Silver diffusivity measurement in ZrC with SIMS to study the release behavior of ^{110m}Ag for nuclear fuel applications

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Abstract

Recently, the diffusion coefficient of silver (Ag) in zirconium carbide (ZrC) at 1500 °C was determined to help elucidate the diffusive behavior of radioactive ^{110m}Ag in the ZrC coating of the tri-structural isotropic (TRISO) nuclear fuel particle. This study was conducted using a recently developed diffusion experimental technique, known as the encapsulating source method. To verify the validity of this experimental method, modifications to the original experimental design have been made within the domain of this method. Primarily, the ability to retrieve the ZrC disk made it possible to create depth profiles using secondary ion mass spectrometry (SIMS) for more precise depth profiling of Ag concentration in ZrC. Applying this improved experimental design, a sample was fabricated and diffusion annealed at 1500 °C for 2 h. Finally, silver concentrations on the ZrC disk were measured using SIMS. Consequently, the diffusion coefficient of Ag in $\text{ZrC}_{0.95}$ at 1500 °C was experimentally determined to be about $1.7 \times 10^{-17} \text{ m}^2/\text{s}$, remarkably consistent with the previously reported value of $2.8 \times 10^{-17} \text{ m}^2/\text{s}$, also obtained by means of the encapsulating source method. This proves that the encapsulating source method is a reliable experimental technique to determine the Ag diffusivity in ZrC.

1. Introduction

The fuel of choice for the high-temperature gas-cooled reactor (HTGR) has been the tri-structural isotropic (TRISO) coated particle fuel [1-8]. In the current TRISO-coated particle fuel design, the coated particle consists of the kernel formed from enriched uranium dioxide (UO_2) or uranium oxycarbide (UCO) in the center and successive layers of porous pyrocarbon buffer, dense inner pyrolytic carbon, silicon carbide (SiC), and dense outer pyrolytic carbon. The SiC

layer serves as the primary barrier to the release of fission products as well as providing structural support to accommodate internal gas pressure [7-11].

Zirconium carbide (ZrC) has been considered as a promising alternative to the SiC fission product barrier of the TRISO-coated fuel particles since the 1970s, because the peak fuel temperature permissible under both normal operating and accident conditions would increase while still retaining a very high degree of passive safety [5,6,12-19]. Therefore it is important to elucidate the release behavior of fission products through the ZrC coating layer. The release of radioactive silver (^{110m}Ag) in particular has been of considerable concern because it can contaminate various surfaces in the primary circuit of a direct-cycle HTGR and make maintenance difficult and thus costly [20,21]. However, there are few studies that address Ag retention in the ZrC TRISO-coated particle [22-24].

For high temperature Ag diffusion experiments in ZrC, it has been difficult to find an effective experimental technique. To overcome such experimental difficulty in the present material system and make it possible to fabricate more reliable diffusion experimental samples, Yang et al. [24] has recently developed a new experimental technique, referred to as the encapsulating source method. They fabricated a sample applying this method, diffusion annealed it, and determined the Ag diffusivity in ZrC at 1500 °C with wavelength-dispersive X-ray spectroscopy (WDS). The salient points of this new technique in the given material system are 1) the diffusion matrix of ZrC is completely encapsulated in a Zr-Ag solid solution, and 2) the diffusion species (Ag atom) originates from gaseous Ag released from this encapsulating material. Fig. 1 shows the schematic experimental setup used to fabricate a diffusion experimental sample based on the encapsulating source method. Note that this setup is the one that has been modified from the previous setup developed by Yang et al. [24], the details of which can be found there.

Fig. 1. Schematic illustration of the experimental setup for fabricating diffusion samples to employ the encapsulating source method: (a) before encapsulation, (b) after encapsulation using arc-melting. Note that the encapsulated sample shown in (b) is subsequently diffusion annealed.

Although a diffusion sample could be successfully fabricated and diffusion annealed using the encapsulating source method in the previous study, it was no easy task measuring Ag concentrations on the diffusion annealed sample because of the limitations of the conventional WDS analysis in terms of both concentration and spatial resolution [24]. This fundamental difficulty in depth profiling with WDS is expected to become more acute for diffusivity measurement at lower temperatures because of lower penetration depths as well as lower concentrations. One potential solution to this limitation is to use, for instance, secondary ion mass spectrometry (SIMS) in place of WDS. SIMS is a measurement technique that provides significant improvement in concentration detection and spatial resolution for depth profiling at a wide range of temperatures. It is generally considered that, when diffusion coefficients are above $10^{-15} \text{ m}^2/\text{s}$, WDS is an effective measurement technique, while higher sensitivity surface measurement techniques such as SIMS or Auger electron spectroscopy (AES) in conjunction with ion beam sputtering can be appropriate for small diffusion distances and low diffusivities in the range of $10^{-16} - 10^{-23} \text{ m}^2/\text{s}$ [25].

Thus, the aim of this work is twofold. The first is to improve the experimental design within the domain of the encapsulating source method, in order to facilitate the use of SIMS. The second is to prove the validity of the encapsulating source method by comparing the previously reported diffusion coefficient with the diffusion coefficient obtained using SIMS in this study.

2. Experimental

The encapsulating source method [24] was employed to determine the diffusion coefficient of Ag in ZrC. Time-of-flight SIMS (ToF-SIMS) analysis was performed on the diffusion annealed sample, fabricated based on this recently developed experimental technique.

2.1. Material's preparation and diffusion annealing

Two samples based on the encapsulating source method were fabricated and annealed at 1500 °C for 2 hours: one was for the diffusion experiment, and another for post-diffusion-anneal metallography. Each sample consisted of an encapsulated ZrC diffusion matrix and an encapsulating Zr-Ag alloy.

Two ZrC rods 3 mm in diameter were custom-manufactured by Applied Physics Technologies, Inc., Oregon. The total carbon present in the rods was measured by ATI Wah Chang Laboratory, Oregon, using a LECO combustion IR. The atomic ratios of carbon to zirconium in the ZrC rods were determined to be about 0.95 (denoted as ZrC_{0.95}) and 0.89. ZrC disks about 2 mm thick and 3 mm in diameter were sliced from the as-received rods to be used for sample fabrication; ZrC_{0.95} was used to fabricate a diffusion experiment sample, while ZrC_{0.89} to fabricate a post-diffusion-anneal metallographic sample. The sliced disks were then mechanically ground with successive grinding steps and finally polished on one face with 0.04 µm grain size colloidal silica. As a result, this polished surface was simply flat and had no rough or raised parts. More detailed information on the ZrC used in this study can also be found in Silva et al. [26]. They used the same materials (as well as other varying stoichiometries of ZrC) as those used in the present study, both of which were from the same manufacturing batch on the same production line. Silva et al. characterized the ZrC using electron microscopy, optical anisotropy, Auger depth profiles, X-ray diffraction, and electron density calculation.

The encapsulating portion of the diffusion samples consisted of three parts: drilled ingot, cap, and stud as in Fig. 1. They were prepared from the alloys fabricated from pure Zr (99.9 wt.% excluding Hf) and Ag (99.9 wt.%) metals by means of multiple arc-meltings, casting, and machining. Each as-cast ingot weighed about 4 g and had cylindrical geometry about 12 mm high and 9 mm in diameter. The nominal compositions of the cast alloys were Zr-8.7 wt.% Ag for the diffusion experiment sample and Zr-8.1 wt.% Ag for the post-diffusion-anneal metallographic sample. Note that these compositions of the resultant Zr-Ag alloys were

determined assuming only Ag evaporates during arc melting and contributes to the slight mass change in the final encapsulating alloy as an approximation. These compositions were selected based on the idea behind the encapsulating source method that the alloy remains as a solid solution at the diffusion anneal temperature.

A small portion of one end of this Zr-8.7 wt.% Ag ingot was then cut for subsequent drilling. Using two drilling steps with end mills of diameters 3.2 mm and 2.9 mm, the center of the diameter of the cylindrical ingot was machined to produce a ledge about 0.4 mm in height where the ZrC disk would rest, forming a dimension controlled gas reservoir as shown in Fig. 1. Meanwhile a small piece of a round bar, as referred to as a stud in Fig. 1 (a), was cast in the form of a rod 3 mm in diameter by arc-melting and subsequent vacuum suction.

Next, a ZrC disk was placed inside the hole, making sure the polished face was toward the gas reservoir. The stud was positioned above the disk to prevent bonding of the ZrC disk with the rest of alloy during encapsulation as illustrated in Fig. 1. A cap of Zr-Ag alloy, with a hole drilled through it, was placed on top allowing trapped oxygen inside the hole (including the gas reservoir of the drilled ingot) to escape during encapsulation. The cap and stud had similar composition to the drilled ingot.

Before encapsulation, the chamber was purged with Ar gas and a pure Zr ball was melted to getter oxygen because Zr is very reactive with oxygen and was indigenous. Encapsulation was performed with a smaller capacity arc melter, where the cap and the top of both the drilled ingot and stud were fused together for only one or two seconds, effectively sealing the ZrC disk inside the alloy. Once encapsulated, the resultant diffusion sample was packed inside a drilled hole of a purified graphite rod 25 mm in diameter to isolate it from the direct furnace environment. The sample was then inserted into an alumina tube furnace pre-heated to the targeted diffusion anneal temperature of 1500 °C to ensure rapid heating and better definition of the annealing time. Ar was flown through the furnace tube during the entire anneal to mitigate undesirable reactions of both the diffusion sample and the graphite rod system with air at such a high temperature. After two hours, the sample, still encased in graphite, was quickly extracted from the furnace and quenched in water, yielding a cooling rate greater than 250 °C/s. Finally, the ZrC disk was retrieved from the diffusion annealed sample by careful sectioning. More details on sample preparation and experimental procedures are described in the next section.

A LEO 1530 field emission SEM was used to examine the surface and cross-sectional microstructure of the ZrC disk from the diffusion sample either in the as-annealed condition or the post-SIMS-analysis conditions. Qualitative chemical analysis was performed on the encapsulating alloy and the diffusion annealed ZrC disk using standardless energy-dispersive X-ray spectroscopy (EDS).

2.2. Improvements on earlier experimental setup and procedures

Several improvements have been made to the experimental design previously used for the encapsulating source method by Yang et al. [24]. First, rapid cooling was successfully employed by quenching in water. Note that the cooling rate was 200 °C/h in the original design. It halted the diffusion process abruptly and thus diffusion annealing conditions were defined more accurately and clearly.

Second, the volume of the gas reservoir inside the fabricated diffusion sample was fabricated in a better controlled manner using the two step drilling and the incorporation of the stud as illustrated in Fig. 1. Note that it was not easy to control the volume of the gas reservoir in the original design. This was expected to help maintain experimental consistency by minimizing volume variations in the gas reservoir.

Third, the volume of encapsulating alloy surrounding the ZrC increased. In general, increased volume would make the encapsulating alloy less sensitive to oxidation, evaporation, or phase reaction which may initiate on the outer surface. This would mitigate the composition changes of the encapsulating alloy near the gas reservoir. As a result, the concentration of the diffusing element of interest would stay unchanged near the gas reservoir, which would ensure the vapor pressure inside the gas reservoir remains constant. Conceptually, there is no limit to the volume of the encapsulating alloy because successive layers of encapsulation can be implemented.

Lastly, and most importantly, the improved experimental design enabled the ZrC to be removed from the diffusion annealed sample. As illustrated in Fig. 1(a), a stud made of similar composition to the rest of the encapsulating alloy was used to ensure that the ZrC disk did not bond with this alloy during encapsulation, which facilitated easier removal of the ZrC disk from the sample. As a result, this modification permitted both the use of SIMS for depth-profiling and the use of samples diffusion annealed for shorter periods due to the very good depth resolution

and the high sensitivity of SIMS. In addition, a much shorter anneal time as well as the aforementioned large volume of the encapsulating alloy would virtually eliminate undesirable compositional changes in the encapsulating alloy during diffusion annealing.

It should be noted that any sample preparation and experimental procedures not specified in Sections 2.1 and 2.2 are essentially identical to those outlined in Ref. 24.

2.3. Concentration measurements

Dual-beam ToF-SIMS was used to measure the Ag concentration as a function of depth into the ZrC disk. For SIMS analysis, the ZrC_{0.95} disk retrieved from the diffusion annealed sample was sent to Pacific Northwest National Laboratory (PNNL) to be analyzed by the Environmental and Molecular Science Laboratory (EMSL), a DOE (Department Of Energy, USA) national user facility. EMSL operated a dual beam Time-of-flight SIMS from ION-TOF USA Inc. that sputtered ions from the sample surface with a 2.0 keV Cs⁺ focused primary ion beam at 125.5 nA. A crater 300 × 300 μm was sputtered in the surface of the ZrC disk with an Ar gun for controlled erosion of the sample, and the primary ion beam was rastered over an area 100 × 100 μm to generate the secondary ions to be analyzed. The resultant sputter crater depth was measured to be 1,521 nm using a Zygo NewView 7000 series profilometer, and thus the sputter rate was determined retrospectively to be 0.5 nm/s. Data was sampled every 10 seconds, essentially yielding a data point every 5 nm until a depth of 1,521 nm below the examined ZrC surface. The ions of interest included (but were not limited to) ⁹⁰Zr, ¹⁰⁷Ag, and ¹⁰⁹Ag. Naturally occurring silver is composed of the two stable isotopes ¹⁰⁷Ag and ¹⁰⁹Ag with ¹⁰⁹Ag being the less abundant (48.161% natural abundance) [27]. However the ¹⁰⁹Ag measurement data instead of ¹⁰⁷Ag were used for determining the diffusion coefficient because detected signals from ⁹⁰ZrOH and ⁹¹ZrO may interfere with those from ¹⁰⁷Ag.

Qualitative chemical analysis was also performed on the post-diffusion-anneal metallographic sample using EDS to measure Ag concentration across the encapsulating alloy.

2.4. Diffusion equation and curve fit

To help better understand the scope and limitations of the encapsulating source method, it is worthwhile to reiterate the well-established solution of the diffusion equation used for curve fitting and determining the diffusion coefficient in the present study. Eq. (1) is the elementary

vector form of Fick's second law of diffusion equation 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.

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

Eq. (1) appropriately simplifies to Eq. (2) for one-dimensional diffusion, where x represents one dimensional diffusion space and D is a diffusivity, the latter of which is both scalar-valued and concentration-independent.

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

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. This is a valid assumption in the present study because the maximum Ag concentration in ZrC was determined to be about 0.05 wt.% at most in the preceding study [24]. 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. A 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) requires two boundary or initial conditions to have a unique concentration at any given location and time. 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:

$$C(x,t) = C_o \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right)$$

3

where erf is the mathematical error function. In order to determine the diffusion coefficient, measured concentrations were fitted to Eq. (3).

3. Results and discussion

3.1. Improvements achieved in sample fabrication

Fig. 2. Improved sample annealed at 1500 °C for 2 h: (a) optical macrograph of the cross-section, (b) Ag concentration measured in the encapsulating portion. Note that the SEM image in (b) is enlarged from the area demarcated with a white rectangle in (a).

Fig. 2(a) shows the optical macrograph of the cross section of the improved sample that has been diffusion annealed at 1500 °C for 2 h. Fig. 2(b) shows the results of the Ag concentration measurement in the encapsulating alloy using EDS. These figures demonstrate three of the improvements achieved using the modified experimental setup and procedures outlined in Section 2.2. First, Fig. 2(a) shows that the volume of the gas reservoir is more precisely controlled compared to that in the preceding study.

Second, it illustrates that the thickness of the encapsulating alloy has increased from about 1 mm (in the previous study) to 3 mm at the thinnest location. Consequently, it is expected that the improved sample tends to be less susceptible to compositional change during diffusion annealing. In addition, this sample was annealed only for 2 h, much shorter than 50 h in the previous study, with the result that the reaction layer (that is, the area between two white arrows) is so thin that it is hardly visible in Fig. 2(a). This also implies that there is not much composition

change in the encapsulating alloy during diffusion annealing. Constant composition is important when applying the encapsulating source method, because it ensures constant vapor pressure of Ag in the gas reservoir during diffusion annealing. Recall that the equilibrium thermodynamic partial vapor pressure of Ag in the given material system is essentially only a function of temperature, and that the constant vapor pressure of Ag and thus the constant Ag concentration at the surface of the ZrC disk is the boundary condition used to derive Eq. (3) [24]. According to the EDS measurement in Fig. 2(b), the Ag concentration in the encapsulating alloy remains practically unchanged along the thickness direction of the encapsulating alloy, although the data fluctuates around Zr-7.5 wt.% Ag (close to the nominal compositions of Zr-8.1 wt.% Ag). Such variations are caused mainly due to the inhomogeneity of the quenched encapsulating alloy. It should be noted that the Zr-Ag alloy in Fig. 2 is composed of fine α -Zr and AgZr₂ (not shown herein), as expected in the Ag-Zr binary phase diagram [28].

Lastly, Fig. 2(b) shows that the one end of the initial stud remained unmelted through the sample encapsulating process, and that the unmelted portion of the stud prevented molten encapsulating alloy from touching the ZrC disk during encapsulation with arc melting. Fig. 2(a) clearly shows that there is no or little, if any, bonding between the ZrC disk and the encapsulating alloy. As a result, the sample is amenable to removal of the ZrC disk from itself after annealing. The ability to remove the ZrC disk makes it possible to create depth profiles using a very high sensitivity surface analysis technique, for example SIMS in the case of the present study.

3.2. Microstructural examination

Fig. 3. SEM micrographs showing the surface morphology of the as-diffusion-annealed ZrC: (a) newly grown ZrC protrusions and thermal etch pits, (b) faceting of etch pit and surface. In (a), a patch of newly grown ZrC is enlarged and shown in the inset.

Fig. 3 shows the surface morphology of the ZrC disk retrieved from the sample diffusion annealed at 1500 °C for 2 h. Rounded or elongated islands were observed on the surface of the annealed ZrC disk as in Fig. 3(a). The surface of these features are well-faceted (that is, having well-developed crystal faces) on a micrometer scale as shown in the enlarged inset in Fig. 3(a). It turns out that these protrusions are comprised of a number of newly grown ZrC crystals (or grains), which was confirmed by EDS compositional analysis (not shown herein) and microstructure observation (as shown later in this section). It is generally accepted that the cause of microscopic faceting in crystal growth is usually associated with a combination of two major factors: 1) the tendency of a crystal to reduce its surface free energy by the development of low energy planes with different crystallographic orientations, and 2) the anisotropic growth kinetics of each crystal surface. Additionally, in the present study, the surface morphology of each crystal in a protrusion is also dependent on the nucleation of that crystal in the initial ZrC disk. Nonetheless, further discussion of the faceted protrusions is beyond the scope of this study.

Thermal etch pits are also observed on the ZrC disk surface in Fig. 3(a). They are usually found to be in parallel with one another. The entire surface inside the pits is all faceted with terraces, steps, and kinks, demonstrated in Fig. 3(b), a close-up of an etch pit. The shapes of the pits are generally elongated and approximately symmetrical along the centerline of the pit's long axis, but the specific shape (for instance, the aspect ratio of the pits) varies depending on the grain (and thus its orientation) on which they sit. In the particular case shown in Fig. 3, most of the pits are fairly long and blade-like with a sharply-tapered acuminate point at one end and a bluntly-tapered point at the other end. It is not clear, however, how and why they are formed, which are questions beyond the scope of this study. Nonetheless, it is likely that the pits are formed through a surface diffusion process rather than sublimation and thermal decomposition, because ZrC is thermally very stable and highly refractory, with a melting point of 3,427 °C at a congruent point [29] and surface diffusion is usually much faster than volume and even grain boundary diffusion.

It is interesting to observe that the seemingly flat surface of the annealed ZrC disk on micrometer scales as in Fig. 3(a) is, in fact, all faceted with pretty straight steps in close-up as

shown in Fig. 3(b). It is most likely that such nanoscale steps are formed through uniting atomistic steps of a vicinal surface that have been created at the initial stage of diffusion annealing. It is also observed that even microscopically curved surfaces are comprised of a number of varying lengths of terraces, not shown in this paper. In fact, the entire surface area on the polished and annealed ZrC disk, without no exception, is all well-faceted either on a micrometer or nanometer scale. This well-developed faceting on the surface of the ZrC disk seems to be indicative of a high degree of surface cleanliness during diffusion annealing due to complete encapsulation of the diffusion matrix, one of the primary advantages of the encapsulating source method. An intuitive (and widely accepted) explanation for faceted surfaces would be that faceting is sometimes thermodynamically favored because it can lower total surface free energy by exposing low energy surfaces despite an increase in total surface area. A full discussion of the development of surface facets on ZrC during annealing, however, would be far more complicated than this simple explanation and beyond the scope of this study.

Fig. 4. Plan view SEM micrographs showing the effect of ion-beam sputtering on the surface topography of the ZrC disk: (a) a newly grown ZrC protrusion and uniformly sputtered crater

bottom, (b) a close-up of the protrusion in (a), (c) a close-up of the deposition layer from the rectangle in (b).

It turns out that the total area of the protrusions situated inside the scanned area for the SIMS analysis accounts for approximately 13% of the total scanned area of $10,000\text{ }\mu\text{m}^2$. Fig. 4 shows plan view SEM micrographs of the flat surface of the ZrC disk and a newly grown ZrC protrusion on it after ion-beam sputtering implemented for the SIMS analysis. Fig. 4(a) demonstrates that most of the ZrC disk surface area is uniformly sputtered and fairly flat except for a protrusion and a thermal etch pit. Fig. 4(b), a close-up of the protrusion, shows that part of it remains shadowed and thus intact during the sputtering process. The area surrounded by a dotted boundary line in this figure is one such masked region. The boxed area within this circled area is revealed at higher magnification in Fig. 4(c).

A thin layer of deposition, whose identity remains unknown herein, is observed in such shaded areas as shown in Fig. 4(b) and (c). The deposits are not uniform but rather patchy and appear to preferentially and only partially deposit on or around the ZrC protrusions as in Fig. 4(b). The amount of deposit coverage is very limited; for example, there is little deposition in the entire area in Fig. 3, unlike the coverage shown on the shaded surface in Fig. 4(b). This non-uniform deposition can be attributed to the various crystallographic orientations present on the surface of the ZrC protrusion, some of which may be more favorable for vapor deposition. A protrusion in itself, for example, contains many grains (as shown in later Fig. 5(d)) and therefore, many different crystallographic planes in terms of the three-dimensional morphology. More crystallographic planes mean a higher probability that some of the faces of the protrusion have favorable nucleation sites for deposition as observed on the sample. It is quite clear that the deposit was formed at the stage of the quenching (not diffusion annealing) because the surface morphology of protrusions are continuous and not interrupted whether their surface areas are bare or covered with the deposition, as illustrated in Fig. 4(c).

The EDS analysis detects a subtle but noticeable amount of oxygen in the deposition (not shown herein) and no other elements. It is likely that the deposition also contains high Ag content because it is expected that, upon quenching, the vapor of Ag and Zr atoms present in the gas reservoir eventually deposit on the surface of the ZrC disk (as well as the inner surface of the encapsulating alloy). However it was not possible to confirm this with EDS analysis because the

spatial resolution of EDS is not high enough to distinguish possible Ag or Zr characteristic X-ray signals of the deposition from those of the background ZrC on which the deposition layer sits.

Fig. 5. SEM micrographs of a cross-section of the diffusion annealed ZrC disk: (a) microstructure showing grains, protrusions, and the location of the SIMS measurement, (b) a close-up of the rectangle in (a) showing a protrusion formed right above excess graphitic carbon pockets, (c) a close-up of the circled area in (b) showing excess graphitic carbon, and (d) a close-up of the circle in (a) showing a protrusion formed with multiple grains, part of which is epitaxially grown.

Fig. 5 shows cross-sectional SEM micrographs of the ZrC disk retrieved from the diffusion annealed sample after SIMS analysis. Only six grains are visible in the bulk ZrC matrix in Fig. 5(a), where each grain is numbered consecutively. The approximate measurement location for the SIMS analysis is indicated as the area between the two white arrows in Fig. 5(a), which reveals that the measurement was probably conducted on a single crystalline grain (indicated as grain number 5 in this figure) of the ZrC disk. Fig. 5(b) is taken from the rectangle in Fig. 5(a), and shows pockets of pre-existing excess carbon, each of which consists of several

islands of graphite. Some of the graphite islands are further magnified in Fig. 5(c). Such islands manifest themselves in the form of a cluster of layered or planar flakes.

Small protrusions are observed, which were formed on the polished ZrC disk surface during diffusion annealing. There are a total of six such protrusions as indicated with thicker arrows in Fig. 5(a). Fig. 5(d) is a close-up of the circled area in Fig. 5(a) showing such a protrusion. It shows that some of the grains in the protrusion were epitaxially grown on the existing ZrC substrate, while the others were freshly formed by a nucleation and growth process. Therefore, it is clear that such protrusions are newly grown ZrC.

It is observed that most of the protrusions are preferentially formed above the excess graphitic carbon pockets as clearly shown in Figs. 5(b) and 5(d). Even in the case that there is no excess graphitic carbon found near a protrusion, it is most likely that excess graphitic carbon exists unnoticed nearby either below or above the cross section of the protrusion, considering metallographic statistics. Fig. 5(d) shows that the center bottom of one such protrusion contains about 20 small grains and the top contains relatively fewer and larger grains because of preferential growth of the latter grains. It also shows that the lower outer part of the protrusion is epitaxially grown from the substrate (that is, the pre-existing bulk ZrC disk), which is indicated as two areas surrounded by dashed lines.

It is not clear, however, whether the major role of the excess carbon is to promote the nucleation of new ZrC grains of a protrusion, and/or to supply carbon atoms to the protrusion. It is also not clear where zirconium atoms, the other constituent of ZrC protrusions, originate from. If the Zr atoms come from the encapsulating Zr-Ag alloy and the C atoms from the excess carbon in the bulk ZrC disk, it is expected that the C/Zr ratio varies with depth below the ZrC disk surface. The reason for this is that, from a thermodynamic viewpoint, the bulk ZrC in the original ZrC disk should increase in C/Zr ratio from a lower amount (the minimum of which is approximately 0.63 [30]) to 0.95 (unaffected carbon content in the ZrC used in this study) with an increase in the depth below the ZrC disk surface. However it turns out this is not the case according to the depth profile with SIMS, the results of which are shown in the next section. How and why ZrC protrusions form is still under scrutiny.

Fig. 6. Illustrations of ion-beam sputtering effect on Ag distribution on the surface of the ZrC disk with a newly-grown ZrC protrusion: (a) right before quenching, (b) right after quenching, (c) during ion-beam sputtering. Note that darker shades of grey indicate higher concentration of Ag.

Fig. 6 schematically outlines the effect of ion-beam sputtering on the resultant Ag distribution on the surface of the ZrC disk with a newly-grown ZrC protrusion in order to illustrate how ion-beam sputtering affects the results of SIMS analysis. The Ag adsorption and morphological changes of the ZrC disk during quenching and ensuing ion beam etching are reconstructed in this figure based on observations made during this study.

Fig. 6(a) represents the surface morphology of the ZrC disk surface near one of the newly-grown ZrC protrusions just before quenching. At this stage, a ZrC protrusion is being formed above a graphite pocket and the disk is absorbing silver liberated from the encapsulating alloy. Note that darker shades of grey indicate higher concentration of Ag. It is not unreasonable to assume that ZrC protrusions have Ag concentration as high as the flat surface of the ZrC disk. This is because Ag adsorption and ZrC growth occurs simultaneously, so Ag does not need to travel long distance by diffusion.

Upon quenching, the vapor of Ag and Zr atoms present in the gas reservoir deposits predominantly on or around the ZrC protrusion and rarely on the flat (although faceted on a nanoscale) surface of the bulk ZrC disk.

During ion-beam sputtering the deposited layer is etched away first except for the deposition situated in the shaded area as illustrated in Fig. 6(c). As the ion-beam etches away the surface of the ZrC disk, the area of the protrusion with high Ag content does not wear off readily. Consequently, the high Ag content in the protrusion yields residual Ag counts during the analysis, meaning the SIMS depth profile can contain elevated counts of Ag, even though the sampling depth may have exceeded the penetration depth of Ag in the bulk ZrC matrix. This interpretation is used to account for the measured Ag concentration profile in the next section.

3.3. Determination of diffusion coefficient

SIMS is difficult to apply for the quantitative analysis of major constituents in many complex samples, such as heterogeneous samples and multilayer samples, and samples that have varying chemistry over themselves. This is mainly because of the strong dependence of ionization probability on the chemical state of the matrix; known as the matrix effect. However, it is generally admitted that the matrix effect remains constant during SIMS analysis, when the concentration of a measured impurity is sufficiently low (roughly below 1 at.%) in the otherwise homogeneous matrix [31-33]. Recall that the maximum Ag concentration in the ZrC, which was fabricated under the conditions similar to those in the present study by Yang et al. [24], was only 0.05 wt.% (0.03 at.%). Consequently, in the present study, it is assumed that the actual concentration at this dilute level varies linearly with the measured secondary ion intensity.

Fig. 7. SIMS depth profiles of relative carbon and zirconium (^{90}Zr) concentrations in the ZrC disk. Diffusion annealing: 1500 °C/2 h. Note that the intensity in the plot represents secondary ion counts collected during the signal extraction period of an SIMS analytical cycle. Color figure available online.

Fig. 7 shows the measured SIMS depth profiles of carbon and ^{109}Ag concentration as a function of depth in the ZrC substrate. Both profiles in this figure match very well, in terms of mean value, on the given scales of each measured species from the very beginning (except for up to the initial 10 nm depth) to the end of the measurement. These results suggest that the stoichiometry of the flat bulk ZrC surface has remained essentially unchanged during diffusion annealing, because each concentration profile is plotted using a linear scale on the ordinate axis and the C/Zr ratio in the original ZrC disk is 0.95 (close to 1). This implies that there was no (or very little) contamination of the ZrC disk with the Zr originating from the Zr-Ag encapsulating

alloy as expected because of the very low vapor pressure of Zr at the diffusion annealing temperature (that is, only about 4.8×10^{-6} Pa for pure Zr [34]). Meanwhile, both profiles also show slight decrease with depth, which is probably associated with topographical disturbance – that is, sputtering rate on the ZrC is not ideally steady state due to the existence of newly grown ZrC protrusions.

Incidentally, SiC in lieu of ZrC coating has been commonly used to fabricate TRISO fuel particles. It is difficult to use the encapsulating source method to determine the Ag diffusivity in SiC, because it is difficult to fabricate an indigenous Si-Ag encapsulating alloy because the Ag solubility in Si is very low. Even the highest calculated solubility is only 1.8×10^{-4} at.% at eutectic temperature of 837 °C [35]. Therefore, it is interesting to consider the possibility that the Zr-Ag alloy might also be used to encapsulate SiC for determining Ag diffusivity in SiC. The use of a Zr-Ag alloy may be feasible because, just as the ZrC was not contaminated, so the SiC is not expected to be contaminated with Zr released from the encapsulating alloy as discussed above.

Fig. 8. Silver (^{109}Ag) concentration profile measured using SIMS and curve fitting for determining the Ag diffusion coefficient in ZrC at 1500 °C.

Fig. 8 represents a silver concentration profile measured using SIMS and curve fitting for determining the Ag diffusion coefficient in ZrC at 1500 °C. It turns out that the curve fitting does not show good match when applying Eq. (3) as is. However, if an appropriate mathematical solution plotted using that equation is shifted by 4.5 counts in the positive direction, this modified mathematical curve fits surprisingly well with the experimental data except for those measured within the initial depth of about 120 nm below the surface.

The occurrence of the transition regime can probably be explained by the notion that the Ag-bearing deposition layer illustrated in Figs. 6(b) and 6(c) is removed during the initial stage of sputtering, causing high Ag counts because it contains high Ag content and/or the ionization rate of Ag in the deposition may be much higher than that in the ZrC disk.

Meanwhile, the shift in curve fitting may well be explained by a combination of the existence of Ag-bearing protrusions and the shadowing effect. Firstly, the newly grown ZrC protrusions containing a high concentration of Ag keep contributing to the Ag counts until the end of the measurement, as discussed in the last paragraph in Section 3.2. Recall that the total area of the protrusions located inside the scanned area for the SIMS analysis accounts for roughly 13% of the total scanned area. Since the Ag concentration at the surface is 46 counts according to the best-fit mathematical curve, the 4.5 counts amounts to about 10% of that concentration, quite close to 13%. Additionally, it is expected that the gradual removal of the outer edges of the shaded areas of the deposited layer maintains the additional contribution to part of the Ag count as further sputtering proceeds until the deposition layer is completely sputtered away. Such annealing-induced disturbance indicates that ZrC with lower C/Zr (thus, containing no or less graphite) is probably more suitable for the encapsulating source method. In such case, ZrC protrusions are less likely to form and thus the morphology of the original ZrC disk surface is less disturbed.

Fig. 8 shows Ag concentration profile measured using SIMS and curve fitting for determining the Ag diffusion coefficient in ZrC at 1500 °C. Note that every five original data points are binned to help clean up the plot by making fewer data points. Five data points in each set are averaged and presented with error bars (one standard deviation) to give an intuitive overview of the measurement reproducibility. Such data binning is not unreasonable because maximum depth variation within the five data points is only 25 nm and concentration variation caused by poor reproducibility of the measurement is much greater than actual concentration variation over such a short distance.

Fig. 8 demonstrates that the measured depth profile seems to be effectively reconciled with the diffusion profile shifted from the one plotted using Eq. (1). Based on the resultant corrected curve fitting, the diffusion coefficient of Ag in (most likely single-crystalline) $\text{ZrC}_{0.95}$ at 1500 °C is determined to be $1.7 \times 10^{-17} \text{ m}^2/\text{s}$.

It is worthwhile to mention how the possible steady decrease of the sputter rate in Fig. 7 may affect the Ag SIMS signal. One plausible explanation for the SIMS signal decrease with sputter depth is that the corners of the protrusions are readily etched with ion-beam bombardment at the initial stage of ion-beam etching and become obtuse (or round) over time. As a rough approximation, it can be assumed that the etch rate of the flat crater bottom of the ZrC disk remains constant, while that of the protrusions decreases linearly with crater depth. According to curve fitting based on the assumption that the sputter rate changes in this way for the Ag SIMS signal, the Ag diffusivity becomes about $1.6 \times 10^{-17} \text{ m}^2/\text{s}$, practically identical to $1.7 \times 10^{-17} \text{ m}^2/\text{s}$. Therefore the possible decrease in sputter rate for Ag concentration measurement is not taken into consideration in Fig. 8.

It is worth comparing this diffusivity value with that obtained by Yang et al. [24] using WDS. They diffusion annealed a virtually single-crystalline $\text{ZrC}_{0.84}$ at 1500°C for 50 h (25 times longer than that applied in the present study) within the same domain of the encapsulating source method. The Ag diffusivity in their work was determined to be $2.8 \times 10^{-17} \text{ m}^2/\text{s}$. A direct comparison between the two results is not possible because the difference in carbon stoichiometry may affect the resultant diffusivity values to an extent; however, the true diffusivity values are estimated to be somewhat, but not by orders of magnitude, different from one another. From an experimental point of view, the two experimental results obtained from either a 2-hour or 50-hour annealing sample are in very good agreement with one another, which supports the validity of the encapsulating source method. At least at this point, the encapsulating source method is clearly the method of choice for determining the Ag diffusivity in ZrC at high temperatures.

3.4. Future research

Although the work detailed in this study provides a viable technique using SIMS to measure Ag diffusivity in ZrC, especially at relatively low temperatures (below about 1500°C), future work should be conducted using graphite-free ZrC to determine the diffusivity more accurately. $\text{ZrC}_{0.95}$ (instead of $\text{ZrC}_{0.84}$) was used in the present study, simply because ZrC with a C/Zr ratio lower than 0.95 was no longer available. Unlike $\text{ZrC}_{0.84}$ used in the preceding study [24], $\text{ZrC}_{0.95}$ contained pre-existing graphite and which eventually led to the formation of ZrC protrusions on the surface of the existing ZrC disk during diffusion annealing as shown in

Section 3.2. The formation of the ZrC protrusions disturbed the surface morphology of the initial ZrC disk, possibly affecting the measured Ag diffusivity to some extent. Consequently, it is advisable to use graphite-free ZrC with a lower C/Zr ratio, which would make it more straightforward to accurately interpret a measured concentration profile for Ag diffusivity determination. It should be noted that the ZrC fabricated in the fluidized bed CVD ZrC for nuclear fuel applications does not usually contain excess graphitic carbon in itself.

Conclusions

Insufficient experimental data on Ag diffusivity in ZrC, mainly due to experimental difficulties, have hindered the modeling efforts that seek to predict and improve fuel performance through basic understanding of the $^{110\text{m}}\text{Ag}$ release in the ZrC TRISO-coated nuclear particle fuel. Recently, a new diffusion experimental technique, known as the encapsulating source method, has been developed to overcome such experimental difficulties. In the present study, several improvements in the experimental setup and procedure were made within the domain of the encapsulating source method. Improved samples were then analyzed using a very high sensitivity surface analysis technique, SIMS. The resultant impurity diffusion coefficient of Ag in virtually single-crystalline $\text{ZrC}_{0.95}$ at 1500 °C was experimentally determined to be approximately $1.7 \times 10^{-17} \text{ m}^2/\text{s}$. Finally, the validity of this method was verified by comparing this result with the previously reported value of $2.8 \times 10^{-17} \text{ m}^2/\text{s}$, which was also obtained by means of the encapsulating source method. This comparison demonstrated that the encapsulating source method was indeed to be valid for determining Ag diffusivities in ZrC. Consequently, it can be expected that the encapsulating source method may be a viable alternative to conventional experimental techniques, when no such traditional methods are available for a given material system.

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