111, Yuseong-gu, Daejeon, 34057, Korea*
[c] *Nuclear Chemistry Research Division, KAERI, Daedeok-daero 989-111, Yuseong-gu, Daejeon, 34057, Korea*
[*] *Corresponding author: hojinryu@kaist.ac.kr*

1. Introduction

The high temperature gas-cooled reactor (HTGR) is spotlighted 4th generation reactor after a severe accident in a nuclear reactor such as Chernobyl, Fukushima accident owing to high safety feature, which is originated from tristructural-isotropic (TRISO) fuel concept. But the one of the current issues in the development of HTGR is what most of the fission products which are diffused through intact TRISO or just released from cracked TRISO is retained in graphite matrix, but some elements such as cesium (Cs), silver (Ag), strontium (Sr) is reported [1-3] whose species have a possibility release out from graphite matrix. The release out of fission product can cause a contamination problem to primary coolant channel. According to this problem, the identification of fission product diffusion behavior in graphite is important to development of HTGR

The diffusion experiment has been actively performed for identifying fission product diffusion in graphite by Carter et al. [4-5] They have measured Cs diffusion coefficient in graphite with the method which impregnates Cs to sample and measures Cs release out quantity. The impregnation process includes the heat treatment at 1100°C for uniform Cs distribution, they calculate the diffusion coefficient from LA-ICP-MS results along radius direction. The methodology is originated from the thermal gradient at 1100°C heat treatment.

The final goal of the study is the confirmation of fission product diffusion behavior, and the previous paper deal with impregnation process and preliminary study to use LA-ICP-MS. Cs distribution in graphite will be discussed in this study, as done in Carter's work [5].

2. Previous study overview

Impregnated sample preparation and the analysis results have been released out in our earlier study [6-7]. The information in this study is an important preliminary study for this paper which will deal with LA-ICP-MS analysis for verifying Cs distribution, so the short explanation is given in the chapter.

2.1 Sample impregnation

The first step of this study is impregnation; fission product such as Cs, Ag is impregnated in the graphite matrix. Impregnation step is used to simulate fission products which have diffused through intact TRISO or just released from cracked TRISO. As mentioned previous chapter, most of these fission products are expected to retain in a graphite matrix, but some elements such as Cs, Ag are released out. Cs is the element which is used in this study.

The graphite which is employed in this study is IG-110, which is manufactured by Toyo tanso and have dimension 6mm diameters and 4mm length pellet as shown in Figure 1. Table 1 is the standard specification of IG-110 provided from the manufacturer.

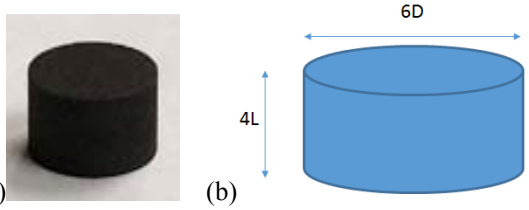


Figure 1. (a) The picture of IG-110 specimen and (b) schematic of specimen

Table 1. IG-110 Physical properties provided by the manufacturer

Bulk Density	1.77 Mg/m^3
Shore Hardness	51 HSD
Electrical Resistivity	11.0 μΩ-m
Flexural Strength	39 MPa
Compressive Strength	78 MPa
Young's Modulus	9.8 GPa
Coefficient of Thermal Expansion	4.5 × 10^{-6} /°C [350-450°C]
Thermal Conductivity	120 W/(m-K)

The impregnation process is similar to Carter's work [4], and the process is briefly described as following;

1. Insert the graphite to solution which contains $CsNO_3$

2. Keep the solution and specimen in the vacuum circumstance
3. Discard the solution and dry specimen to remove water in oven (50°C) over one day
4. Seal the specimen into quartz tube which is vacuum circumstance
5. Heat up quartz tube in furnace for converting $CsNO_3$ to Cs and distributing uniformly

The specimen after preparing above process is analyzed to confirm the impregnation process by measuring impregnated Cs quantities and Cs distribution with the following process.

2.2 ICP-MS analysis

The amount of Cs after impregnation is analyzed by using ICP-MS machine which is located in KAIST Analysis Center for Research Advancement (KARA).

The pre-treatment process has been performed in the solution which consists of 70% HNO_3 7ml + 35% HCl 3ml at 200°C during 30minutes since the liquid sample is necessary for ICP-MS analysis, so solid sample should be converted to the liquid sample. At this time, Cs can be just dissolved to the solution after the pre-treatment process. Thus, graphite is ground to fine powder as much as possible before the pre-treatment process.

The results of ICP-MS analysis is several hundred ppm, about 146~652ppm range. In comparison with Carter's work [4], the results isn't measured by ICP-MS but measured by Instrumental Neutron Activation Analysis (INAA). The results of Carter's work is estimated in the range about 206~271ppm, and the results are judged comparable because the results are overlapped.

2.3 LA-ICP-MS analysis

As mentioned before, LA-ICP-MS is used to verify Cs distribution in the specimen. The preliminary study using LA-ICP-MS was contained in the previous paper [7], the detail contents including both previous study and new contents will be shown in next chapter.

3. Methods and results

3.1 LA-ICP-MS overview

The principle of LA-ICP-MS is briefly explained in Figure 2. The surface of the specimen is vaporized locally by laser ablation machine, and the vaporized quantities in each element are measured by using ICP-MS.

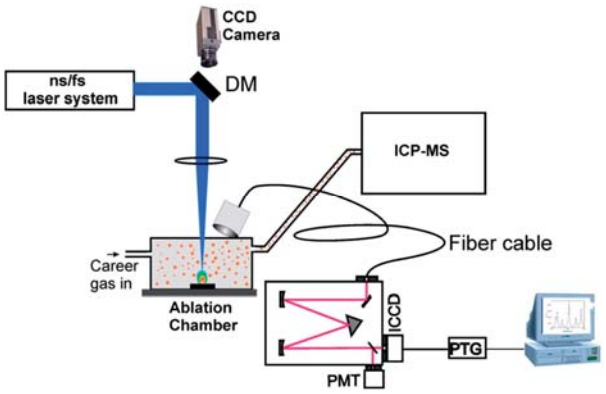


Figure 2. Schematic of LA-ICP-MS [8]

The two LA-ICP-MS machines which are used in this study are located in Korea Institute of Science and Technology (KIST) and Korea Atomic Energy Research Institute (KAERI). The provided data about each LA-ICP-MS is shown in Table 2.

Table 2. LA-ICP-MS instrument information

Institute	Instrument	Manufacturer	Instrument
KIST	LA	Applied Spectra	J100
	ICP-MS	Thermo	I cap Q
KAERI	LA	CETAX	LSX 213
	ICP-MS	Thermo	Element XR

3.2 Measurement methods

The specimen cutting has to be performed to measure the Cs distribution inside of specimen. Therefore, the specimen have been cut three times for each specimen as shown in Figure 3.

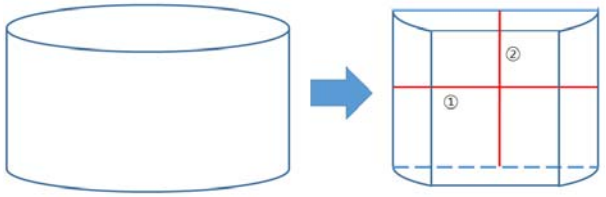


Figure 3. Cutting method for making LA-ICP-MS sample

The largest surface is analyzed after cutting, because the axial and radial direction analysis can be performed at the same time.

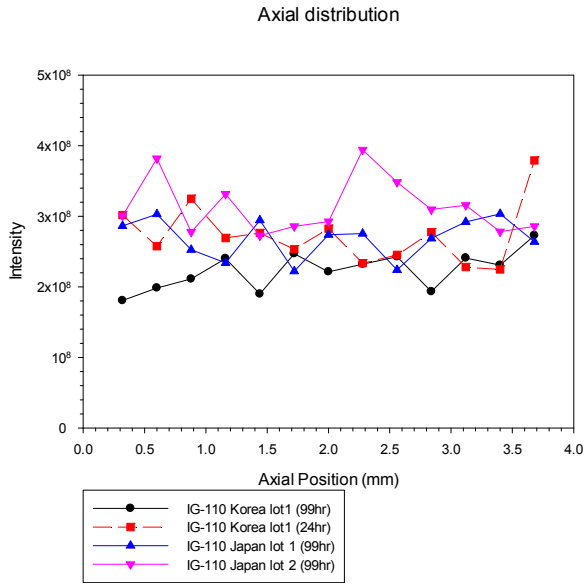
Two measurement methods are used to analyze Cs distribution; line scanning and mapping. First, line scanning is performed to verify 1D linear distribution along with axial and radial direction. In detail, the laser shoots the surface through linear line along an axial or radial direction at a regular interval, and the signal is

measured and recorded by ICP-MS. The second method is called as mapping, which analyzes the Cs distribution to a 2D plane.

3.3 Results

The partial results are shown in this chapter, and the line scanning results which was performed in KIST are shown as Figure 4.

(a)



(b)

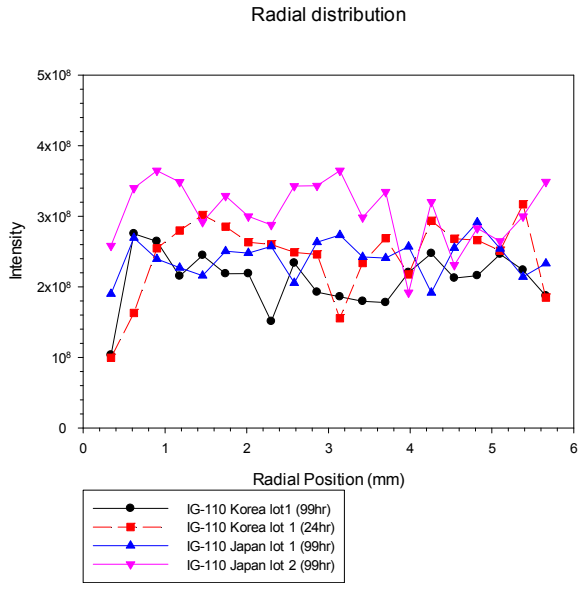
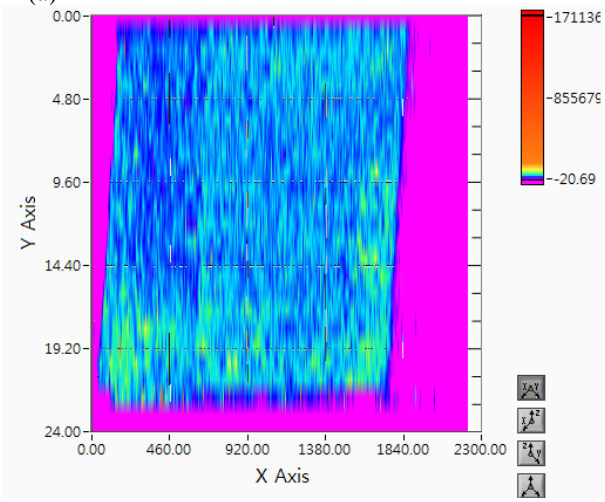


Figure 4. (a) Axial and (b) radial Cs distribution in the sample

The tests are performed on the four specimens both axial and circumferential direction, most intensity data are in the range of 10^8 to 4×10^8. Intensity mean signal frequency for each data point. As a consequence, the results can be interpreted that Cs is distributed consistently if data scattering is considered.

(a)



(b)

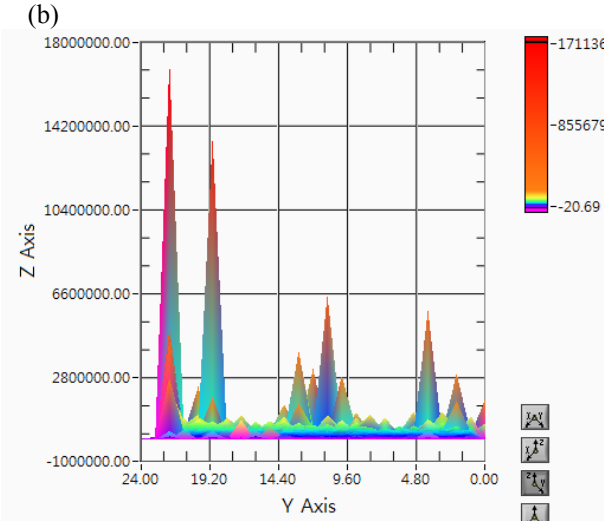


Figure 5. Mapping results (a) X axis (Axial direction) verse Y axis (Radial direction) and (b) Y axis (Radial direction) verse Z axis (Intensity) by using IG-110 Japan lot 1 (99hr)

Mapping results for the 2D plane are shown in Figure 5, X and Y axis mean location of axial and radial in the plane and Z axes show intensity at each point. Most of the surface detects very low Cs contents, but Cs peak can be detected in local regions.

The variation in results between line scanning and mapping is expected due to the difference in measurement mechanisms. In the line scanning method, the total intensity is measured at each point as an average value. But in the mapping method, the intensity measurement follows a line from an initial point to an end point where the detectable spot size is determined by the motion of laser source. This mechanism is called gridding with a spacing between lines to be approximately 0.18mm. As a result, the intensities

measured by the mapping method might be detected at lower focal spot than line scanning method.

4. Conclusion

The study has been performed to confirm the fission product diffusion behavior. Among several fission products, Cs which can easily release out to primary coolant and also have volatile characteristic is selected to study.

The impregnation process is performed to simulate Cs retained graphite. Impregnated Cs quantity is analyzed by using ICP-MS, and the Cs quantity after impregnation is in the range of 146~652 ppm.

Cs distribution after the impregnation process is measuring by using LA-ICP-MS. The line scanning results are interpreted that Cs is spread to overall sample uniformly with scattering. But, it is noticeable that Cs is expected to contain some local region from the mapping results.

Acknowledgment

This study was supported by NRF-2015M2A8A2023296. And the LA-ICP-MS analyses have been supported by Dr. Jong-Yun Kim, Dr. Sang Ho Lim, and Dr. JeongMook Lee who are affiliated to Nuclear Chemistry Research Division of KAERI and Mr. Taehee Kim who is affiliated to Nuclear Fuel Laboratory of KAIST. I would like to appreciate all researchers who supported this study

REFERENCES

[1] Hayashi, K., et al. (1983). "Distribution of fission and activation products in the graphite sleeves of HTGR fuel rods: first and second OGL-1 fuels." *Journal of Nuclear Materials* 116(2): 233-243.

[2] Hayashi, K., et al. (1987). "In-pile release behavior of metallic fission products in graphite materials of an htgr fuel assembly." *Journal of Nuclear Materials* 149(1): 57-68.

[3] Hayashi, K., et al. (1987). "In-pile release behavior of metallic fission products in graphite materials of an htgr fuel assembly." *Journal of Nuclear Materials* 149(1): 57-68.

[4] Carter, L. M., et al. (2015). "Measurement of cesium diffusion coefficients in graphite IG-110." *Journal of Nuclear Materials* 460: 30-36.

[5] Carter, L. M., et al. (2015). "ICP-MS measurement of diffusion coefficients of Cs in NBG-18 graphite." *Journal of Nuclear Materials* 466: 402-408.

[6] Je-Kyun Baek, et al. (2015). “A Preliminary Study for Diffusion Experiments of Metallic Fission Products in Graphite for HTGR” *Korea Nuclear Society*, Autumn meeting

[7] Je-Kyun Baek, et al. (2016). “A study on the diffusion of volatile fission products in the graphite matrix of HTGR” *The Minerals, Metals and Materials Society*, 145th Annual meeting & Exhibition

[8] LaHaye, N. L., Harilal, S. S., Diwakar, P. K., & Hassanein, A. (2014). Characterization of laser ablation sample introduction plasma plumes in fs-LA-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 29(12), 2267-2274.