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Original Article

COMPARISON OF DIFFUSION COEFFICIENTS AND ACTIVATION ENERGIES FOR AG DIFFUSION IN SILICON CARBIDE

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ABSTRACT

The migration of silver (Ag) in silicon carbide (SiC) and ^{110m}Ag through SiC of irradiated tristructural isotropic (TRISO) fuel has been studied for the past three to four decades. However, there is no satisfactory explanation for the transport mechanism of Ag in SiC. In this work, the diffusion coefficients of Ag measured and/or estimated in previous studies were reviewed, and then pre-exponential factors and activation energies from the previous experiments were evaluated using Arrhenius equation. The activation energy is $247.4 \text{ kJ}\cdot\text{mol}^{-1}$ from Ag paste experiments between two SiC layers produced using fluidized-bed chemical vapor deposition (FBCVD), $125.3 \text{ kJ}\cdot\text{mol}^{-1}$ from integral release experiments (annealing of irradiated TRISO fuel), $121.8 \text{ kJ}\cdot\text{mol}^{-1}$ from fractional Ag release during irradiation of TRISO fuel in high flux reactor (HFR), and $274.8 \text{ kJ}\cdot\text{mol}^{-1}$ from Ag ion implantation experiments, respectively. The activation energy from ion implantation experiments is greater than that from Ag paste, fractional release and integral release, and the activation energy from Ag paste experiments is approximately two times greater than that from integral release experiments and fractional Ag release during the irradiation of TRISO fuel in HFR. The pre-exponential factors are also very different depending on the experimental methods and estimation. From a comparison of the pre-exponential factors and activation energies, it can be analogized that the diffusion mechanism of Ag using ion implantation experiment is different from other experiments, such as a Ag paste experiment, integral release experiments, and heating experiments after irradiating TRISO fuel in HFR. However, the results of this work do not support the long held assumption that Ag release from FBCVD-SiC, used for the coating layer in TRISO fuel, is dominated by grain boundary diffusion. In order to understand in detail the transport mechanism of Ag through the coating layer, FBCVD-SiC in TRISO fuel, a microstructural change caused by neutron irradiation during operation has to be fully considered.

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1. Introduction

Tri-structural isotropic (TRISO)-coated particle fuel, which will be used in the very-high-temperature gas-cooled reactor, has been studied extensively from the beginning of the 21st century around the world. TRISO-coated particles, embedded in a graphite matrix as fuel, are used originally in high-temperature gas-cooled reactors as these particles are intended to stay intact and effectively retain and contain FPs (fission products) during normal operation as well as postulated accidents [1].

Considered from the inside outward, an individual TRISO-coated fuel particle has a fuel kernel, a 300–500 μm diameter sphere of UO_2 , UC_2 , or a mixture of the two which has been termed uranium oxycarbide or UCO [2]. Kernels based on Pu or Th are also possible. The kernel is surrounded by successive layers of: (1) a low-density pyrolytic carbon (buffer; PyC), 90–100 μm thick; (2) high-density pyrolytic carbon (inner pyrolytic carbon; IPyC), 35–40 μm thick; (3) silicon carbide [SiC by a fluidized-bed chemical vapor deposition (FBCVD)] with ~ 35 μm ; and (4) high-density pyrolytic carbon (outer pyrolytic carbon; OPyC), 35–40 μm thick [3–6]. In general, $\sim 3,700$ – $16,000$ TRISO particles are then packed into a graphite matrix, which takes the form of a pebble or a rod.

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. The processes occurring in TRISO fuel after a high burn-up are schematically shown in Fig. 1 [7]. These include oxide fuel kernel migration (via the transport of carbon from the cool to hot side); intralayer crack formation, noble gas (Kr, Xe), Ba, silver (Ag), Sr, and 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 palladium (Pd) attack on SiC and noble gas, Pd, Ba, Sr, Cs, and Ag, transport via bulk diffusion, grain boundaries, and cracks through the coating layers [7,8].

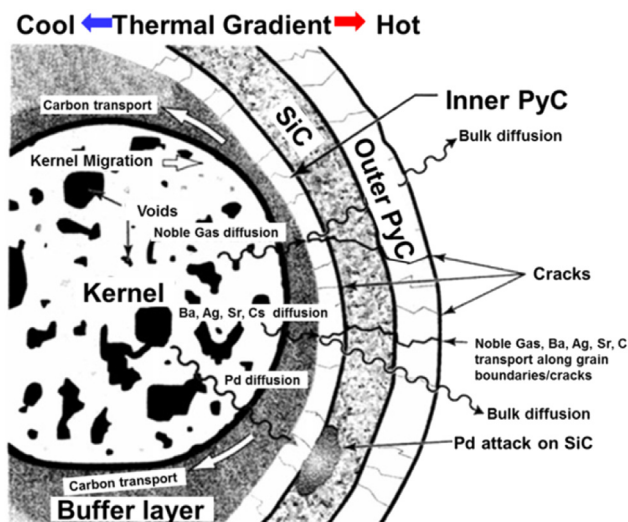


Fig. 1 – Processes in high burn-up TRISO fuel affecting the TRISO fuel life-time [7]. TRISO, tri-structural isotropic.

The different layers of the particle provide containment for FPs that can withstand the high operating temperatures ($>1,100^\circ\text{C}$) in a high-temperature gas-cooled reactor environment. During fuel irradiation testing or/and reactor operation, most FPs, such as cesium, iodine, xenon, and krypton, including metallic FPs, silver, palladium, etc., are retained by the combination of PyC and SiC layers. The kernel is the first barrier to FP release, as FPs must first diffuse to its outer surface. SiC is considered as the main diffusion barrier against the release of FPs. The SiC layer, that is, in a TRISO-coated particle has primarily two functions; (1) the pressure vessel providing structural support, and (2) the main barrier for the retention of metallic FPs. This makes the SiC layer the most important constituent of the fuel particle for the qualification of the fuel for use in Gen-IV very-high-temperature gas-cooled reactors. Only the cubic polymorph of SiC (β -SiC) is desired for nuclear applications due to its dimensional stability under irradiation [5].

Despite the numerous advantages of the TRISO design, release of some metallic fission products (e.g., Ag) with a relatively long half-life remains problematic. Evidence of the release of certain metallic FPs, especially Ag and Pd, through intact TRISO particles have been seen for about the past three to four decades around the world, as well as in the recent high flux reactor (HFR)-EU1bis and Advanced Gas Reactor (AGR-1) Fuel Development and Qualification program's first irradiation experiment [9–11]. For direct cycle high-temperature reactors utilizing low-enriched uranium fuel, the production, release, transport, and subsequent deposition of Ag fission and activation products in the main power system may pose maintenance problems due to excessive radiation levels to the operating personnel [12]. For higher operating temperature designs, $^{110\text{m}}\text{Ag}$ release from fuel and deposition on high-maintenance components may lead to more expensive maintenance concepts or limit the planned power and outlet temperature.

Many previous observations of Ag release during fuel testing and operation have raised concerns that the SiC layer may not be as effective for Ag. Because of the long half-life of about 253 days and a high γ -ray emitter of $^{110\text{m}}\text{Ag}$, Ag release from SiC coated fuel not only has important safety implications (increase of the total activity levels in the primary circuits of high-temperature gas reactors) but also significant economic and operational implications (maintenance more difficult and costly) because it limits the operational temperature and burn-up of the fuel. However, the specific mechanisms of transport have not been established and have been a subject of debate for many years [2,13–17]. A basic understanding of the atomic level mechanisms controlling fission product transport is essential for predicting the impact of irradiation, doping, and microstructural changes on fission product release [18].

In this paper, the diffusion coefficients of Ag measured and estimated in and/or through SiC are compared based on the following experimental methods: (1) measuring Ag diffusion through the use of ion-implanted cubic (3C) SiC and 6H-SiC samples and annealing; (2) measuring Ag diffusion through the use of 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 and/or 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 the past 40 years by many researchers [2]. Compared with transport through the SiC layer, transport through the UO_2 kernel and PyC layer is relatively quick in TRISO fuel. The diffusion coefficients of Ag in the UO_2 kernel and PyC layers are a few hundred times larger than SiC diffusion coefficient at $1,000^\circ\text{C}$ [2]. Both German and United States fuel development programs have suggested the same diffusion coefficients for UO_2 kernel and PyC layers [19].

Best estimate UO_2 : $D = 6.70 \times 10^{-9} \cdot e^{-165/RT} \text{m}^2 \cdot \text{s}^{-1}$

Best estimate PyC: $D = 5.30 \times 10^{-9} \cdot e^{-154/RT} \text{m}^2 \cdot \text{s}^{-1}$

Also, the transport of Ag in SiC has been studied using ion-implanted various SiC samples [3,12–15], diffusion couple [11,20–25], and fractional/integrated Ag release from irradiated TRISO fuel [16,26,27] to obtain the diffusion coefficients.

In this section, the diffusion coefficients of Ag are summarized and compared depending on the experimental methods (ion implantation and Ag paste) and 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 diffusion coefficients in SiC from experiments using 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 [3,12–15]. The diffusion coefficients are summarized in Table 1. The calculated diffusion coefficient at $1,569^\circ\text{C}$ [23] and the simulated values for Ag in $\Sigma 3$ GB (grain boundary) modeling [29] are also included in Table 1.

The diffusion coefficients observed experimentally among the samples ranged from $<10^{-19}$ to $<10^{-21} \text{m}^2 \cdot \text{s}^{-1}$, which is at least a two-order of magnitude difference, and estimated analytically among the samples ranged from $<10^{-17}$ to $<10^{-23} \text{m}^2 \cdot \text{s}^{-1}$, which is at least a six-order of magnitude difference. Friedland et al. [14] has found using α -particle channeling spectroscopy, electron microscopy, and vacuum annealing at temperatures up to $1,600^\circ\text{C}$ that Ag diffusion was observed in the polycrystalline CVD–SiC samples, but that no diffusion of Ag was observed in the 6H–SiC (single-crystal) experiments [15]. Fairly strong silver diffusion was observed after an initial 10 hour annealing period at $1,300^\circ\text{C}$ in both polycrystalline and single crystalline SiC, which is mainly due to implant induced radiation damage. After further annealing at this temperature no additional diffusion took place in the 6H–SiC samples, while it was considerably reduced in the

Table 1 – Diffusion coefficients of Ag from ion implantation.

Refs	$D(\text{m}^2 \cdot \text{s}^{-1})$	T (K)	t (h)	Remarks
[14,15]	$<10^{-21}$	1,573	>10	6H–SiC
[14,15]	$<5 \times 10^{-21}$ ($D_0 = 4.30 \times 10^{-12}$)	1,773	>10	6H–SiC
[3,13]	$<5 \times 10^{-21}$	1,773	210,480	CVD–SiC
[14,15]	1.41×10^{-20}	1,473	10	CVD–SiC
[14,15]	$2.8 \pm 0.2 \times 10^{-20}$	1,573	>10	CVD–SiC
[14,15]	1.46×10^{-19}	1,673	10	CVD–SiC
[12]	$<10^{-19}$	1,453	0.5	CVD–SiC
[23]	1.31×10^{-17a}	1,842	–	Calculation
[29]	4.00×10^{-18a}	1,873	–	Simulation in $\Sigma 3$ GB
[29]	1.10×10^{-18a}	1,773	–	Simulation in $\Sigma 3$ GB
[29]	2.00×10^{-19a}	1,673	–	Simulation in $\Sigma 3$ GB
[29]	3.90×10^{-20a}	1,573	–	Simulation in $\Sigma 3$ GB
[29]	5.00×10^{-21a}	1,473	–	Simulation in $\Sigma 3$ GB
[29]	5.00×10^{-22a}	1,373	–	Simulation in $\Sigma 3$ GB
[29]	3.90×10^{-23a}	1,273	–	Simulation in $\Sigma 3$ GB

^a Evaluated values from ion implantation data.

CVD–SiC. The latter was obviously due to grain boundary diffusion and could be described by the Fick diffusion equation. Annealing of 6H–SiC above $1,400^\circ\text{C}$ shifted the silver profile without any broadening towards the surface, where most of the silver was released at $1,600^\circ\text{C}$. The fact that significantly higher effective diffusion coefficients of Ag in the CVD–SiC 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 [14,15]. Nabelek et al. [12] attributed no change in the Ag concentration profile after 0.5 hours at $1,180^\circ\text{C}$ 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. The calculated coefficient of $1.31 \times 10^{-17} \text{m}^2/\text{s}$ aligns well with the other reported experimental values for Ag diffusion in surrogate CVD–SiC [14,29] and simulated values for Ag in $\Sigma 3$ GBs [29]. The magnitude of the calculated diffusion coefficients implies the GB diffusion mechanism is not representative of the system for release from TRISO fuel. Khalil et al. [29] showed that Ag diffusion along $\Sigma 3$ GBs of SiC is significantly faster than diffusion in the bulk.

2.2. Ag diffusion coefficients in SiC from experiments using diffusion couple (silver paste)

The diffusion of Ag in SiC (SiC–LT deposited at $1,300^\circ\text{C}$ with 9.1 vol% methyltrichlorosilane (MTS) concentration and SiC–PR deposited at $1,300^\circ\text{C}$ 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 FBVD reactor were performed using Ag paste and a heating test [20,21,28]. Then, Ag was trapped between two layers of SiC. López-Honorato et al. [21] reported Ag diffusion along SiC grain boundaries had been observed. This finding is contrasted by the previous results [12–15] that was unable to find any significant migration of Ag in Ag ion-implanted SiC annealed at elevated

temperatures. An estimate of the diffusion coefficients were calculated with the following relation [20,21]:

$$D = x^2 \cdot t^{-1}$$

where D is the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), x is the diffusion distance (m), and t is the time under heat treatment (s). The calculated diffusion coefficients are given in Table 2. Detailed information on this experiment can be found in [28].

The diffusion coefficients observed among the samples spanned from $\geq 1.6 \times 10^{-15} \text{m}^2 \cdot \text{s}^{-1}$ to $< 1 \times 10^{-18} \text{m}^2 \cdot \text{s}^{-1}$, 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 [19,27].

2.3. Ag diffusion coefficients estimated from 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 [12,16,17]. 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 (UO_2 , UC_2 , ThO_2 , mixtures, etc.) and for reference quality fuel [UO_2 , (U, Th) O_2] and published in [16]:

$$\text{All fuel types: } D = 4.5 \times 10^{-9} \cdot e^{-218/RT} \text{m}^2 \text{s}^{-1}$$

$$\text{Reference fuel only: } D = 3.6 \times 10^{-9} \cdot e^{-215/RT} \text{m}^2 \text{s}^{-1}$$

Shrader et al. [24] summarized the pre-exponential factors and activation energies for the reported diffusion coefficient of Ag in SiC, in the form of $D = D_0 \cdot \exp(-Q/k_B \cdot T)$, published from previous experiments [12,16,17]. These values are shown in Table 3. The pre-exponential estimated from the release rates measured during isothermal heating ranged from $3.60 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$ to $6.80 \times 10^{-11} \text{m}^2 \cdot \text{s}^{-1}$ (diffusion coefficient; from $1.50 \times 10^{-15} \text{m}^2 \cdot \text{s}^{-1}$ to $2.78 \times 10^{-17} \text{m}^2 \cdot \text{s}^{-1}$), which is at least a two-order of magnitude difference. The activation energy is in the range of 1.83 eV ($176.6 \text{kJ} \cdot \text{mol}^{-1}$) to 2.26 eV ($218.1 \text{kJ} \cdot \text{mol}^{-1}$).

Table 2 – Calculated diffusion coefficient of Ag.

Refs	D ($\text{m}^2 \cdot \text{s}^{-1}$)	T (K)	t (h)	Remarks
[20]	3.46×10^{-18}	1,223	240	Silver paste
[20]	1.55×10^{-17}	1,423	240	Silver paste
[20]	2.99×10^{-15}	1,773	240	Silver paste
[21]	$< 1 \times 10^{-18}$	1,473	240	Silver paste
[21]	$\geq 1.6 \times 10^{-15}$	1,473	240	Silver paste
[21]	7.0×10^{-17}	1,473	240	Silver paste
[21]	3.9×10^{-17}	1,473	240	Silver paste
[21]	1.6×10^{-17}	1,473	240	Silver paste
[21]	$< 1 \times 10^{-18}$	1,473	240	Silver paste

Table 3 – Reported diffusion coefficient of Ag in SiC, in the form of $D = D_0 \cdot \exp(-Q/k_B \cdot T)$. The temperature range shown gives the range of temperature values used to fit the Arrhenius expression for D [22].

Refs	D_0 ($\text{m}^2 \cdot \text{s}^{-1}$) ^a	Q (eV)	T (K)	Measurement
[16]	5.00×10^{-10}	1.89	1,273–1,773	Integral release
[16]	3.50×10^{-10}	2.21	1,473–2,573	Integral release
[16]	3.60×10^{-9}	2.23	1,273–1,773	Integral release
[16]	6.80×10^{-11}	1.83	1,473–1,673	Integral release
[17]	4.50×10^{-9}	2.26	1,273–1,773	Integral release
[12]	6.76×10^{-9}	2.21	1,073–1,773	Integral release

^a Diffusion coefficients can be calculated taking the middle of temperature from the range of temperature value.

2.4. Ag diffusion coefficients evaluated from fractional release of Ag during irradiation tests of TRISO fuels

van der Merwe [19,27] 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 [2,27]. The estimated diffusion coefficients are shown in Table 4 [19,27]. 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

Table 4 – Summary of estimated diffusion coefficient [19,27].

Fuel sphere	Best estimate (average)	
	Center fuel temp. ($^{\circ}\text{C}$)	Diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)
<i>HFR-K3; Christ data</i>		
1	1,247	7.63×10^{-18}
4	1,278	2.55×10^{-17}
<i>HFR-K3; Venter data</i>		
1	1,231	7.75×10^{-18}
2	1,121	6.58×10^{-18}
3	1,115	5.96×10^{-18}
4	1,285	2.63×10^{-17}
<i>FRJ2-K13</i>		
1	1,131	1.67×10^{-17}
2	1,149	1.71×10^{-17}
3	1,148	1.43×10^{-17}
4	1,127	1.79×10^{-17}
<i>FRJ2-K15</i>		
1	920	7.63×10^{-18}
2	1,095	2.55×10^{-17}
<i>FRJ2-K12</i>		
1	1,123	1.50×10^{-18}
2	1,289	7.82×10^{-18}
<i>R2-K13</i>		
1	1,211	1.64×10^{-17}
4	1,020	3.33×10^{-18}
<i>FRJ2-K11</i>		
1	1,168	4.93×10^{-17}
2	1,164	4.99×10^{-17}

program spanned from $1.43 \times 10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$ to $7.82 \times 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$, which is at least one-order of magnitude difference.

The following best estimate and design limit diffusion coefficients were derived by fitting all results to a straight line, as shown in Fig. 2 [19,27]:

$$\text{Best estimate : } D = 1.14 \times 10^{-13} \cdot e^{-109/RT} \text{ m}^2 \cdot \text{s}^{-1}$$

$$\text{Design limit : } D = 2.28 \times 10^{-13} \cdot e^{-109/RT} \text{ m}^2 \cdot \text{s}^{-1}$$

2.5. Ag diffusion coefficient from experiments and estimations

The diffusion coefficients assessed among the ion-implanted samples including single crystal (6H-SiC) ranged from $<10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$ to $<10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$, which is at least six-order of magnitude difference. The diffusion coefficients observed among the samples used Ag paste differed from $\geq 1.6 \times 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$ to $<1 \times 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$, which is at least a three-order of magnitude difference. The diffusion coefficient estimated from the Ag integral release fraction of the samples spanned from $1.50 \times 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$ to $2.78 \times 10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$, 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 ranged from $1.43 \times 10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$ to $7.82 \times 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$, which was at least one-order of magnitude difference.

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

$$D = D_0 \exp\left(-\frac{Q_{eV}}{k_B T}\right) = D_0 \exp\left(-\frac{Q_J}{RT}\right)$$

$$\log D = \log D_0 - \frac{Q_J}{2.3 RT} \quad (\text{or } \ln D = \ln D_0 - \frac{Q_J}{RT})$$

$$(Q_J = Q_{eV} \cdot 2.3R/k_B)$$

where, D is the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$), D_0 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 ($8.6173 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$)

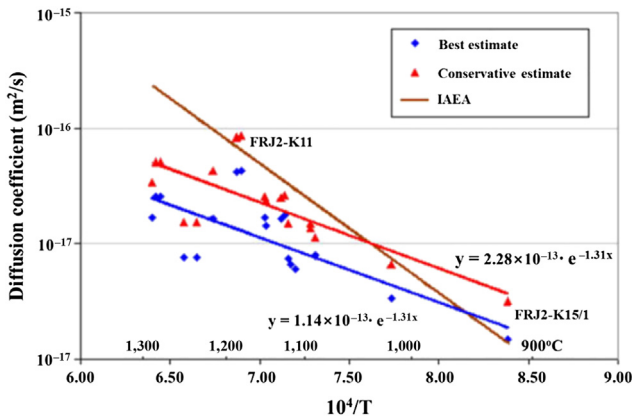


Fig. 2 – Diffusion coefficients from the detailed evaluation [19].

$= 1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$, 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 International Atomic Energy Agency (IAEA) diffusion coefficient line [19,27], which in turn is based on experimental work performed on fuel manufactured before 1978, is also plotted against the temperature in Fig. 3.

3. Results and discussion

Using the Arrhenius relationship, it is therefore convenient to analyze the known and calculated diffusion coefficients in terms of activation energy Q . As given in Table 5, the diffusion coefficients are derived by fitting nine groups to a straight line in Fig. 3. All calculated diffusion coefficients for the experiments and estimations are below the recommended IAEA diffusion coefficient line [19,27] except for a few diffusion coefficients, as shown in Fig. 3. It appears that the currently recommended diffusion coefficient is overly conservative.

It indicates that the diffusion coefficient (or the pre-exponentials) and the activation energy are very different, depending on the 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.

3.1. Ion implantation

From ion-implanted single crystal (6H-SiC), the pre-exponential of Ag ions and the activation energy for Ag diffusion are estimated as $1.572 \times 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$ and $216.3 \text{ kJ} \cdot \text{mol}^{-1}$ from Fig. 3, respectively. In the case of ion-implanted CVD-SiC experiments, the pre-exponential of Ag ions and the activation energy for Ag diffusion are estimated as $3.018 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ and $274.8 \text{ kJ} \cdot \text{mol}^{-1}$. For example, comparing this pre-exponential factor with $D_0 = 4.30 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ for 6H-SiC in Table 1, it is a three-order of magnitude difference for ion-implanted single crystal, and almost same of magnitude for ion-implanted CVD-SiC. It can be derived that the diffusion coefficient of Ag ions is also remarkably different from those in Table 1.

In the case of ion implantation excluding 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 $1.329 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. However, from the simulated in $\Sigma 3$ GB, the pre-exponential of Ag ions and the activation energy for Ag diffusion are estimated as $1.980 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ and $444.2 \text{ kJ} \cdot \text{mol}^{-1}$.

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. Maclean et al. [3] explained that the path might be more mechanical than

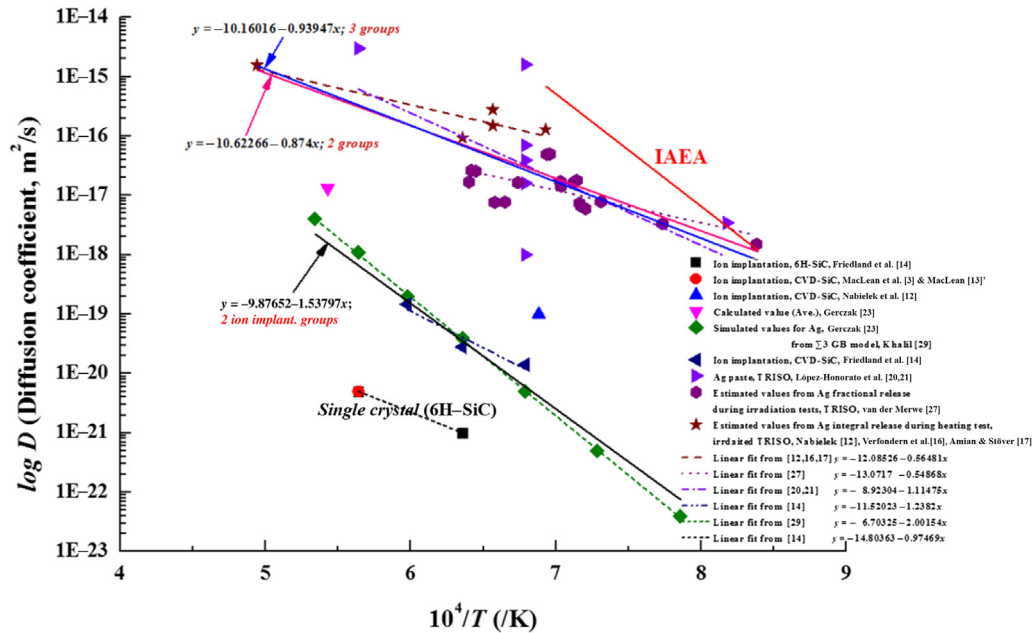


Fig. 3 – Diffusion coefficients plotted against temperatures.

microstructural although it is likely that the microstructure would play a critical role in allowing mechanical paths to develop. It was also 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 $\Sigma 3$ GBs of SiC, which supports the hypothesis that grain boundary diffusion is responsible for the fast release of Ag from TRISO particles [18,23,24].

3.2. Ag paste

The pre-exponential of Ag and the activation energy for Ag diffusion using Ag paste are estimated as $1.194 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ and $247.4 \text{ kJ} \cdot \text{mol}^{-1}$ from Fig. 3, respectively. Comparing them with the estimated data from the irradiated TRISO, the pre-exponential is at least four- to five-order of magnitude

difference, and the activation energy is approximately twice greater. This is shown that the transport of Ag in SiC depends on neutron irradiation as well as microstructure of SiC, which can be changed during FBCVD-SiC process and irradiation test.

López-Honorato et al. [20] 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 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 nano-cracks [21], 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. Interestingly, Tan et al. [30] has shown that the SiC coatings of TRISO particles, deposited at $1,400^\circ\text{C}$, have a high concentration of high-angle grain boundaries, and that the strains detected in the microstructure increase with the coating thickness. Because it has been observed that a higher concentration of high-angle/high-energy grain boundaries can greatly enhance the diffusivity [31], these types of characteristics can be very important. Very recent work suggests that a model for Ag migration through SiC coating in TRISO particles proposed by Geng et al. [25], that is, a combined reaction and wetting process, could be responsible for the high Ag release rates observed in irradiated TRISO fuel.

3.3. Integral release

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

Table 5 – 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(single crystal)	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 ^a	1.329×10^{-10}	341.3
Ag paste	1.194×10^{-09}	247.4
Integral release	8.218×10^{-13}	125.3
Irradiation test	8.478×10^{-14}	121.8
2 groups ^b	2.384×10^{-11}	193.9
3 groups ^c	6.916×10^{-10}	208.5

^a Except ion implanted 6H-SiC.

^b Integral release and irradiation test.

^c Ag paste, integral release, and irradiation test.

125.3 kJ·mol⁻¹ from Fig. 3, respectively. Comparing this pre-exponential factor with $D_0 = 6.80 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ to $6.76 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ in Table 3, it differs by at least two- to three-orders of magnitude difference, and this activation energy with an activation energy of 176.6 kJ·mol⁻¹ to 218.1 kJ·mol⁻¹ calculated from Table 3, is about 0.6-times the magnitude. The activation energy from the correlation of a straight line, $y = 1.14 \times 10^{-13} \cdot e^{-1.31x}$ and $2.28 \times 10^{-13} \cdot e^{-1.31x}$, as shown in Fig. 2 is calculated as 126.4 kJ·mol⁻¹ in this study. However, the activation energy in references [19,27] is estimated as 109 kJ·mol⁻¹. This is a difference of about 16 kJ·mol⁻¹. Also, the pre-exponential factors are almost the same values.

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 [12]. Previous work [3,12] has shown that Ag alone is not mobile in SiC even along the grain boundaries. Amian and Stöver [17] have concluded that the probable pathway for Ag migration in SiC coatings is the grain boundary, when comparing with data published for the diffusion of some elements in SiC single crystals and pyrolytic coatings. The scattering of data can be explained and understood to be due to the individual defect structure of the material (SiC) and the presence of Pd or similar fission products induced by neutron irradiation.

3.4. Irradiation test

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 kJ·mol⁻¹ from Fig. 3, respectively. This activation energy is the same value as the activation energy of 126.4 kJ·mol⁻¹ calculated from the correlation of a straight line in Fig. 2 [19,27]. However, this estimated activation energy differs from 109 kJ·mol⁻¹ in [19,27]. The difference of activation energy between them is about 13 kJ·mol⁻¹. Also, the pre-exponential between $8.478 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ in this study and $1.14 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ ($2.28 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$) in Fig. 2 differs at least one-order of magnitude. Also, this activation is similar to that of the integral release (125.3 kJ·mol⁻¹), the pre-exponential between integral release and irradiation test differs at least one-order of magnitude. 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 [16]. Bulk diffusion would only give a diffusion rate of $<10^{-21} \text{ m}^2/\text{s}$ (at 1,300°C), which is at least four-order of magnitude lower than those measured in coated particles [19,27]. Furthermore, theoretical work has suggested that bulk diffusion would only dominate the diffusion process at the large grain sizes ($>10 \mu\text{m}$) and at much higher temperatures ($>1,600^\circ\text{C}$) [32]. For these reasons, it is likely that the Ag detected at the grain boundaries is the result of a diffusion process partially controlled by grain-boundary diffusion and even triple junctions [10,32].

4. Conclusion and recommendations

In general, the activation energy for diffusion depends on the diffusion mechanism. At any temperature the magnitudes of

grain boundary diffusion ($D_{g,b}$) and surface diffusion (D_s) relative to the diffusivity through defect-free lattice diffusion (D_l) or volume diffusion (D_v) are such that diffusion coefficient is D_l (or D_v) $< D_{g,b}$ $< D_s$ or activation energy is Q_l (or Q_v) $> Q_{g,b}$ $> Q_s$.

Grain boundary diffusion is orders of magnitude faster than lattice (or volume) diffusion. Volume diffusion only becomes significant at high temperature, and is revealed within a single crystal (or grain).

As shown in Fig. 3 and Table 5, Ag transport by ion implantation can be different with the grain boundary and surface (or vapor) diffusion mechanisms. The activation energies for Ag diffusion and the pre-exponentials (or diffusion coefficients) from both integral release and irradiation testing (neutron irradiation) resemble each other. However, these activation energies are about half of that from using Ag paste. And, the magnitude of difference of the activation energy among Ag paste, integral release, irradiation testing, two groups (integral release, irradiation testing), and three groups (Ag paste, integral release, irradiation testing) Ag paste, integral release, irradiation testing) in Table 5 can be explained by the microstructural change of SiC and the presence of fission products (e.g., Pd) in SiC induced by neutron irradiation. In the case of experiments using Ag paste, it is impossible to directly simulate the effect of Pd compared with the others. Presently, many previous works of Ag migration in SiC have proposed that Ag transport through SiC does not proceed via bulk volume diffusion, grain boundary diffusion that may be significantly enhanced either by neutron bombardment or by the presence of fission products such as Pd [9,33–37].

It was observed that a microstructural evolution of SiC (by CVD) is strongly dependent on temperature [5,38]. The effect of cracks in the SiC layer, which can provide a fast gaseous-diffusion path for Ag, on the Ag release has been investigated [39]. The cracks can be considered to instantaneously transport any incident Ag atoms from the inner to outer positions of the crack. It is expected that the presence of reflective PyC/SiC interfaces and radiation-induced trapping features decreases the amount of Ag release, while the presence of cracks and grain boundary networks in the SiC layer can accelerate Ag release. Further work [11] has led to a suggestion that Ag is not transported through SiC by diffusion but by a vapor transport mechanism, and an alternative vapor transport model suggests that Ag leaks through nano-sized cracks in the SiC layer.

The mechanism of Ag transport in the SiC layer of TRISO fuel has been studied for the past four decades without arriving at a satisfactory explanation for Ag transport in intact coated particles. The magnitude difference of pre-exponential factors (or diffusion coefficients) can then be explained as the microstructural changes (grain size, grain shape and defect nucleation, swelling, etc.) of the SiC layer (by FBCVD) of TRISO fuel during irradiation or operation conditions. And, 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.

Therefore, 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, especially FBCVD-SiC coating process, because the microstructure of SiC can be changed by the condition of FBCVD-SiC coating process. Also, it is necessary that changes of Ag diffusion properties including changes by chemical reaction with fission product (Palladium) 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.

Conflicts of interest

The authors declare no conflicts of interest.

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