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ICP-MS measurement of diffusion coefficients of Cs in NBG-18 graphite

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HIGHLIGHTS

- A method for analysis of fission product diffusion in graphite by ICP-MS was applied to nuclear-grade graphite NBG-18.
- The design simulates HTGR conditions.
- Diffusion coefficients for cesium in NBG-18 graphite were obtained.

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ABSTRACT

Graphite is used in the HGTR/VHTR as moderator and it also functions as a barrier to fission product release. Therefore, an elucidation of transport of fission products in reactor-grade graphite is required. We have measured diffusion coefficients of Cs in graphite NBG-18 using the release method, wherein we infused spheres of NBG-18 with Cs and measured the release rates in the temperature range of 1090–1395 K. We have obtained:

$$D_{Cs,NBG-18} = \left(1.0 \times 10^{-7} m^2 \big/ s\right) \exp\left(\frac{-1.23 \times 10^5 J/mol}{RT}\right)$$

These seem to be the first reported values of Cs diffusion coefficients in NBG-18. The values are lower than those reported for other graphites in the literature.

1. Introduction

Release of fission products from nuclear reactors is a fundamental safety concern. The High Temperature Gas-Cooled Reactor (HTGR/VHTR) uses graphite as a moderator and as a barrier to fission product release in the reactor core. The VHTR is expected to operate with a maximum core outlet temperature of 950 °C, and in an accident scenario may reach temperatures in excess of 1600 °C. At these temperatures, diffusion becomes an important mechanism of fission product transport and release from the core. Improvements in manufacturing techniques coupled with unavailability of historical graphite grades (e.g. H-451) have led to the development of contemporary grades of nuclear graphite including IG-110, NBG-18, and PCEA, and these and other candidate graphites need to be well qualified [1]. Currently, material properties and diffusion/oxidation behavior of candidate graphites are being intensely investigated. Measurements of diffusion coefficients for fission products in graphite are required for source term estimations and reactor safety.

We have previously measured diffusion coefficients for Cs in IG-110 graphite using the release method, in which graphite spheres were infused with Cs and subsequent release of Cs measured by ICP-MS [2], and we have illustrated infusion procedures and instrument calibration for Cs in NBG-18 graphite [3]. In this paper we

Abbreviations: HTGR, High Temperature Gas-Cooled Reactor; ICP-MS, Inductively Coupled Plasma-Mass Spectrometry; LA-ICP-MS, Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry; INAA, Instrumental Neutron Activation Analysis; FP, Fission Product.

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apply the technique to diffusion of Cs in NBG-18 graphite, and focus on the results for NBG-18 and comparisons with IG-110.

We note that IG-110 graphite is a very fine-grained petroleum coke filler-based graphite produced by Toyo Tanso in Japan using an isostatic rubber press process. NBG-18 is manufactured using a vibrational molding process by SGL Carbon GmbH in Germany, using a much larger grain size and coal coke filler. Differences in manufacturing techniques and materials impart wide variation among the properties of nuclear graphites, including pore size distribution, concentration of impurities, density, and grain sizes. These characteristics are expected to have an effect on fission product diffusion coefficients in graphite. A summary of relevant characteristics for IG-110 and NBG-18 is given in Refs. [1,4,5].

2. Theory

Transport of Cs in certain graphites has been shown to occur via a pore surface diffusion mechanism which consists of series of random “jumps” of Cs atoms between diffusion sites [6–11]. The permeability of a material to a particular diffusant is characterized by the diffusion coefficient. The diffusion coefficient generally follows an Arrhenius type dependence on temperature, specifically:

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \tag{1}$$

where D is the diffusion coefficient (m^2/s), D_0 is the diffusion coefficient at infinite temperature, E_a is the activation energy (J/mol), R the gas constant (J/mol·K), and T the temperature (K). In graphite, the diffusion coefficient may be a function of other factors in addition to temperature, including pore size distribution, oxidation, irradiation, and concentration of contaminants.

Here we consider a spherical graphite sample of radius $r = R$ which has been infused with a particular fission product (FP). As the sample is heated, the concentration of the FP changes at a time dependent rate governed by the diffusion equation, as the FP atoms diffuse through and out of the sphere through its surface. Under the assumption that the mass distribution of the FP is spherically symmetric, we have [2,9,12,13]:

$$\frac{\partial C(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D\, r^2 \frac{\partial C(r,t)}{\partial r}\right) \tag{2}$$

With boundary condition:

$$C(R,t) = 0. \tag{3}$$

Here, $C(r,t)$ is the concentration of the FP (g/cm^3), and t is the time (s). Note that $C(r,t)$ is non-negative and is finite everywhere. This mass transfer equation is well known, and may be solved using separation of variables, transform techniques, or numerical methods.

The series solution of Eqns. (1) and (2) is known to be:

$$C(r,t) = \sum_{n=1}^{\infty} A_n \Psi_n(r) Exp\left(-\lambda_n^2 Dt\right) \tag{4}$$

Where,

$$\begin{aligned} &\lambda_n = n\pi/R \\ &\Psi_n(r) = sin(\lambda_n r)/r \\ &A_n = \frac{2}{R}\int_0^R r^2 C(r,0)\Psi_n(r)\mathrm{d}r \end{aligned} \tag{5}$$

Where $C(r,0)$ is the initial condition, the concentration profile in the sphere, at $t = 0$.

The mass loss rate (g/s) of FP from the sphere is expressed as:

$$\begin{aligned} \dot{m}(t) &= -4\pi R^2 D \frac{\partial}{\partial r} C(r,t)\Big|_{r=R} \\ &= 4\pi RD \sum_{n=1}^{\infty} A_n (-1)^{n-1} \lambda_n Exp\left(-\lambda_n^2 Dt\right) \end{aligned} \tag{6}$$

And, the cumulative fractional release $F(t)$, defined as the ratio of mass of FP released from the sphere (up to time t) to the total initial FP mass, is thus:

$$\begin{aligned} F(t) &= \frac{1}{m_0}\int_0^t \dot{m}(t')\,\mathrm{d}t' \\ &= \frac{4\pi RD}{m_0}\sum_{n=1}^{\infty} A_n(-1)^{n-1}\frac{1}{\lambda_n D}\left[1 - Exp\left(-\lambda_n^2 Dt\right)\right] \end{aligned} \tag{7}$$

Where m_0 is the total initial total mass of the FP in the sphere,

$$m_0 = 4\pi\int_0^R r^2 C(r,0)\mathrm{d}r \tag{8}$$

If the initial distribution of FP, $C(r,0)$ is known, (6) or (7) may be fit to experimental release data to determine the diffusion coefficient. In particular, if we take,

$$C(r,0) = \alpha + \beta(r/R) \tag{9}$$

Where α and β are some constants, then we find:

$$A_n = -\frac{2R}{n^3\pi^3}\left\{2\beta + (-1)^n\left[-2\beta + n^2\pi^2(\alpha+\beta)\right]\right\} \tag{10}$$

And, Eqn. (7) can be written as:

$$\begin{aligned} F(t) = \frac{8R^3}{m_0\pi^3}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^4}\left[1 - e^{-\left(\frac{n\pi}{R}\right)^2 Dt}\right]\Big\{2\beta + (-1)^n\Big[-2\beta \\ + n^2\pi^2(\alpha+\beta)\Big]\Big\} \end{aligned} \tag{11}$$

An alternative and more convenient expression for $F(t)$ corresponding to Eqn. (11), valid for short time, can be found using the Laplace Transform technique. We have found this solution, to order t to be (we call it, $F_{short}(t)$ to distinguish it from the above series solution)

$$F_{short}(t) = \frac{4\pi R^3}{m_0}\left[\alpha\left(2\sqrt{\tau/\pi} - \tau\right) + 2\beta\left(\sqrt{\tau/\pi} - \tau\right)\right] \tag{12}$$

Where, the non-dimensional quantity τ is defined as (this combination appears in Eqn. (11) above also):

$$\tau = \frac{Dt}{R^2} \tag{13}$$

For the case of flat initial profile, $\beta = 0$, and Eqn. (12) is then the same as we had used in our previous work on IG-110. Also, as for the flat profile, we have found that Eqn. (12) is surprisingly accurate even for fairly large times (we have compared $F(t)$ and $F_{short}(t)$ for a range of parameter; generally for good accuracy, it is necessary to retain about 100 or more terms in the series as it converges very slowly for short times).