Journal of Nuclear Materials 476 (2016) 30–35

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Diffusion of cesium and iodine in compressed IG-110 graphite compacts

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HIGHLIGHTS

- A method for analysis of fission product diffusion in graphite by ICP-MS was applied to pressed IG-110 graphite compacts containing cesium and iodine.
- Diffusion coefficients for cesium and iodine were obtained.
- The measurement design simulates HTGR conditions of high temperature and flowing helium.

ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form
12 April 2016
Accepted 15 April 2016
Available online 21 April 2016

ABSTRACT

Nuclear graphite grade IG-110 is currently used in the High Temperature Engineering Test Reactor (HTTR) in Japan for certain permanent and replaceable core components, and is a material of interest in general. Therefore, transport parameters for fission products in this material are needed. Measurement of diffusion through pressed compacts of IG-110 graphite is experimentally attractive because they are easy to prepare with homogeneous distributions of fission product surrogates. In this work, we measured diffusion coefficients for Cs and I in pressed compacts made from IG-110 powder in the 1079–1290 K temperature range, and compared them to those obtained in as-received IG-110.

1. Introduction

The HTGR/VHTR utilizes graphite as a moderator, structural material, and barrier to fission product release. Diffusion coefficients for fission products in graphite are required for source term estimation, radiological surveillance, and reactor safety. Diffusion coefficients for fission products in graphite may be dependent on many variables including graphite type and properties (porosity, BET surface area, impurity concentration, and irradiation history), fission product identity, and concentration. The manufacturing method used to produce the graphite results in a characteristic microstructure described by the porosity, BET surface area, and pore size distribution. Irradiation causes structural defects in the graphite microstructure which include formation of vacancies, interstitials, and in-plane topological changes.

The diffusion coefficients of fission products in graphite can be measured using a release method [1–7]. Advantages of the release method include non-destructive analysis and real time data collection. One challenge of the release method is in choosing the appropriate size of the graphite sample. A large sample may best represent the properties of bulk graphite but the time required to achieve a uniform distribution to satisfy the Booth model [4] using a technique that isopiestically infuses the element into the graphite [1–3,5,6,8] can be prohibitive. Conversely, a uniform distribution of an infused element can be achieved quickly with a small graphite sample but the sample may not represent bulk graphite due to variability of the pore structure. A second important limitation of the release method is the difficulty of infusing low-volatility elements into graphite samples. For example, the challenge of loading a graphite sphere with Sr has limited the usefulness of the release method for measuring the Sr diffusion coefficient. These two challenges may be overcome by measuring diffusion in graphite compacts made from graphite powder instead of bulk graphite.

Abbreviations: HTGR, high temperature gas-cooled reactor; ICP-MS, inductively coupled plasma-mass spectrometry; INAA, instrumental neutron activation analysis; FP, fission product; VHTR, very high temperature reactor; BET, Brunauer-Emmett-Teller surface area; MURR®, University of Missouri Research Reactor.

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http://dx.doi.org/10.1016/j.jnucmat.2016.04.024

Surprisingly, it has been reported that Sr diffusion coefficients obtained from diffusion measurements in some bulk graphites are similar to those obtained from pressed graphite compacts made from powdered graphite of the same type [9]. This suggests that the mechanism of Sr diffusion is relatively insensitive to differences in the microstructure of pressed graphite pellets and manufactured graphite. An additional advantage of compacted graphite is that it is relatively simple to load multiple elements to fabricate a surrogate fission spectrum.

The objective of the present work is to compare the measured diffusion coefficients of Cs and I in pressed graphite pellets and bulk graphite. If the diffusion in compacted graphite and bulk graphite is similar, then compacted graphite may be used to approximate the diffusion of Ag, Sr, and other important fission products in bulk graphite when isopiestic infusion is not feasible. Differences between the graphite microstructure of the pressed pellets and the manufactured graphite should result in different Cs and I diffusion coefficients. The underlying mechanisms of I transport in graphite are not described well by Fickian kinetics [5]. However, for the purposes of fuel performance modeling codes, I diffusion is handled using Fickian kinetics with an effective diffusion coefficient that encompasses pore diffusion, grain diffusion, trapping, and other complex transport mechanisms [10]. In this work, we compare the diffusion of Cs and I in compacted IG-110 graphite to our previously published work on Cs and I diffusion in bulk IG-110 graphite [1,5].

The diffusion of Cs and I in graphite compacts in measured using the release method, where the source of Cs and I in graphite compacts is CsI. As noted above, we investigated graphite compacts because it is desirable to start with a graphite sample that contains a uniform distribution of diffusant to simplify the boundary conditions for the diffusion equation.

2. Theory

For our purposes here, the diffusion of a species in a sample is described by the equations:

$$\begin{aligned} \frac{\partial C(\mathbf{r},t)}{\partial t} &= D\nabla^2 C(\mathbf{r},t) \\ C(\mathbf{r},0) &= C_0 \\ C(\mathbf{r}_s,t) &= 0 \end{aligned} \tag{1}$$

where, $C(\mathbf{r},t)$ is the concentration of the fission product (g/m^3), $C(\mathbf{r}_s,t)$ is the concentration of the fission product at the surface of the sample, D is the diffusion coefficient (m^2/s), $\mathbf{r}$ is the distance vector (m), and t is the time (s). C_0 is a constant; the initial uniform concentration (g/m^3). We also assume that $C(\mathbf{r},t)$ is finite everywhere. The diffusion coefficient D is determined by comparing the experimental fractional release rate, $f(t)$ or the cumulative fractional release $F(t)$ with the corresponding theoretical results. The release rates are defined as:

$$f(t) = \frac{1}{VC_0}\int\left(-D\frac{\partial C(\mathbf{r}_s,t)}{\partial n}\right)dS \tag{2}$$

And,

$$F(t) = \int_0^t f(t')dt' \tag{3}$$

Where V is the volume of the sample, and $\mathbf{n}$ is a unit normal vector at $\mathbf{r}_s$ a point on the surface and is directed outwards from the body.

For a finite-cylindrical sample of radius R and length h, one gets:

$$F(t) = \sum_{m=1}^{M}\sum_{n=1}^{N} b_{m.n}(1-\exp[-\lambda_{m.n}Dt]) \tag{4}$$

Where:

$$b_{m,n} = \frac{32}{m_0^2 n^2 \pi^2}, \text{ if n is odd; } 0, \text{ otherwise}. \tag{5}$$

Also,

$$\lambda_{m.n} = \left(\frac{m_0}{R}\right)^2 + \left(\frac{n\pi}{h}\right)^2 \tag{6}$$

Here m_0 is the m th root of the Bessel Function of order zero, J_0. The series converges slowly as M and N go to infinity (we have later used $M = 100$ and $N = 100$, and explored up to $M = 200$ and $N = 200$). Note that $\sum_{m=1}^{M}\sum_{n=1}^{N} b_{m.n} \to 1$, as $M, N \to \infty$. For fast computations, we have separated the terms and summations in Equation (4) as:

$$\begin{aligned} F(t) &= \frac{32}{\pi^2}\left(\sum_{m=1}^{M}\frac{1}{m_0^2}\right)\left(\sum_{n=1,3,5,..}^{N}\frac{1}{n^2}\right) - \frac{32}{\pi^2}\left(\sum_{m=1}^{M}\frac{1}{m_0^2}\exp\left[-\left(\frac{m_0}{R}\right)^2 Dt\right]\right)\left(\sum_{n=1,3,5,..}^{N}\frac{1}{n^2}\exp\left[-\left(\frac{n\pi}{h}\right)^2 Dt\right]\right) \\ &\approx 1 - \frac{32}{\pi^2}\left(\sum_{m=1}^{M}\frac{1}{m_0^2}\exp\left[-\left(\frac{m_0}{R}\right)^2 Dt\right]\right)\left(\sum_{n=1,3,5,..}^{N}\frac{1}{n^2}\exp\left[-\left(\frac{n\pi}{h}\right)^2 Dt\right]\right) \end{aligned} \tag{7}$$

And this works as well as the series solution for a sphere. Still, since the series converges slowly, it is useful to consider a short time approximate solution also. For a sphere of radius R_s the short time solution is particularly simple:

$$F_{short}(t) = 6\sqrt{\frac{\tau}{\pi}} - 3\sqrt{\tau} \tag{8}$$

Where the dimensionless quantity τ is the reduced time, *viz*:

$$\tau = \frac{Dt}{R_s{}^2} \tag{9}$$

Equation (8) is accurate to an experiment time that results in a fractional release up to about 90% of the diffusant (i.e. for values of τ less than approximately 0.2) [11]. With appropriate normalizations, Equation (8) is also suitable for describing diffusion from non-spherical samples at short time scales. The surface flux of diffusant, at short times, emanates from a layer close to the sample