The measurement of silver diffusivity in zirconium carbide to study the release behavior of ^{110m}Ag in the ZrC TRISO-coated nuclear fuel particle

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Abstract

The tri-structural isotropic (TRISO) coated particle fuel has been developed and used for high temperature gas-cooled reactors (HTGRs). It provides a unique robustness of the first barrier for the fission products. The TRISO fuel particle has typically consisted of a UO_2 or UCO kernel, surrounded by successive layers of porous carbon, dense inner pyrocarbon, silicon carbide, and dense outer pyrocarbon. During operation, however, the SiC layer has been known to release radioactive silver ^{110m}Ag which makes maintenance more difficult and thus costly. Zirconium carbide has been considered as a promising alternative to the SiC fission product barrier. ZrC exhibits high temperature stability and possibly possesses superior Pd resistance, while the retention properties especially for silver have not been adequately studied.

To help elucidate the diffusive behavior of silver in the ZrC coating of the TRISO-coated particle, a new diffusion experimental technique, called the *encapsulating source method*, has been developed by constructing a constant source diffusion couple between ZrC and Ag gas originated from Zr-Ag solid solution. ~~SEM, WDS, EBSD~~ Scanning electron microscopy (SEM), wavelength-dispersive X-ray spectroscopy (WDS), electron backscatter diffraction (EBSD) and optical methods were used to analyze the diffusion couple annealed at 1500 °C. The resultant diffusion coefficient of Ag in single-crystalline $\text{ZrC}_{0.84}$ at 1500 °C was experimentally determined to be about $2.8 (\pm 1.2) \times 10^{-17} \text{ m}^2/\text{s}$.

Keywords: fission product; silver; zirconium carbide; TRISO particle; VHTR; HTGR

1. Introduction

1.1. TRISO-coated particle fuel

The very high temperature reactor (VHTR), or high-temperature gas-cooled reactor (HTGR), is one of the six classes of reactor designs in the Generation IV initiative [1]. The VHTR reference concept is a helium-cooled, graphite moderated, thermal neutron spectrum reactor with target coolant outlet temperatures of 1000 °C. Such high temperatures offer higher efficiency electricity generation and new opportunities for a broad spectrum of process heat applications, including hydrogen production by thermo-chemical water splitting or high-temperature electrolysis. [2-3].

The fuel of choice for the VHTR is the tri-structural isotropic (TRISO) coated particle fuel [4-10]. The VHTR aims to achieve enhanced levels of safety, which is in part based on the capability of coated fuel particles to confine the radiological fission products even at high temperatures. The TRISO-coated particle is designed to act as a miniature pressure vessel; it withstands high temperatures and prevents significant release of fission products from the reactor core under normal and postulated accident conditions [9-13]. In the current reference TRISO-coated particle design, the kernel (microsphere) is typically formed from enriched uranium dioxide (UO_2) or uranium oxycarbide (UCO) and is surrounded by successive layers of porous pyrocarbon buffer, dense inner pyrolytic carbon (IPyC), silicon carbide (SiC), and dense outer pyrolytic carbon (OPyC), as schematically illustrated in Fig. 1. Note that this figure is drawn to scale based on the design used in the AGR-1 experiment at the Idaho National Laboratory (INL), USA [14]. A lot of TRISO-coated particles are packed together into spherical or cylindrical fuel elements to be used in reactor cores.

Fig. 1. Schematic cutaway drawing of a TRISO fuel particle showing the fuel kernel and coating layers. Note that the numbers in parentheses refer to the thicknesses of the coatings and the diameter of the fuel kernel.

The SiC layer in the TRISO particles, in particular, provides structural support to accommodate internal gas pressure and serves as the primary barrier to the release of fission products. It retains gases and most metallic fission products below 1600 °C. It has long been known, however, that silver exhibits relatively high release from intact SiC-coated TRISO fuel particles if they are maintained at sufficiently high temperatures for sufficiently long times [15-23]. The release of radioactive ^{110m}Ag in particular is of considerable concern since this strong γ -ray emitter (half-life of 249.8 days) can plate out on the various helium-wetted surfaces in the primary circuit of direct-cycle HTGRs and thus significantly complicate plant operations and maintenance [24-25]. Furthermore, SiC begins to gradually lose mechanical integrity especially above 1700 °C, by transformation of β -SiC to α -SiC and later thermal decomposition [26-28]. It is also widely noted that the SiC layer is subject to attack from palladium and rare earth elements [21, 29-34], although some studies led to contradictory results, showing significant Pd corrosion of SiC has not been identified [16,35].

1.2. ZrC and Ag retention

Zirconium carbide has been considered as a promising alternative to the SiC fission product barrier of the TRISO-coated fuel particles since the 1970s, since the peak fuel temperature permissible under operating and accident conditions would increase while still retaining a very high degree of inherent-reactor-passive safety [7,8,36-42]. It has been demonstrated that the ZrC-coated TRISO fuel possesses much greater high temperature stability than that coated with SiC [38]. In one Japanese side-by-side test of TRISO particles of both SiC (36 μm thick) and ZrC (25 μm thick), irradiated to a burn up of 4.5% FIMA for about 100 effective full-power days at temperatures ranging from 1400 to 1650 °C, there was complete coating failure of only one of 2400 particles with ZrC, as opposed to 20 failures in the same number of particles with SiC [40]. In other Japanese studies [38,43], irradiated particles with ZrC survived at much higher rates when subsequently exposed to high-temperature heating tests. When heated to 2400 °C at 1 °C/min and held for more than 1.6 hours, there was only a 1% failure of particles with ZrC, compared to 90% failure in particles with SiC by the time the temperature reached 2400 °C. The ZrC coating layer has also been known to exhibit immunity to

Pd attack, although in a recent study Pd has not been found concentrated at the inner surface of ZrC layers, indicating possible migration through the coating rather than being retained [40,44].

With respect to Ag retention in the ZrC TRISO-coated particle, there are only a few studies that addressed this issue [44,45]. In order to assess the extent of silver retention in the ZrC layer under various operating conditions, it would be a good starting point to measure reliable silver diffusion coefficients in un-irradiated ZrC, although such a diffusion process is expected to be complicated further in actual service conditions by effects such as irradiation-enhanced trapping and adsorption.

Very few diffusion data on the transport of silver in zirconium carbide have been reported thus far, while there is a relatively large amount of research on that in silicon carbide (nevertheless, the Ag migration mechanism in the SiC coating layer has still not been well understood until now) [15,17,45-5961]. This paucity of studies is not due to lack of interest but rather to the difficulty of carrying out experiments as discussed in the next section.

To the best of authors' knowledge, there is only one single study that explored Ag diffusivity in ZrC. In the former USSR, Chernikov et al [45] investigated the diffusion behavior of Ag in ZrC (C/Zr unknown) coating layer over a wide range of temperatures (1730 to 2230 °C). ^{110m}Ag solution was deposited on the surface of what they called “simulators”, which were unirradiated cylindrical ZrC pellets. After diffusion annealing, the distribution of the nuclide in the ZrC coating layer was determined by removing the ZrC stepwise until 10 μm thickness. Two linear regions with two different slopes ~~based on the nuclide concentration and distribution of the diffusant (^{110m}Ag)~~ were obtained in a diagram of the ^{110m}Ag activity versus the penetration depth squared. Chernikov et al considered that the first region was due to the migration of silver ~~along the short circuit paths in the grain volumes~~ and the second region was due to that ~~in the grain volumes along the short circuit paths~~. However, they did not explain why the slope could vary depending on the diffusion depth ~~of the diffusing species~~.

Recall that it is well known that in polycrystalline metals the slope in an Arrhenius diffusion plot may vary with temperature (not diffusion depth) due to the change of the dominant diffusion mode, whether lattice or grain boundary diffusion. However the slope change with diffusion depth in likely homogeneous materials is not well known. We speculate that such a peculiar diffusion behavior is somehow associated with some of the experimental difficulties

outlined in the next section. Therefore it seems worthwhile to revisit Ag diffusion in ZrC from a different experimental perspective.

1.3. Experimental difficulties measuring Ag diffusivity in ZrC

~~A number of different experimental techniques are used to measure diffusion coefficients. The selection of the most appropriate method depends primarily on the nature of the material system under investigation at the given temperatures.~~ For Ag diffusion experiments in ZrC at high temperatures, such as 1500 °C, it is difficult to find an effective laboratory technique. Let us consider thin film method and the ion-implantation method as examples of experimental difficulties. Thin film method is used now almost exclusively for the measurement of diffusion coefficients, assuming that the entire deposited layer starts to dissolve instantaneously and diffuse into the matrix upon the initiation of diffusion annealing. To employ this type of method, a very thin section is deposited on the substrate applying various techniques. This thin layer contains atoms which are distinguishable from those in the substrate (or matrix). However, it is sometimes difficult to interpret diffusion profiles acquired using the thin film method mainly due to the following reasons [6062]. First, deposited material tends to evaporate during the high temperature diffusion anneal. Secondly, deposited material lingers on the surface of the matrix even significantly after initiation of the diffusion anneal caused by very low solubility and/or diffusivity. Third, the coating layer and/or the matrix are subject to oxidation. Lastly, some thin films have poor wettability on certain substrates. In the Zr-C-Ag system, in particular, overcoming all these four obstacles is extremely challenging. It should be pointed out that the melting point of Ag (962 °C) is quite low compared to the diffusion anneal temperature of, for instance, 1500 °C, the Ag solubility limit in ZrC is also very low at 1500 °C, and ZrC is also very reactive with oxygen. The deposited Ag thin film melts and agglomerates due to the low melting point and poor wettability on ZrC above the melting point of Ag.

In the case of an ion-implantation diffusion experiment with the Zr-C-Ag system, the very low solubility of Ag in ZrC is expected to complicate interpretation of the diffusion profiles due to phase separation rather than broadening of the dissolved solute concentration profile along the depth direction upon diffusion annealing.

To overcome experimental difficulties determining diffusion coefficients with traditional methods in the given material system, we developed a new experimental method, named the *encapsulating source method*. The salient points of this new approach are a completely encapsulated diffusion matrix and the existence of a gas reservoir of the diffusing substance. This experimental technique is a type of a constant-source diffusion experiment. Although this concept is not new, the idea that a gaseous diffusion source originates from an encapsulating material has never been adopted in any published work. Full details of this experimental technique are discussed in Section [3.2.2.3](#).

2. Experimental

2.1. Material's preparation and diffusion annealing

A [high purity](#) zirconium carbide disk 2 mm thick and 3 mm in diameter was used to measure the diffusion coefficient of silver in zirconium carbide. It was custom manufactured by Applied Physics Technologies, Inc., Oregon, USA utilizing a float-zone refining technique.

~~Starting materials were sintered ZrC. The molten zone was suspended via surface tension between the starting sintered stock and the seed crystal. The seed was initially another length of sintered stock to attempt to keep the samples polycrystalline for purposes other than the present study. Therefore the resultant rods consist of a limited number of columnar grains; typically only a few grains observed on the cross section normal to the zone refining direction. Elemental analysis of this zirconium carbide was performed by ATI Wah Chang Laboratory, Oregon, USA using a LECO Instruments combustion IR. This analysis determined the total carbon present in the sample and showed the C/Zr molar ratio of the ZrC used in the present study was 0.84 (denoted as $\text{ZrC}_{0.84}$). The standard deviation of the stoichiometry determined was 0.0062, and the value presented here is rounded to the 2nd decimal point.~~

~~The chemical analysis of $\text{ZrC}_{0.945}$ from the same production line as $\text{ZrC}_{0.84}$ used in this work, of some selected 75 impurity elements between atomic number of 3 (lithium) and 92 (uranium), was conducted using inductively coupled plasma mass spectrometry (ICP MS). The measurement results showed that the total impurity was below about 810 ppm weight (0.0810 wt.%). Ag concentration, in particular, did not exceed 1 ppm weight, and Hf was 30 ppm weight.~~

A Zr-Ag solid solution was alloyed from pure hafnium-free Zr (99.9 wt.%, Hf: < 63 ppm weight) and silver (99.9 wt.%) using an arc melter. Arc melting was carried out in an argon back-filled atmosphere at a pressure of about 50 kPa (~~about 0.5 atm.~~). The alloy was melted four times with the small ingot being flipped over between successive operations for better homogenization. The resultant alloy weighed about 10 grams and measured to be about Zr-8.1 wt.% Ag of average composition according to a post-fabrication wavelength dispersive X-ray spectroscopy (WDS) measurement. ~~This quantitative approximation was made based on averaging individual point measurements after the matrix corrections for the individual raw X-ray counts since the sample was microscopically inhomogeneous.~~

Fig. 2. Schematic illustration of experimental setup for fabricating a diffusion couple to employ the *encapsulating source method*: (a) before encapsulation, (b) after encapsulation using arc-melting.

Fig. 2 shows the schematic experimental setup used to fabricate a diffusion couple for utilization of the *encapsulating source method*. First, the Zr-8.1 wt.% Ag alloy was cut into smaller pieces. Two of them were used to fabricate a diffusion couple, one of which was drilled with a hole about 3 mm in diameter to accommodate the ZrC disk (the lower Zr-Ag alloy piece in Fig. 2(a)). The other piece was also drilled with a smaller venting hole to remove residual oxygen during purging with Ar (the upper Zr-Ag alloy piece in Fig. 2(a)).

Once the ZrC disk was placed inside the Zr-Ag alloy as in Fig. 2(a), the disk was encapsulated by the surrounding Zr-Ag alloy using a smaller capacity arc melter different from

the one mentioned previously. To do this, two of the Zr-Ag alloy pieces and the ZrC disk were loaded into the melter as in Fig. 2(a) and the melting chamber was evacuated, purged with Argon, and evacuated again. This procedure was repeated five times to remove most of the oxygen. The chamber was then filled to ~~0.5 atm~~ about 50 kPa with Ar. Pure Zr was arc-melted before encapsulation to act as an oxygen getter to minimize any trace amounts of oxygen remaining after purging since Zr is indigenous and thermodynamically very reactive with oxygen [64,63]. Next, the encapsulation was performed in the arc melter with one melt cycle of one or two seconds to seal the Zr-Ag alloy by means of local melting of the surrounding container of Zr-Ag alloy. As a result, a diffusion couple between ZrC and (Ag gas from) the encapsulating Zr-Ag alloy was constructed as illustrated in Fig. 2(b).

The diffusion couple prepared using arc encapsulation outlined above was then located inside a graphite rod 25 mm in diameter to prevent oxidation during subsequent exposure at high temperature. It was placed in an alumina tube furnace previously heated up to 1500 °C, annealed for 50 hours under Ar-flow at 80 cm³/min with loosely fitted plugs to seal the alumina tube during annealing, and finally cooled at 200 °C/hr. This annealing temperature was chosen since typical estimated maximum fuel temperature is about 1500 °C in the case of a depressurized loss of forced cooling accident in a small modular HTGR with spherical fuel elements, ~~although typical limits are somewhat arbitrary and in fact depend on the type of fuel, irradiation history, manufacturing processes and many other factors [4,5,9]. Including a 100 °C uncertainty, the upper design limit for maximum fuel temperature of the modular HTGR under both normal operation and accidents is usually set at 1600 °C [5,12]. The demonstrated fission product retention at 1600 °C establishes the basis for the design of small modular HTGRs which inherently limit the temperature to 1600 °C by passive means [62].~~

The diffusion annealed sample was cross sectioned, mounted, ground, and polished for SEM-Scanning electron microscopy (SEM) imaging, orientation image mapping (OIM), and chemical analysis. All images presented in this paper were taken in the as-polished condition without etching.

3.4.2. Diffusion equation

To give better insight into the *encapsulating source method* and to help understand the scope and limitations of this new experimental technique, it is worthwhile to review the well-established solution of the diffusion equation used for curve fitting and determining the diffusion coefficient in the present study.

$$\frac{\partial C}{\partial t} = \nabla \cdot (\mathbf{D} \nabla C) \quad \text{Eq. 1}$$

where C denotes a concentration at the location and time t in question, $\nabla \cdot$ the divergence operator, and $\mathbf{D}$ a diffusivity which is tensor-valued and concentration-dependent. Eq. (1) is the elementary vector form of Fick's second law of the diffusion equation, ~~which is based on two assumptions. One is that no external driving forces, such as electric, magnetic, or stress field are exerted on the system, which is quite obviously true in the present diffusion system. The other is that the internal driving force for diffusion is expressed as the concentration gradient in lieu of the chemical potential gradient. This is also a valid assumption because Ag concentrations are very low and these low concentrations make Ag atoms virtually isolated in the ZrC matrix and not interact with other Ag atoms. As it turns out in Section 3.5, the maximum Ag concentration in ZrC is determined to be only about 0.05 wt.%.~~

Eq. (1) appropriately simplifies to Eq. (2) for the one-dimensional diffusion.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{Eq. 2}$$

where x represents one dimensional diffusion space and D is a diffusivity, the latter of which is both scalar-valued and concentration-independent. To derive Eq. (2) from Eq. (1), two conditions have to be met. First, the diffusivity is independent of concentration and remains constant. This requirement can be fulfilled when a trace amount of the diffusing impurity element of interest is involved in the otherwise homogeneous matrix, ~~which is the case with the present material system as shown in Section 3.5. This is a valid assumption in the present study because the maximum Ag concentration in ZrC is determined to be only about 0.05 wt.% as shown in Section 3.2.~~ Second, diffusivity is a scalar value. In general, however, it is not a scalar but a vector even in a microscopically homogeneous medium. It can be scalar-valued only when the medium is isotropic in terms of diffusion. The solid with cubic crystallographic symmetry is an example of an isotropic medium, which is the case with the crystal structure of ZrC. Now we can use Eq. (2) to adequately describe the diffusion system in the present study.

Eq. (2) ~~is a linear second-order partial differential equation, which~~ requires two boundary or initial conditions to have a unique concentration at any given location and time. ~~Assuming that the sample is semi-infinite and imposing an initial condition and a boundary condition, the equation can be solved analytically.~~ The semi-infinite solution can be applied when the diffusion depth is negligibly shallower than the sample thickness in the diffusion direction, which is the case with the diffusion-annealed sample used in the present system. If the initial condition is that $C = 0$ for $x > 0$ when $t = 0$, and the boundary condition is that $C = C_0$ at the sample surface (that is, $x = 0$) for all t when $t > 0$, the latter of which defines the constant-source diffusion condition. The well-known solution for Eq. (2) with these restraints is:

$$C(x,t) = C_0 \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right) \quad \text{Eq. 3}$$

where erf is the mathematical error function. Eq. (3) is the starting point of our analysis. The validity of the boundary condition in our diffusion system is also discussed in sections ~~3.2, 3.3 and 3.5 in the next section.~~

3.2.3. Encapsulating source method

Fig. 2 schematically illustrated how to fabricate a diffusion couple to employ the *encapsulating source method*. The complete encapsulation as shown in this figure provides better protection against detrimental oxidation on the matrix ZrC since oxygen has to permeate the barrier layer of the encapsulating alloy before reaching and reacting with the ZrC disk. It should be noted that wettability on the surface of the matrix is not an issue ~~herein in the present experimental system, unlike in the thin film method mentioned in Section 1.3,~~ since the diffusion source is no longer condensed matter.

It is possible for Zr to evaporate into the gas reservoir in Fig. 2(b). However, the vapor pressure of pure Zr is very low, close to an ultra-high vacuum (that is, only about 4.8×10^{-6} Pa ($\sim 3.6 \times 10^{-8}$ Torr) at 1500 °C [6764]). Therefore, the partial vapor pressure of Zr in the reservoir is most likely negligible, although the actual pressure may be somewhat different from the vapor pressure of pure Zr. Consequently, the possible Zr gain on the surface of the ZrC disk from the gaseous Zr originating from the Zr-Ag solid solution is not likely to change the concentration of the ZrC disk significantly within the given experimental time.

On the other hand, the partial vapor pressure of Ag in Zr-8.1 wt.% Ag is expected to dominate in the reservoir. This relatively higher partial vapor pressure of Ag can be indirectly deduced from the high Ag loss rate during arc-melting for alloying about Zr-8 wt.% Ag solid solutions. The authors' experience showed that, during arc melting even with the previously alloyed Zr-Ag solid solutions, mass loss of the arc-melted materials occurred mainly due to Ag evaporation. Therefore it is concluded that only Ag vapor, except a small amount of initial inert Ar gas, prevails inside the reservoir.

It is the gas reservoir that provides the source of Ag which permeates into the ZrC disk with time. The gas pressure of evaporated Ag in the reservoir is designed to remain constant throughout the diffusion annealing (except for the initial stage of sample heating), in order to satisfy the boundary condition used to derive Eq. 3 and make it possible to construct a constant-source diffusion couple between the ZrC disk and Ag gas. The Ag gas pressure virtually remains constant, if the average composition of the encapsulating alloy does not change significantly during diffusion annealing and the Ag atoms is equilibrium with those dissolved in the ZrC disk. The reason for this is that the thermodynamic partial equilibrium vapor pressure is only a function of the composition of the corresponding condensed matter and temperature. To ensure a macroscopically constant Ag concentration in the encapsulating Zr-Ag alloy, the total amount of Ag permeating into the ZrC should be negligible compared to that remaining in the surrounding Zr-Ag alloy. This is the case in the present study since, as it turns out in Section 3.4.3.2, diffusivity and concentrations of Ag in ZrC are very low.

In the above paragraph, the discussion was made based on the assumption that the Ag in the gas reservoir does not migrate to the ZrC disk but in fact it is constantly consumed due to permeation into the ZrC disk. However, it is expected that Ag vapor pressure in the reservoir still remains constant and thus the aforementioned boundary condition remains valid. The reason is that Ag atoms are continuously supplied to the reservoir at the same rate that they are consumed, because the diffusion of Ag from the Zr-Ag alloy into the reservoir is expected to be much faster than that from the reservoir into the ZrC disk [6865]. The real question is how slowly this transport phenomenon occurs in the ZrC disk, which is being investigated in this work. Consequently, low vapor pressure of Zr and dominant and constant vapor pressure of Ag inside the reservoir make it possible to construct a constant-source diffusion couple between the ZrC disk and Ag gas.

3.3. Diffusion-annealed sample

Fig. 3. The binary Zr-Ag phase diagram at the Zr-rich side showing that the solidus of 8.1 wt.% Ag is above 1500 °C; reconstructed based on [6966]. Note that the blue lines and words were added by the authors. Color figure available online.

Fig. 3 shows the binary Zr-Ag phase diagram. The solidus of Zr-8.1 wt.% Ag alloy is sufficiently higher than 1500 °C to avoid liquation of the encapsulating alloy during diffusion annealing. Therefore, no liquid is expected to exist in the sample at 1500 °C, assuming that the ZrC is chemically inert with Ag gas in the system due to high thermal stability. Although chemical inertness in the given system cannot be true from the strictest thermodynamic point of view, a gas/solid interface between Ag gas in the reservoir and the ZrC disk should be present assuming Ag gas does not readily react with ZrC. In fact, the most accurate prediction of what will happen on the ZrC disk during diffusion annealing requires the complete information of phase equilibria and kinetics of the Zr-C-Ag system, which is not available thus far. Nonetheless, there was no sign of Ag vapor condensation or phase transformation of ZrC observed on the surface of the diffusion annealed ZrC disk. Therefore, Ag transport behavior at a very low concentration in the ZrC using the *encapsulating source method* can be adequately described with Eq. (3) applying the aforementioned boundary condition.

2.2.2.4. EPMA measurement and data evaluation

Quantitative chemical electron probe micro analyzer (EPMA) analyses were conducted using ~~WDS a Cameca SX-51 electron microprobe with five WDS spectrometers. To improve the spatial resolution, a comparatively low incident electron energy of 10 keV for WDS analysis was chosen on balance, while not too much sacrificing the efficiency of X ray excitation. The quantitative chemical analysis was conducted using WDS with a 5 spectrometer electron microprobe, using Probe for EPMA (electron probe micro analyzer) software.~~ Operating conditions were a 10 kV of accelerating voltage with a beam current of 150 nA for Ag with a take-off angle of 40°. Lines measured were Ag L (using 3 PET crystals). No peak interference is anticipated in the given peak measurement system. Ag was acquired for 210 seconds for each of the three spectrometers making the total counting time 630 seconds for each measurement. The 3 separate Ag counts were summed to lower the Ag detection limit down to about 0.007 wt.% Ag. The Phi-Rho-Z matrix correction was implemented. Standards used were 99.9 wt.% pure Ag and ZrC_{0.84}.

It should be noted that the measured concentration is pushing the limits of the EPMA technique in terms of concentration and/or spatial resolution in this study [6367]. The data from a nominal analytical area can be affected by neighboring inhomogeneous areas far beyond the area of an incident electron beam ~~even when the beam is well confined in a homogeneous area of the sample surface.~~ This can happen because the actual analytical volume that generates characteristic X-ray peaks of interest is usually larger than the size of the beam. This larger area of the interaction volume can contain multiple phases including the sample edge. Therefore, this edge effect can sometimes significantly skew the resultant X-ray counting and thus measured composition when compositions are measured close to the sample edge as is the case in the present study.

Table 1

PENEPMA simulation parameters

Beam energy of incident electron	10 (keV)
Number of electrons simulated for each point	6.0×10^6 (electrons)
Take-off angle for EPMA detector	40 (°)
Material bombarded by electrons	Zr _{11.51} C _{87.45} Ag _{1.04} (wt.%)
Density of material simulated	6.76 (g/cm ³)

To evaluate the sample edge effect ~~with a volumetric incident electron beam~~ in the present study, and thus validate the measurement result, X-ray generation was simulated using the computer software PENEPMA [6468,6569] developed by X. Llovet and F. Salvat. ~~This simulation code adopts the most elaborate interaction models thus far. It utilizes PENELOPE-2008, a general purpose Monte Carlo code system for electron and photon transport which uses the most elaborate interaction models available for complex materials and sample geometries. The parameters used for the simulation are summarized in Table 1. In particular, a material selected for the simulation was 1.04 wt.% Ag (~ 0.5 at.% Ag), although the highest concentration of Ag in ZrC actually measured was only about 0.05 wt.% as shown in Section 3.4. This concentration was chosen to increase calculation statistics within a reasonable time when utilizing a personal computer.~~

~~Once simulated data representing X-ray counting were acquired, these raw intensity density data were converted into an actual concentration by applying a matrix correction to address the effects of absorption, fluorescence, electron backscattering, and efficiency of X-ray generation on the characteristic intensity collected in the detectors. The matrix correction was conducted using the matrix correction utility program CalcZAF available to the scientific community from Probe Software, Inc. [66]. An additional point was selected far inside the ZrC from the sample edge for a 10-times longer simulation for better calculation statistics. This data was then used as a standard concentration when performing the matrix correction.~~

The X-ray simulation result indicated that the composition measurements from the areas deeper than about 0.4 μm from the sample edge (or sample surface in 3-D) were virtually unaffected by the presence of the adjacent edge. For instance, the characteristic X-ray intensity of silver measured at a location 0.4 μm away from the edge showed only about 5% reduction compared to that measured at a location far away from the edge. This result is used to validate the actual EPMA measurement data presented in Section ~~3.4~~3.3.2.

3. Results and Discussion

~~3.3~~3.3.1. Diffusion annealed sample

Fig. 4. Sample cross section: (a) overall optical macrograph, (b) higher magnification SEM image. Diffusion annealing: 1500 °C for 50 hours.

Fig. 4 shows a cross section of the sample used for the diffusion coefficient measurements in this study. This sample is previously diffusion annealed at 1500 °C for 50 hours. Fig. 4(a) shows a reaction layer where the original encapsulating alloy reacts with carbon from the graphite containment and is transformed into new ZrC, which was confirmed with electron backscatter diffraction (EBSD) analysis but not shown herein. Fig. 4(b) shows that the ZrC disk used in this diffusion experiment comprised of two large grains according to SEM imaging, where they are distinguished by the different contrast. The importance of this bi-crystallinity is also discussed [in section 3.4 later in this section](#). Fig. 4(b) also shows that the ZrC disk consists of a single phase. There is no excess carbon as expected from the stoichiometry of the ZrC used.

It turns out that the top area of the ZrC disk in the sample is broken off during encapsulation and two small pieces of broken ZrC are found embedded in the Zr-Ag alloy as indicated in Fig. 4. This fracturing appears to be associated with the large grain size of the ZrC disk although ZrC is considered to be thermally stable and resistant to thermal shock. Other experiments conducted by the authors (not shown herein) showed that polycrystalline ZrC was much more resistant to thermal shock in similar encapsulation conditions. This fracturing probably happened only once, at the initial contact of liquid with the ZrC disk during the encapsulation process. However this does not imply that the disk was contaminated by the liquid, because the reservoir is expected to have sustained a small amount of Ar gas once it was closed by the liquid. This breakage in the present experiment is unintentional and merely coincidental

but seems beneficial since it can provide an in-situ highly-fresh surface which normally cannot be obtained.

Dark columnar features in Fig. 4(b) indicate that there were phase transformations involved during fabrication of the diffusion couple and during/after the diffusion annealing process. According to EDS-energy-dispersive X-ray spectroscopy (EDS) analysis, it shows that those dark features are α -Zr (probably, proeutectoid phase) and the brighter background is composed of very fine α -Zr and AgZr_2 (probably, eutectoid phases considering the phase diagram in Fig. 3) among those columnar features.

3.4. Determination of Ag diffusivity

Fig. 5. Measurement location for EPMA and scan area for EBSD. Note that the EPMA measurement location is sufficiently away from both the grain boundary and the local bonding.

Fig. 5 shows the measurement direction and areas for EBSD and EPMA from the diffusion sample. The ZrC disk was cross sectioned parallel with the cylindrical direction since the fresh surface is practically parallel with the original surface of the disk before breakage. This means that the data acquired can still represent one-dimensional diffusion properly. It should be pointed out that it is not possible that measured concentrations are affected by the bonding since the data measurement were carried out far away (about 1 mm) from the bonding area as shown in this figure. It should also be pointed out that, although the ZrC disk and the encapsulating alloy across the reservoir were not in equilibrium from a strict thermodynamic viewpoint, there is no sign of Ag vapor condensation or phase transformation of ZrC observed in the vicinity of the

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surface of the ZrC disk in Fig. 5. Therefore, the constant boundary condition applied to solve Eq. (3) still seems to remain reasonable.

Fig. 6. Secondary electron SEM image (left) and IPF map (right) at the location on the ZrC disk, indicated in Fig. 5. Color figure available online.

It was shown in Fig. 4 that the ZrC disk used in the diffusion experiment comprised of two large grains according to SEM imaging, where they were distinguished by the contrast. This bi-crystallinity is also confirmed using EBSD analysis. Fig. 6 shows the crystallographic orientation map (right) corresponding to the SEM secondary electron image (left), where these images are taken from the area demarcated in Fig. 5. The map in Fig. 6 is an as-obtained raw inverse pole figure (IPF) image without any further so-called cleanup process. The step size for the mapping is 0.5 μm . According to the orientation mapping, the misfit angle between the two grains is determined to be only 2° at the most.

The bi-crystallinity of the given ZrC disk is especially important since it can eliminate complexities of the measurement data analysis arising from high-diffusivity paths such as interfaces or grain boundaries although the dependence of grain boundaries on Ag diffusion should also be eventually addressed. Due to this reason, the sample area used for the diffusion experiment and analysis is chosen in an area of a virtually single crystal. It should be also noted that ZrC does not exhibit diffusion anisotropy relative to the crystal axes. This is because it has cubic symmetry (cF8) in the crystal structure [70]. A detailed mathematical description about the crystal structure effect on diffusion anisotropy can be found elsewhere such as ref. [71].

3.2. Ag diffusivity

Before presenting measured EPMA diffusion data, it should be noted that Ag was detected only near the original diffusion surface and not elsewhere in the ZrC disk except the localized bonding area indicated in Fig. 5.

Fig. 7. Three sets of measured Ag concentration data with WDS and the corresponding concentration profiles obtained based on the solution of the diffusion equation. Note that the diffusion sample was previously heat-treated at 1500 °C for 50 hours.

Due to limitations of EPMA in terms of concentration detection resolution and spatial resolution, measured data may not be ideal for curve fitting with an analytical solution. This is especially the case when the concentration of the diffusing element is very low and a very shallow area near the sample surface is measured. However, it turns out that the concentration profile demonstrates a measurable variation, at least, in the relative concentrations of silver. Fig. 7 shows such measurement data points and solid curves calculated applying the analytical solution expressed as Eq. (3). The data points in this figure are measured in the area and along the direction specified in Fig. 5. The depth is measured from the sample surface and thus the sample edge after cross sectioning. Three sets of Ag concentration data are plotted with respect to the penetration depth using three different types of marks, circles or two different squares. Each set of data is measured about 15 μm away from one another along the direction parallel to the boundary normal.

Only data points from an area greater than 1.5 μm in depth are considered to be valid for curve-fitting. This is based on possible deviation in locating electron beams in addition to the simulation results mentioned in Section 2.2.4. Two additional curves as well as one best-fit curve are presented to give an outlook for possible deviation from the best fitting. According to

the curve fitting shown in Fig. 7, the experimental data best fit with $2.8 (\pm 1.2) \times 10^{-17} \text{ m}^2/\text{s}$, where the uncertainty is determined solely in terms of approximate curve fitting. Thus the diffusion coefficient of Ag in single crystalline $\text{ZrC}_{0.84}$ at 1500°C was determined as $2.8 (\pm 1.2) \times 10^{-17} \text{ m}^2/\text{s}$. It should be noted that Fig. 7 also shows that the highest Ag concentration by extrapolation is about 0.05% at the ZrC surface, which indicates that the assumption of a dilute solution in Section [3.1-2.2](#) is valid.

It is worthwhile to compare this diffusivity value to those obtained by extrapolating the data from the aforementioned Chernikov et al [45]. Recall that, in their study, two linear regions with two different slopes based on the nuclide concentration and distribution of $^{110\text{m}}\text{Ag}$ were obtained. They inferred that the first region was due to the migration of silver ~~along the short circuit~~ in the grain volumes paths and the second region was due to that ~~in the grain volumes~~ along the short circuit paths. Extrapolation of their data to 1500°C yields approximately $6.0 \times 10^{-17} \text{ m}^2/\text{s}$ for the first region and $8.9 \times 10^{-15} \text{ m}^2/\text{s}$ for the second region. Considering the experimental difficulties, two lattice diffusion coefficients (that is, $6.0 \times 10^{-17} \text{ m}^2/\text{s}$ from Chernikov et al's work and $2.8 \times 10^{-17} \text{ m}^2/\text{s}$ from the present study) are in fairly good agreement with one another. Therefore, it seems that both diffusivity data from this study and from Chernikov et al's work reflect the real nature of Ag transport in ZrC within experimental uncertainty, although either or both of values obtained by Chernikov et al may be to some extent affected by or related to the aforementioned experimental difficulties.

As a final note in this section, it seems also appropriate to compare the silver diffusivity in zirconium carbide with that in silicon carbide since ZrC is a candidate to replace SiC as a coating material in TRISO fuel particles. However, a direct comparison of these two types of diffusion coefficients is not possible because the published values with SiC exhibit significant scatter up to greater than six orders of magnitude; they vary from virtually zero ($< 5 \times 10^{-21} \text{ m}^2/\text{s}$) to about $4 \times 10^{-15} \text{ m}^2/\text{s}$ at 1500°C [45-59]. Detailed reviews can also be found in Malherbe [72] and Kim et al [73].

3.3. Future research

Although the work detailed in this study provides another step forward in understanding silver transport in zirconium carbide, much further work remains to be done using the

encapsulating source method. For instance, the Ag diffusivity in ZrC at 1600 °C should be determined for modular HTGR licensing purposes. Note that the demonstrated fission product retention at this temperature establishes the basis for the design of small modular HTGRs which inherently limit the temperature to 1600 °C (including a 100 °C uncertainty) by passive means [74]. In addition, a follow-up study should be conducted to evaluate the effect of the non-stoichiometry of ZrC on Ag diffusivity, since stable ZrC has a large range of C/Zr ratio varying from 0.63 to 0.98 [75].

4. Conclusions

A new diffusion experimental technique, called the *encapsulating source method*, has been developed to construct and diffusion anneal a constant source diffusion couple composed of ZrC and Ag vapor originated from Zr-8.1 wt.% Ag solid solution. Concentrations were measured from a diffusion annealed sample using WDS. Consequently, the impurity diffusion coefficient of Ag in single-crystalline ZrC_{0.84} at 1500 °C was experimentally determined to be about $2.8 (\pm 1.2) \times 10^{-17} \text{ m}^2/\text{s}$. This is the first reported value of this diffusion coefficient at 1500 °C.

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