A Preliminary Study for Diffusion Experiments of Metallic Fission Products in Graphite for HTGR

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1. Introduction

The high temperature gas-cooled reactor (HTGR) is a system of Generation IV reactors, operated at a high temperature with gas coolants. The concept of coated particulate fuel is usually adopted in the design of HTGR fuel for high temperature core conditions [1]. There are several coated particulate fuel such as BISO (Bistructural-isotropic coated particulate fuel) TRISO (Tristructural-isotropic coated particulate fuel), QUADRISO (Quadruple-isotropic coated particulate fuel), etc. Graphite matrix compact including coated fuel particles is formed as cylindrical pellets or spherical pebbles [1].

TRISO which is a representative coated particulate fuel type consists of fuel kernel, a buffer carbon layer, an inner pyro-carbon layer, a SiC layer, and an outer pyro-carbon layer [1]. Most fission products are retained in TRISO particles but some fission products can be released to the graphite matrix because of possible transportation through the coating layers or the failure of coating layers [2]. The graphite matrix also retains most of the fission products, but some metallic fission products such as Cs, Ag are released out from graphite matrix [3]. The release of fission products affects the radiation safety of reactor systems because of primary coolant contamination. Thus, diffusion behavior of metallic fission products in the graphite matrix should be estimated to confirm the radiation safety of HTGR.

2. Review of metallic fission product diffusion in graphite

The possibility of primary coolant contamination by the release of fission products from graphite compact is critical concerns. There are several reports that observe the diffusion behavior of fission products which are released out from the graphite matrix such as Cs, Ag, etc.

2.1 Diffusion coefficients of metallic fission products in graphite

2.1.1. Irradiated HTGR fuel

Recently, fission product diffusion data of irradiated HTGR fuel have been reported [3-6]. The diffusion data about irradiated fuel are mainly related to the fission product release from entire graphite compact, rather than diffusion coefficients of fission products in irradiated graphite. But Hayashi et al. [3] measured the Cs diffusion coefficient in the graphite matrix, as shown in equation (1).

$$D=(9.0\times10^{-6})\exp(-1.57\times10^{5}/RT) \quad (1)$$

When compared Cs diffusion data in irradiated graphite and un-irradiated graphite, the diffusion coefficients in irradiated graphite is lower than that those in un-irradiated graphite by 3-4 orders of magnitude. These results are caused by the effect of radiation damage in graphite under irradiation.

2.1.2. Non-irradiated HTGR fuel

Most of the non-irradiated fuel tests were performed in 1980s or earlier, and Cs diffusion coefficient data from non-irradiated fuel tests are summarized as Table 1. The Ag diffusion coefficient data from non-irradiated fuel tests are summarized as Table 2.

Table 1. Cs diffusion data [4, 8-12]

Investigators	Graphite type / test method	$D=D_0\exp(-E/RT)$	
		D_0 (m^2/s)	E (J/mol)
Meyers and Hill	H-451, cylinder/ sectioning	$D=2.20\times10^{-10}$ ~ 1.31×10^{-9}	
Leyers	A3, sphere/ release	2.01×10^{-4}	1.98×10^{5}
Hoinkis	A3-3, cylinder/ release	1.99×10^{-4}	1.81×10^{5}
Evans et al.	HS1-1 / sectioning	4.44×10^{-2}	1.27×10^{5}
Hayashi and Fukuda	IG-110, cylinder / sectioning	1.2×10^{-4} (Test A) 1.7×10^{-4} (Test B)	1.12×10^{5} (Test A) 9.5×10^{4} (Test B)
Carter et al.	IG-110, sphere / release	1.0×10^{-7}	1.1×10^{5}

Table 2. Ag diffusion data [7, 13]

Graphite type	Temperature range (°C)	$D=D_0\exp(-E/RT)$	
		D_0 (m^2/s)	E (J/mol)
LTI pyrocarbon		5.3×10^{-9}	1.54×10^5
	1000 ~ 1630	5.3×10^{-4}	1.93×10^5
Matrix graphite	800 ~ 1300	68	2.62×10^5
	800 ~ 1300	1.3	2.46×10^5
	800 ~ 1300	1.6	2.58×10^5
	800 ~ 1000	8.7×10^7	4.14×10^5
Structural graphite	490 ~ 800	1.6	2.58×10^5
	750 ~ 1030	6.3×10^{-3}	2.64×10^5
	850 ~ 1100	1.6×10^2	3.64×10^5
GR001CC (Boyle et al.)	1150	$D = 2.385\times10^{-15}$ m^2/s	

2.2 Diffusion mechanisms of metallic fission products in graphite

The graphite matrix has a porous structure and the structure has lots of defects in the irradiation environment, so the diffusion behavior of metallic fission products in the graphite matrix is very complex. There are several fission product diffusion models in the porous graphite because fission product diffusion in graphite cannot be explained by the simple homogeneous Fickian diffusion model. The other complicated models have been proposed such as two-phase diffusion model, coupled fast-slow diffusion model, diffusion-trapping model, etc. [2] In order to understand complicated diffusion mechanisms of metallic fission products in irradiated graphite, diffusion experiments with microstructure-controlled graphite are necessary.

3. Experiment preparation

There are several methods measuring diffusion coefficients of fission products in the graphite matrix. Among them, the profile method and the release method have been selected to perform diffusion tests. In the profile method, a long cylindrical pellet of graphite contacting with another thin graphite disk which is impregnated by fission products such as Cs, Ag is annealed. The concentrations of fission products in the thin sectioned regions of the long cylindrical pellet are measured after annealing. Meanwhile, the impregnated graphite compact spheres is annealed in the inert gas flow and the released concentrations of fission products are measured in the release method [4, 7-13].

3.1 Graphite fabrication

First of all, the resinated graphitic powder should be prepared to fabricate the matrix graphite samples. Natural graphite, electro-graphite and phenolic resin with alcohol are mixed to pass through several powder production processes, such as mixing, pasting, drying, milling, etc. This resinated graphitic powder is used to fabricate cylinders, disks and spheres of matrix graphite [1].

Two types of graphite cylinder and graphite cell should be prepared for the profile method. Long graphite cylinders are fabricated by using die pressing. Thin source disks to be impregnated by Cs or Ag are to be fabricated by polishing of thicker graphite disks.

Carter et al. [4] have performed a diffusion test of Cs by using the release method, and they used spherical graphite matrix balls. In this study, cold isostatic pressing (CIP) method is used to fabricate spherical graphite samples.

All the graphite compacts pass the two stages of heat treatment, carbonization and annealing. The carbonization process is performed in an inert gaseous atmosphere at 800°C, the mixed resin binder in the graphite powder has a more strength after carbonization. Next, the annealing process is performed under vacuum over 1800°C to eliminate the impurities in the graphite matrix [1].

Fig. 1. The cold isostatic pressing equipment used for producing spherical matrix graphite samples

Fig. 2. A spherical graphite sample and the two semi-spherical mold after cold isostatic pressing

3.2 Impregnation

Impregnation of Cs or Ag is one of the most important steps in the fission product diffusion experiments because homogeneous distribution of impregnated elements can affect experimental results significantly. Because Cs or Ag cannot be impregnated directly to the graphite matrix, nitrate solutions containing Cs or Ag, such as $CsNO_3$ and $AgNO_3$, are usually used. First, graphite is impregnated by a nitrate solution and then the graphite is heated to convert the nitrate into Cs or Ag.

By reviewing all the impregnation conditions in previous studies [4, 7-13], several impregnation conditions have been used to confirm how the impregnation conditions affect the final fission product concentration in the graphite matrix. Destructive chemical analyses have been used to check the fission product concentrations in the graphite matrix, unlike other previous research using neutron activation analysis (NAA) to confirm Cs or Ag contents [4].

But any impregnation conditions haven't been identified as a standard, impregnation conditions should be confirmed to guarantee constant impregnation results. There are several test parameters, such as heat treatment ambient, heat treatment conditions, concentration of the nitrate solution, specimen types, and time to impregnate. The results of impregnation with varied conditions will be released in the paper.

4. Conclusions

Diffusion behavior of metallic fission products in the graphite matrix has been analyzed in order to design diffusion experiments for Cs or Ag impregnated graphite matrices or structural graphite samples. When Cs diffusion data in irradiated graphite are compared with those for un-irradiated graphite, the diffusion coefficients in irradiated graphite is lower by 3-4 orders of magnitude. These results are caused by the effect of radiation damage in graphite under irradiation.

When the possible theories of fission products transport in graphite were reviewed, several processes such as two-phase diffusion model, coupled fast-slow diffusion model, diffusion-trapping model, etc. have been identified as important mechanisms for metallic fission product transport in graphite.

The resinated graphitic powder is used to fabricate different graphite matrix compacts with a cylinder, a disk or a sphere shape. Because well-organized impregnation processes haven't been published in the previous studies, the variation of major impregnation parameters, such as impregnation solution concentrations, impregnation times, and specific surface areas of samples are tested. By using chemical composition analyses, the quantities of metallic fission products in graphite matrix samples have been measured to identify the effect of each parameter.

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