

Diffusion Coefficients and Activation Energies for Ag Transport through SiC

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1. Introduction

One of the desired functions of TRISO coating is to prevent the release of fission products from inside the particle into the coolant. Among these layers, the retention of fission products is accomplished primarily by the SiC layer of the coating. These processes include oxide fuel kernel migration (via the transport of carbon from the cool to hot side); intra-layer crack formation, noble gas (Kr, Xe), Ba, Ag, Sr, Cs diffusion out of the kernel; pressure build-up due to noble gas release from the kernel and CO from released oxygen in ungettered oxide kernel; a Pd attack on SiC and noble gas, Pd, Ba, Sr, Cs, Ag, transport via bulk diffusion, grain boundaries, and cracks through the coating layers [1,2].

In this paper, the measured and estimated diffusion coefficients of Ag in and/or through SiC are compared based on the following experimental methods: 1) measuring Ag diffusion through ion-implanted cubic (3C) SiC and 6H-SiC samples and annealing, 2) measuring Ag diffusion through a diffusion couple and annealing, and 3) fitting the overall integrated/fractional Ag release from a batch of TRISO fuel particle during heating after irradiation and irradiation testing. Also, the pre-exponential factor and activation energy of Ag diffusion in or/and through SiC is estimated based on the Arrhenius relationship and compared with the previous results.

2. Ag diffusion coefficients

The transport of Ag through the coating layers of a coated particle has been studied in depth for last 40 years by many researchers [3]. Compared to transport through the SiC layer, transport through the UO₂ kernel and PyC layer is relatively quick in TRISO fuel. The diffusion coefficients of Ag in the UO₂ kernel and PyC layers are a few hundred times larger than SiC diffusion coefficient at 1000°C [3]. Both German and United States fuel development programs have suggested the same diffusion coefficients for UO₂ kernel and PyC layers [4]. The transport of Ag in SiC has been studied using ion-implanted various SiC samples [5-9], diffusion couple [10-16], and fractional/integrated Ag release from irradiated TRISO fuel [17-20] to obtain the diffusion coefficients.

In this section, the diffusion coefficients of Ag are summarized and compared regarding the experimental methods (ion implantation and Ag paste), estimation methods from the integral release of Ag during heating tests of irradiated TRISO fuel and the fractional release of Ag during irradiation tests in HFR for German TRISO fuel development program.

2.1 Ag ion implantation

The diffusion of Ag in single crystalline (hexagonal 6H-SiC) and polycrystalline CVD-SiC was investigated using ion implantation and a heating test. Detailed information on the ion implantation and heating test can be found in the references [5-9]. The diffusion coefficients observed among the samples differed from $<10^{-19}$ to $<10^{-21}$ m²·s⁻¹, which is at least a two-order of magnitude difference. Friedland *et al.* [8,9] has found that Ag diffusion was observed in the polycrystalline samples, but that no diffusion of Ag was observed in the single-crystal experiments. The fact that significantly higher effective diffusion coefficients have been determined in Ag release studies must therefore be either due to SiC coatings containing diffusion enhancing impurities in their grain boundaries or structural imperfections like cracks or pores [8,9]. Nabilek *et al.* [6] attributed no change in the Ag concentration profile after 0.5 h at 1180°C to Ag ions trapped in SiC grains during implantation not being able to diffuse along the grain boundaries. It can be considered that most of the implanted Ag ions are stopped within the SiC grains, and the measurement yields the bulk diffusion coefficient, which is expected to be very low.

2.2 Diffusion couple (Silver paste)

The diffusion of Ag in SiC (SiC-LT deposited at 1300°C with 9.1 vol% methyltrichlorosilane (MTS) concentration and SiC-PR deposited at 1300°C with 9.1 vol% MTS and 0.5 vol% propylene) deposited on the top of the IPyC layer and SiC deposited on top of a highly dense IPyC using an FBCVD reactor were performed using Ag paste and a heating test [11,12,21]. The diffusion coefficients observed among the samples differed from $\geq 1.6 \times 10^{-15}$ to $< 1 \times 10^{-18}$ m²·s⁻¹, which is at least a three-order of magnitude difference. Also, these diffusion coefficients were within the range of values recently calculated as best estimates for Ag diffusion in SiC using the results of the German HTR program [4].

2.3 Integral release of Ag during annealing test of irradiated TRISO fuels

Integral releases of Ag from irradiated SiC-layered coated particles have been measured during isothermal annealing in the temperature ranges [6,17,22]. The release rates measured have been evaluated with numerical treatment based on a simple diffusion model (Fick's law of diffusion), which assumes that fission

products are preliminary transported through the fuel materials. Different particle types have different fuel kernel materials with slight variations in the coating dimensions. Diffusion coefficients for Ag in SiC was derived for all types of kernels (UO₂, UC₂, ThO₂, mixtures, etc.) and for reference quality fuel (UO₂, (U, Th)O₂) [17]. D. Shrader *et al.* [15] summarized the pre-exponential factors and activation energies for the reported diffusion coefficient of Ag in SiC published from previous experiments [6,17,22]. The pre-exponential estimated from the release rates measured during isothermal heating differed from 3.60×10⁻⁹ to 6.80×10⁻¹¹ m²·s⁻¹ (diffusion coefficient; 1.50×10⁻¹⁵ to 2.78×10⁻¹⁷ m²·s⁻¹), which is at least a two-order of magnitude difference. The activation energy is in the range of 1.83 eV (176.6 kJ·mol⁻¹) to 2.26 eV (218.1 kJ·mol⁻¹).

2.4 Fractional release of Ag during irradiation tests of TRISO fuels

J.J. van der Merwe [4] has predicted and estimated the Ag transport and release from TRISO particle spherical fuel in the German fuel development program. Detailed information, such as the maximum fuel temperature, burn-up, fractional Ag release and fuel type, of each irradiation test in German fuel development program can be found in the references [3,20]. The temperatures and diffusion coefficients listed are the average (best estimate) center fuel temperatures for each test sphere and the diffusion coefficients at those specific temperatures. The diffusion coefficient evaluated from TRISO particle spherical fuel in the German fuel development program differed from 1.43×10⁻¹⁷ to 7.82×10⁻¹⁸ m²·s⁻¹, which is at least one-order of magnitude difference. The best estimate and design limit diffusion coefficients were derived by fitting all results to a straight line, as shown in Fig. 2 [4].

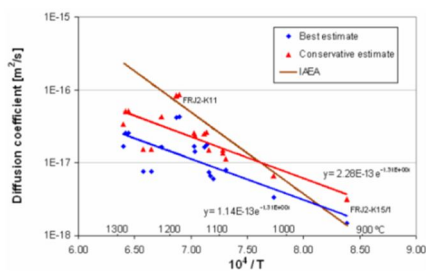


Fig. 2. Diffusion coefficients from the detailed evaluation [4].

2.5 Ag diffusion coefficient from experiments and estimations

Diffusion coefficients of Ag through SiC from previous papers are summarized in Table 1. The calculated diffusion coefficient at 1569°C [14] and the simulated values for Ag in Σ 3 grain boundary modeling [23] are also included in Table 1. The diffusion coefficients observed among the ion-implanted samples including single crystal (6H-SiC) differed from <10⁻¹⁹ to <10⁻²¹ m²·s⁻¹, which is at least two-order of magnitude

difference. The diffusion coefficients observed among the samples used Ag paste differing from $\geq 1.6 \times 10^{-15}$ to $< 1 \times 10^{-18}$ m²·s⁻¹, which is at least a three-order of magnitude difference. The diffusion coefficient estimated from the Ag integral release fraction of the samples differed from 1.50×10⁻¹⁵ to 2.78×10⁻¹⁷ m²·s⁻¹, which is at least a two-order of magnitude difference. Also, the diffusion coefficient evaluated from TRISO particle spherical fuel in the German fuel development program differed from 1.43×10⁻¹⁷ to 7.82×10⁻¹⁸ m²·s⁻¹, which at least one-order of magnitude difference.

Table 1. Summarized diffusion coefficients from previous studies [14,23].

Reference	D (m ² ·s ⁻¹)	T (K)	Measurement/Evaluation
8,9(6H-SiC)	< 10 ⁻²¹	1573	Ion implantation
8,9(6H-SiC)	< 5×10 ⁻²¹	1773	Ion implantation
5,7	< 5×10 ⁻²¹	1773	Ion implantation
8,9	1.41×10 ⁻²⁰	1473	Ion implantation
8,9	2.8×10 ⁻²⁰	1573	Ion implantation
8,9	1.46×10 ⁻²⁰	1673	Ion implantation
6	< 10 ⁻¹⁹	1453	Ion implantation
14	1.31×10 ^{-17*}	1842	Calculation
23	4.00×10 ^{-18*}	1873	Simulation in Σ 3 GB
23	1.10×10 ^{-18*}	1773	Simulation in Σ 3 GB
23	2.00×10 ^{-19*}	1673	Simulation in Σ 3 GB
23	3.90×10 ^{-20*}	1573	Simulation in Σ 3 GB
23	5.00×10 ^{-21*}	1473	Simulation in Σ 3 GB
23	5.00×10 ^{-22*}	1373	Simulation in Σ 3 GB
23	3.90×10 ^{-23*}	1273	Simulation in Σ 3 GB
11	3.46×10 ⁻¹⁸	1223	Silver paste
11	1.55×10 ⁻¹⁷	1423	Silver paste
11	2.99×10 ⁻¹⁵	1773	Silver paste
12	< 1×10 ⁻¹⁸	1473	Silver paste
12	$\geq 1.6 \times 10^{-15}$	1473	Silver paste
12	7.0×10 ⁻¹⁷	1473	Silver paste
12	3.9×10 ⁻¹⁷	1473	Silver paste
12	1.6×10 ⁻¹⁷	1473	Silver paste
12	< 1×10 ⁻¹⁸	1473	Silver paste
17	2.78×10 ⁻¹⁷	1523	Integral release
17	1.50×10 ⁻¹⁵	2023	Integral release
17	1.50×10 ⁻¹⁶	1523	Integral release
17	9.31×10 ⁻¹⁷	1573	Integral release
22	1.49×10 ⁻¹⁶	1523	Integral release
6	1.29×10 ⁻¹⁶	1443	Integral release
4	7.63×10 ⁻¹⁸	1520**	Irradiation (HFR-K3)
4	2.55×10 ⁻¹⁷	1551**	Irradiation (HFR-K3)
4	7.75×10 ⁻¹⁸	1504**	Irradiation (HFR-K3)
4	6.58×10 ⁻¹⁸	1394**	Irradiation (HFR-K3)
4	5.96×10 ⁻¹⁸	1388**	Irradiation (HFR-K3)
4	2.63×10 ⁻¹⁷	1558**	Irradiation (HFR-K3)
4	1.67×10 ⁻¹⁷	1404**	Irradiation (FRJ-K13)
4	1.71×10 ⁻¹⁷	1422**	Irradiation (FRJ-K13)
4	1.43×10 ⁻¹⁷	1421**	Irradiation (FRJ-K13)
4	1.79×10 ⁻¹⁷	1400**	Irradiation (FRJ-K13)
4	1.50×10 ⁻¹⁸	1193**	Irradiation (FRJ-K15)
4	7.82×10 ⁻¹⁸	1368**	Irradiation (FRJ-K15)
4	7.39×10 ⁻¹⁸	1396**	Irradiation (R2-K12)
4	1.68×10 ⁻¹⁷	1562**	Irradiation (R2-K12)
4	1.64×10 ⁻¹⁷	1484**	Irradiation (R2-K13)
4	3.33×10 ⁻¹⁸	1293**	Irradiation (R2-K13)
4	4.93×10 ⁻¹⁷	1441**	Irradiation (FRJ2-K11)
4	4.99×10 ⁻¹⁷	1437**	Irradiation (FRJ2-K11)

* Evaluated values from ion implantation data

** Average center fuel temperature.

In general, the dependence of diffusion coefficient D on temperature T can be approximately described by an Arrhenius relationship:

$$D = D_o \cdot \exp\left(-\frac{Q_{eV}}{k_B T}\right) = D_o \cdot \exp\left(-\frac{Q_J}{RT}\right) \quad (Q_J = Q_{eV} \cdot 2.3R/k_B)$$

where D is the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), D_o is the temperature independent pre-exponential constant ($\text{m}^2 \cdot \text{s}^{-1}$), Q is the activation energy for diffusion (eV or $\text{kJ} \cdot \text{mol}^{-1}$), k_B is the Boltzmann constant ($8.6173 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1} = 1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), R is the molar universal gas constant ($= 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and T is temperature (K). Using the above equations, all diffusion coefficients were plotted against the heating temperatures and average fuel center temperatures as shown in Fig. 3. The recommended IAEA diffusion coefficient line [4], which in turn is based on experimental work performed on fuel manufactured before 1978, is also plotted against the temperature in Fig. 3.

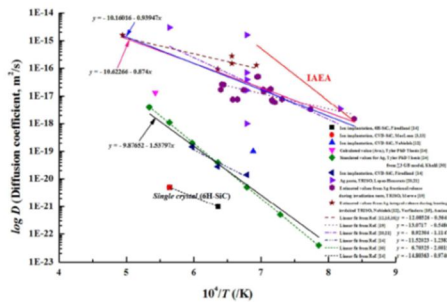


Fig. 3. Diffusion coefficients plotted against temperatures from Table 1.

3. Results and Discussion

To sum up the previous description, the pre-exponentials and activation energies are summarized in Table 2, which indicates that the diffusion coefficient (or the pre-exponentials) and the activation energy are very different, depending on experimental method. Here, it is found that the diffusion of Ag in SiC by ion implantation is too slow to account for the diffusion of Ag using Ag paste, the integral release of Ag from irradiated TRISO fuel and the fractional release of Ag from TRISO fuel during the irradiation tests. It was found that key atomic level parameters that control the diffusion (formation energy of Si vacancy and formation energy of Ag interstitials) are significantly lowered in $\Sigma 3$ grain boundaries of SiC, which supports the hypothesis that grain boundary diffusion is responsible for the fast release of Ag from TRISO particles [14,15,23].

Table 2. Estimated pre-exponential and activation energy.

Method	Pre-exponential ($\text{m}^2 \cdot \text{s}^{-1}$)	Activation energy ($\text{kJ} \cdot \text{mol}^{-1}$)
Ion implantation		
6H-SiC	1.572×10^{-15}	216.3
CVD-SiC	3.018×10^{-12}	274.8
Simulated in $\Sigma 3$ GB	1.980×10^{-07}	444.2
2 ion implant. groups*	1.329×10^{-10}	341.3
Ag paste	1.194×10^{-09}	247.4
Integral release	8.478×10^{-14}	121.8
Irradiation test	8.218×10^{-13}	125.3
3 groups**	6.916×10^{-10}	208.5

* Except ion implanted 6H-SiC

** Except ion implantation group.

In the case of ion implantation excluded 6H-SiC and the heating test, the activation energy for Ag diffusion was calculated as $341.3 \text{ kJ} \cdot \text{mol}^{-1}$. Also, the pre-exponential of Ag ions is estimated as $1.329 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. This result means that Ag ions do not transport by diffusion, either in the matrix or along the grain boundaries, in CVD SiC or single crystalline for the conditions studied in the ion implantation and heating tests. If Ag does not diffuse to SiC, then Ag release from coated particle fuel must be controlled by transport along another path. H.J. Maclean *et al.* [2] explained that the path might be more mechanical than microstructural although it is likely that the microstructure would play a critical role in allowing mechanical paths to develop.

From using Ag paste and an annealing test, the pre-exponential of Ag and the activation energy for Ag diffusion are estimated as $1.194 \times 10^{-09} \text{ m}^2 \cdot \text{s}^{-1}$ and $247.4 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. E. López-Honorato *et al.* [11] confirmed that the SiC microstructure has a big impact on the release of Ag, thus suggesting that subtle microstructural differences such as the characteristics of the grain boundaries (i.e., high-angle grain boundaries, strains, amorphous phases, defects) are playing a fundamental role in enhancing or retarding Ag diffusion. It was then proposed that that it was possible to greatly reduce Ag diffusion by carefully controlling the microstructure of SiC. However, the idea of Ag diffusing due to the presence of nanocracks [12], and the irradiation effect has not been supported. The importance of reducing the volume of high angle random grain boundaries in order to reduce the diffusion of fission products was also stressed. Very recent work suggests that a model for Ag migration through SiC coating in TRISO particles proposed by Xin Geng *et al.* [16], that is, a combined reaction and wetting process, could be responsible for the high Ag release rates observed in irradiated TRISO fuel.

The pre-exponential of Ag and the activation energy for Ag diffusion are estimated as $8.478 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ and $121.8 \text{ kJ} \cdot \text{mol}^{-1}$ from Ag integral release during a heating test, respectively. The exact mechanism of Ag release from TRISO fuel particles has largely been attributed to grain boundary diffusion leading to a requirement of small crystal size in the SiC coatings [6]. Previous work [5,6] has shown that Ag alone is not mobile in SiC even along the grain boundaries.

The pre-exponential of Ag and the activation energy for Ag diffusion are estimated as $8.218 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ and $125.3 \text{ kJ} \cdot \text{mol}^{-1}$ from a fractional Ag release during irradiation test, respectively. This activation is similar to that of the integral release. Although Ag can nucleate at the grain boundaries during cooling in a process governed by bulk diffusion, bulk diffusion has been already disregarded as the dominant factor in Ag diffusion [17]. Bulk diffusion would only give a diffusion rate of $< 10^{-21} \text{ m}^2/\text{s}$ (at 1300°C), which is at

least four-order of magnitude lower than those measured in coated particles [4,24].

4. Conclusions and recommendations

The mechanism of Ag transport in the SiC layer of TRISO fuel has been studied for the last four decades without arriving at a satisfactory explanation for Ag transport in intact coated particles. The causes of uprising Ag transport through SiC, the coating layer of TRISO fuel are complex depending on the temperature during operation or irradiation testing. Although Ag transport depends on the microstructure of SiC (such as grain boundary stoichiometry, SiC grain size and shape, the presence of free silicon, nano-cracks, etc.), neutron irradiation, irradiation temperature, Pd attack, thermal decomposition, transmutation products, layer thinning and coated particle shape, etc., Ag diffusion along the grain boundary of SiC plays a major role.

Considering that the current Ag diffusion coefficient is summarized and compared from previous studies, it might also be possible that, considering the irradiation effects of SiC, the Ag retention ability of a TRISO particle somehow improves during the TRISO particle-making process. Therefore, it is necessary that changes of Ag diffusion properties in SiC and microstructural changes of SiC with fluence and burnup of the SiC materials be studied in the ranges of the operation and/or irradiation conditions. In addition, the natural Ag contamination of the fuel matrix material has to be specified because natural Ag contamination can be the dominant source term for HTR cores under lower power and temperature conditions.

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