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DIFFUSION OF METALLIC FISSION PRODUCTS IN
PYROLYTIC CARBON

by

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IN NUCLEAR SCIENCE ABSTRACTS

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ABSTRACT

The diffusion of strontium and cesium through thin layers (100μ) of isotropic pyrolytic carbon has been measured over the temperature range 1000° to 1700°C . Diffusion coefficients observed for cesium are orders of magnitude lower than those for strontium. The diffusion rates for both series are much lower than those observed in polycrystalline graphite, where little difference is seen between cesium and strontium. When constant chemical potential sources are used, chemical- and self-diffusion measurements for strontium give identical results in the concentration range 1.0×10^{-4} g to 2.0×10^{-3} g Sr/g graphite. There is apparently no concentration effect for cesium over the range 1.0×10^{-7} g to 1.5×10^{-3} g Cs/g graphite.

The difference between strontium and cesium diffusion in pyrolytic carbon is attributed to the greater steric effect of the pyrolytic carbon defect structure relative to that of cesium.

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I. INTRODUCTION

Pyrolytic carbon-coated nuclear fuel particles, while demonstrating excellent fission gas retention, exhibit a relatively high release of certain metallic fission products.⁽¹⁻⁴⁾ Studies have been reported of the diffusion of Ni, Ag, Sr, Ba, Ce, Ra, Pa, and Th in various types of graphites, with the conclusions that diffusion proceeds principally via defects in the graphite structure.⁽⁵⁻⁷⁾ It is desirable to extend such studies to the diffusion of several metallic fission-product elements in pyrolytic carbon to elucidate the release mechanism and to provide data which can be used to predict the transport of fission products in HTGR fuel elements.

Small spherical particles (200 μ to 500 μ diameter) are not well suited for a detailed analysis of concentration gradients through their coatings. Rather than to use macrospecimens of pyrolytic carbon to predict the behavior of these coatings, it is preferable to study the diffusion of metallic nuclides in specimens that are identical in as many respects as possible to the coatings on the particles. For this reason, small wafers of porous graphite were mixed with fuel particles and coated along with them in typical coating runs. The flat surfaces of the wafers allow precision removal (lapping) of the surface layers. If a radioactive fission product has diffused into the coating, its concentration in each layer removed is easily determined by standard counting techniques, and a concentration profile is obtained from which a diffusion coefficient can be calculated.

Data were obtained for the diffusion of both strontium and cesium over the temperature range 1000 $^{\circ}$ to 1700 $^{\circ}$ C, using Sr⁸⁵, Sr⁸⁹, and Cs¹³⁷ as tracers. While both chemical- and self-diffusion measurements were made for strontium, it was only possible to measure chemical diffusion for cesium. Self-diffusion data are preferable because the experimental conditions approximate reactor steady-state operating conditions. Strontium diffusion was

measured using constant chemical potential sources of 1.0×10^{-4} g and 2.0×10^{-3} g Sr/g C. Cesium was measured at 1.0×10^{-7} g and 1.5×10^{-3} g Cs/g C.

In an earlier attempt to measure the diffusion of metallic fission products, porous graphite discs were first impregnated with uranium and then given a coating of pyrolytic carbon. The intent was to irradiate the coated specimens, thus generating fission products internally, and then to measure the outward diffusion of metallic fission products by determining their concentration profiles in the coatings as a function of annealing time and temperature. Control samples were run to correct for the fission products in the pyrolytic carbon due to migration of fuel during the coating process and due to recoil during the irradiations. In this approach, the high uranium concentration in the coatings precluded the use of these specimens as a source of basic diffusion data of the metallic fission products. A typical example is shown in Fig. 1, where neutron activation of an unannealed control specimen reveals the concentration gradient of uranium, by measurement of its fission product, Ba^{140} , in a wafer coated with isotropic pyrolytic carbon. This approach, however, did provide a method for studying fuel migration during the coating process.

Fig. 1 -- Distribution of Ba^{140} from U^{235} in a fueled graphite wafer coated with pyrolytic carbon

II. PROCEDURE

Graphite Wafers

Porous graphite wafers (Speer 780S), 5/16-in. diameter by 1/16-in. thick, were coated along with fuel particles in routine coating runs. The pyrolytic carbon coatings, about 100- μ thick (density = 2.1 g/cm³), were deposited at 2200°C and were isotropic (anisotropy factor ~ 1.3).⁽⁸⁾ To ensure precision sectioning after the diffusion anneals, the surfaces of the wafers were ground flat ($\pm 2.5\mu$) and parallel before and after the coating step. This was particularly important after deposition of the coating because pyrolytic carbon builds up at the edges, as shown in Fig. 2.

Constant Chemical-Potential Sources

For these diffusion studies, the constant chemical-potential technique is preferred over the thin film method because (1) this approach approximates actual reactor operating conditions, and (2) diffusion in PyC as a function of source concentration can easily be measured.

To produce constant-chemical potential sources of any desired concentration, a slurry was made of spectrographic grade graphite powder (5 g to 10 g) and a solution of the desired fission product, using isopropyl alcohol as a wetting agent. The slurry was evaporated to dryness. Thus, constant chemical-potential sources corresponding to a wide range of concentrations of the element in graphite are possible, with the lower limit of concentration that can be studied being determined by the detection limit of carrier-free isotopes.

Diffusion Anneals

Diffusion anneals were performed at a series of fixed temperatures, with the coated wafers pressed into a bed of the graphite powder containing

GRAPHITE WAFER WITH
PYROLYTIC CARBON

SURFACES GROUND PARALLEL -
READY FOR DIFFUSION ANNEAL

SAMPLE IS MOUNTED AND
EDGES OF SAMPLE ARE
REMOVED ON A LATHE

SAMPLE READY FOR SECTIONING

Fig. 2--Preparation of pyrolytic-carbon-coated samples

the fission product of interest. For the less volatile strontium, screw top tantalum containers were used, but, for the more volatile cesium, the tantalum containers had to be sealed by welding.

A resistance heated graphite tube furnace with a helium atmosphere was used. Temperatures were easily maintained within $\pm 3^{\circ}\text{C}$ of the reported temperature.

Self-Diffusion

Strontium. Wafers were saturated with strontium (Sr^{89} -tagged) at a level of 2.0×10^{-3} g Sr/g graphite by annealing for 25 hours at 1700°C in a bed of graphite powder containing strontium at that level. For these experiments, saturation is defined as achieving 80% of the constant source concentration at a depth of 90μ . One specimen was sectioned, and the strontium distribution, determined by means of the Sr^{89} tracer, established that the concentration at a depth of 90μ exceeded 80% of that of the source.

Self-diffusion of strontium was then determined by performing diffusion anneals in another constant source of 2.0×10^{-3} g Sr/g graphite but now using Sr^{85} as a tracer. The Sr^{89} , being a pure beta-emitter, does not interfere with gamma spectrometry measurements of Sr^{85} .

Cesium. Calculations using diffusion data obtained for chemical diffusion indicated that for cesium an anneal of 150 hours at 2000°C would be required to saturate coatings. Since it was felt that the saturation treatment itself might affect the coatings, self-diffusion measurements were not attempted with cesium.

Sectioning

After a diffusion anneal, the wafer was mounted flat on the end of a piston, and the outer edge was machined away, leaving a disc of about 1/4-in. diameter (Fig. 2). (The piston fits into a jig which holds it perpendicular to the abrasive paper while the surface of the sample is sectioned.) A section was removed from the exposed surface by drawing it once across 4/0 emery

polishing paper mounted on a granite surface plate. A five pound weight for uniform pressure was used, and the specimen was drawn over a 24 cm length of polishing paper; a layer of 4μ to 6μ was removed with each pass. A micrometer gauge was used to measure the thickness of the removed section. The micrometer gauge, granite surface plate, piston (with a mounted sample), and jig are shown in Fig. 3. The pyrolytic carbon adheres to the emery paper and each strip of paper is trimmed and counted. Gamma spectrometry was used for Sr^{85} and Cs^{137} ; the beta-emitter Sr^{89} was measured by proportional counting. A typical concentration profile is shown in Fig. 4. The concentration profiles were found to fit the diffusion equation corresponding to a constant source at the boundary of a semi-infinite medium,

$$\frac{C}{C_0} = \text{erfc} \frac{X}{2\sqrt{Dt}}, \quad (1)$$

where X = depth (cm)

t = annealing time (sec)

C = concentration at X

C_0 = concentration at surface ($X = 0$)

D = Diffusion coefficient (cm^2/sec).

The solid line in Fig. 4 is the curve of best fit corresponding to Eq. 1.

Data Analysis

Diffusion coefficients D were calculated from

$$D = \frac{X^2}{4t(Z)^2} \text{ cm}^2/\text{sec} , \quad (2)$$

where Z was obtained from the relationship $\text{erfc } Z = C/C_0$.

To analyze diffusion profiles, a computer program was devised applying the method of least squares fit to n^{th} order polynomial fitting of

Fig. 3--Lapping equipment

Fig. 4--Diffusion of strontium in isotropic pyrolytic carbon during a 2-hr anneal at 1100°C

relative concentration (C/C_0) versus depth (X). A second order fit usually gives the best values for diffusion coefficients. The required input data are (1) micrometer readings after each section is removed, (2) counts/minute for each section, and (3) annealing time in seconds.

Results

Diffusion coefficients obtained in these studies are shown in Table 1. Arrhenius plots ($\log D$ vs $1/^\circ K$) of the diffusion data are shown in Figs. 5 and 6. Figure 5 shows that there is no difference between the chemical diffusion of Sr at a level of 1.0×10^{-4} g Sr/g C and the self-diffusion of tracer Sr at a level of 2.0×10^{-3} g Sr/g C. From a least squares fit of the data, constants were evaluated to give the diffusion equation

$$D_{Sr} = 4.4 \times 10^{-2} \exp\left(-\frac{48,000}{RT}\right) \text{ cm}^2/\text{sec} . \quad (3)$$

Likewise, the cesium diffusion equation was determined from the Arrhenius plot of the diffusion coefficient determined for a level of 1.0×10^{-7} g Cs/g C as

$$D_{Cs} = 9.7 \times 10^{-7} \exp\left(-\frac{42,000}{RT}\right) \text{ cm}^2/\text{sec} . \quad (4)$$

These equations correspond to the classical diffusion equation

$$D = D_0 \exp(-E_a/RT) ,$$

where D_0 = empirical constant (cm^2/sec)

E_a = empirical activation energy ($\text{cal/mole-}^\circ K$)

R = gas constant ($1.987 \text{ cal/mole-}^\circ K$)

T = temperature ($^\circ K$).

In accordance with the atomic theory of diffusion,⁽⁹⁾ D_0 and E_a are related to the relative entropy and enthalpy of the "activated complex" (i. e. , the state corresponding to the barrier through which an atom must

Table 1
DIFFUSION COEFFICIENTS FOR STRONTIUM AND
CESIUM IN ISOTROPIC PYROLYTIC CARBON

Temperature (°C)	D_{Sr} (cm ² /sec)	
	Chemical Diffusion	Self-Diffusion
	Conc = 1.0×10^{-4} g Sr/g C	Conc = 2.0×10^{-3} g Sr/g C
1000	----	8.5×10^{-11}
1100	8.0×10^{-10}	1.5×10^{-9}
1200	3.7×10^{-9}	----
1300	1.0×10^{-8}	7.8×10^{-9}
1400	2.3×10^{-8}	----
1500	4.4×10^{-8}	4.4×10^{-8}
1700	----	3.5×10^{-7}
	D_{Cs} (cm ² /sec)	
	(Chemical Diffusion)	
	Conc = 1.0×10^{-7} g Cs/g C	Conc = 1.5×10^{-3} g Cs/g C
1000	5.8×10^{-14}	----
1200	5.8×10^{-13}	----
1400	8.6×10^{-12}	3.6×10^{-12}
1700	1.4×10^{-11}	8.2×10^{-11}

Fig. 5--Diffusion coefficients for strontium in isotropic pyrolytic carbon

Fig. 6--Diffusion coefficients for cesium in isotropic pyrolytic carbon

pass in jumping from one stable site (defect) to another) as follows:

$$\log_{10} D_0 = \log_{10} (\gamma a_0^2 \nu) + \frac{\Delta S_a}{2.303R}, \quad (5)$$

and

$$E_a = \Delta H_a,$$

where γ = geometric factor

a_0 = jump distance (average root mean square distance between defects) (cm)

ν = average jump frequency (sec^{-1})

ΔS_a = difference between entropy of "activated complex" state and normal state of atoms (in the carbon matrix)

ΔH_a = corresponding enthalpy difference.

III. DISCUSSION

The diffusion coefficients found for strontium and cesium in the pyrolytic carbon are several orders of magnitude lower than those for porous nuclear grade graphites. Thus, at $10^4/T = 5$ (1727°C), Bryant, et al.⁽¹⁰⁾ found that, for porous AUC graphite, $D_{\text{Sr}} \approx 0.9 \times 10^{-3} \text{ cm}^2/\text{sec}$ and $D_{\text{Cs}} \approx 1.1 \times 10^{-3} \text{ cm}^2/\text{sec}$ (with activation energies of 60 kcal/mol and 40 kcal/mole, respectively). We find, however, that $D_{\text{Sr}} \approx 3 \times 10^{-7}$ and $D_{\text{Cs}} \approx 3 \times 10^{-11} \text{ cm}^2/\text{sec}$. Bromley and Large⁽¹¹⁾ have also reported diffusion coefficients for metallic fission products in polycrystalline graphite, and, extrapolating their data for Type A graphite (normal British reactor grade), we obtain $D_{\text{Sr}} \approx 0.8 \times 10^{-3}$ and $D_{\text{Cs}} = 1.3 \times 10^{-4} \text{ cm}^2/\text{sec}$, which agree reasonably well with the data of Bryant, et al. However, the data of Bromley and Large correspond to much lower activation energies than found by Bryant, et al. (9.0 kcal/mole and 16.4 kcal/mole for Sr and Cs, respectively) and thus do not agree at lower temperatures. Anderson and Zumwalt⁽¹²⁾ found values of D for Ba and Sr in polycrystalline nuclear graphite between those estimated from the data of Bryant, et al., and the data of Bromley and Large; however, Anderson and Zumwalt found that the value of D_{Ba} depends largely on concentration.

At first consideration, the much lower value of D_{Cs} than that of D_{Sr} of the pyrolytic carbon is rather striking, particularly in view of the facts that (1) in the case of polycrystalline graphites, D_{Cs} and D_{Sr} are similar, (2) the diffusion of electropositive metals in pyrolytic carbon (graphite)^{*} and polycrystalline graphite appears to be by the same mechanism, and (3) the metals often have diffusion coefficients of the same order of magnitude.

^{*}Note: The terms pyrolytic graphite and pyrolytic carbon are used for the same materials by different workers. The term pyrolytic graphite has been used particularly for the forms of pyrolytic carbon that have large crystallites and are more anisotropic.

Wolfe, et al.,⁽⁵⁾ report that Ni, Ag, Ra, U, and Th diffusion in graphites proceeds via the defect structure, both in the case of polycrystalline graphite and in the case of pyrolytic graphite. Autoradiographs indicated diffusion along grain boundaries, experiments with polycrystalline graphite of different porosity eliminated the possibility of pore diffusion, and experiments with annealed pyrolytic graphite eliminated the possibility of interstitial and vacancy diffusion. Also, they found that the diffusion coefficients for U in the various types of graphite were quite similar.

Evans, et al.,⁽⁶⁾ performed similar experiments using both autoradiographic and concentration profile analysis techniques and found that the diffusion behavior of all actinides that were studied (Pa, U, Th) was similar in pyrolytic carbon and porous graphite. They concluded that diffusion in the perpendicular (c) direction of the anisotropic pyrolytic carbons that were studied is controlled by defects which can be eliminated by heat treatment (at $\sim 2900^{\circ}\text{C}$).

Faircloth, et al.,⁽⁷⁾ using the technique of electron probe microanalysis as well as a sectioning technique, have recently reported on studies of the diffusion of Sr, Ba, and Ce. In comparing diffusion in polycrystalline graphite and pyrographite (pyrolytic carbon), they concluded that diffusion in the a direction of pyrographite occurs by the same mechanism as in polycrystalline graphite, namely along defects such as grain boundaries and microcracks. The mechanism for diffusion in the c direction was not clear.

In view of these reported findings, it would seem reasonable to postulate that, in our experiments, Sr has diffused through the carbon coating (which by X-ray measurements has a crystallite size in the c direction $\sim 150 \text{ \AA}$,⁽⁷⁾ the size in the a direction probably being of the same order of magnitude) by migration along defects in the a direction. Movement in the c direction may also occur, but, for a nearly isotropic material (with approximately random orientation of the crystallites), this need not be postulated. Since various electropositive metals behave similarly on

graphite, it is assumed that Cs diffused by the same mechanism. The lower activation energy for Cs compared to that of Sr is not unexpected because the chemical affinity of alkali metals is lower than that of alkaline earth elements, as is evidenced by the greater stability of the carbides of the latter. The substantially lower $\log D_0$ value (-6.01 vs. -1.36) of Cs compared to that of Sr is believed to be due to a greater steric effect of the pyrolytic carbon defect structure (i.e., microcracks and grain boundaries) relative to that of the larger Cs atoms. Atom and ion sizes are (1) single bond metallic radii, Cs = 2.35 Å, Sr = 1.914 Å, and (2) ionic radii, Cs⁺ = 1.69 Å, Sr⁺⁺ = 1.13 Å. (13) Both atom and ion sizes are given since Cs and Sr should have some ionic character, when they are associated with defects in the pyrolytic carbon structure, the nearest carbon atoms will tend to act as electron acceptors.

The precise nature of the steric effect is to change the vibrational frequencies of the Cs pyrolytic carbon or the Sr pyrolytic carbon atom system. Thus, if the frequencies of a carbon structure are designated ν_{10} and the frequencies after the introduction of Cs or Sr atoms in certain structural arrangement (such as "activated complexes") are ν_{1a} , then the entropy change is

$$\Delta S_a = R \sum_i \ln \frac{\nu_{10}}{\nu_{1a}} \quad (6)$$

and the difference of Sr and Cs activation entropies (ΔS_a) would be

$$(\Delta S_a)_{Sr} - (\Delta S_a)_{Cs} = R \sum_i \ln \frac{(\nu_{1a})_{Cs}}{(\nu_{1a})_{Sr}} \quad (7)$$

If the $\log (\gamma a_0^2 \nu)$ is assumed to be about the same for Cs and Sr, our experimental data give, from Eq. (5),

$$(\Delta S_a)_{Sr} - (\Delta S_a)_{Cs} = 2.303R [(\log D_0)_{Sr} - (\log D_0)_{Cs}] = 21.4 \text{ eu} \quad (8)$$

and we then calculate

$$\sum_i \ln \frac{(\nu_{1a})_{Cs}}{(\nu_{1a})_{Sr}} = 9.3 \quad (9)$$

The steric effect is thus seen to have a rather large effect on the frequencies of the "activated complex" state, with the frequencies of the cesium "activated complex" being substantially greater than those of the strontium "activated complex" in the pyrolytic carbon.

From a practical viewpoint, the difference in the D_0 values, and thus the diffusion coefficients of Sr and Cs, makes pyrolytic carbon fuel particle coatings a much better diffusion barrier for fission product cesium than for fission product strontium. This is supported by observations on the release behavior of irradiated fuel particles annealed to high temperatures. (2-4)

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