Silver Diffusion in Coated Fuel Particles

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II. Experimental Procedure

A detailed description of the CVD machine used can be found elsewhere.¹ Two types of SiC coatings were deposited on top of the inner pyrolytic carbon layer (Fig. 1) in a hydrogen environment as follows: SiC-LT—at 1300°C with 9.1 vol% methyltrichlorosilane (MTS) concentration; SiC-PR—at 1300°C with 9.1 vol% MTS and 0.5 vol% propylene. Then silver paste (Johnson Matthey E8100, Johnson Matthey, London, U.K.) was applied on top of the particles and heat treated up to 690°C in air to burn out the organic components. Particles were then dip coated in a solution containing polycarbosilane (PCS) in xylene and dried in air. A detailed description of the preparation of a PCS layer has been reported elsewhere.⁸ Samples were first heat treated in air at 200°C for 2 h and then in an argon atmosphere at 950°C for 0.5 h in order to transform the PCS into SiC+C.⁹ About 50 coated SiC/Ag/PCS particles were then loaded together with 30 g of alumina spheres into the reaction chamber where another layer (external layer) of SiC coating was deposited with a similar deposition temperature and MTS concentration (but different surface area/volume ratio) as that for the deposition of the original SiC layer (inner layer) before the application of Ag. Samples were then heat treated for 240 h at 950°C to 1500°C in an argon atmosphere.

Samples were embedded in copper-loaded resin and polished to the cross section. As-deposited samples were chemically etched for an hour in 100 mL of boiling water containing 10 g of NaOH and 10 g of FeK₃(CN)₆. The microstructures were analyzed using a Philips XL30 FEG-SEM (Philips, Eindhoven, the Netherlands) microscope coupled with an energy-dispersive X-ray spectrometer (EDX). Stoichiometry was characterized by Raman spectroscopy using a Renishaw-1000 system (Renishaw plc., Gloucestershire, U.K.) with a He/Ne laser with a 633 nm wavelength. Transmission electron microscopy (TEM) samples of the as-deposited coatings were made by focused ion beam milling (Dual beam FIB/SEM-FEI Nova Nanolab 600, FEI Company, Hillsboro, OR) and observed with a TEM-FEI Tecnai G2 F30 (FEI Company).

III. Results and Discussion

Figure 1 shows an SEM image providing clear evidence that silver can be successfully trapped between two layers of SiC, both deposited by fluidized bed chemical vapor deposition. Without the PCS layer we observed that the silver would melt away before any SiC could be deposited in time to trap the thin layer of silver. It should be noted that the intermediate layer of SiC+C is 1–5 µm thick. For most of the samples only the inner SiC coating was analyzed because this coating is in direct contact with the silver. In some cases, Ag was found to diffuse on the external SiC because Ag diffused through a broken SiC+C layer produced from PCS.

Figure 2 shows that SiC-LT has a clear diffusion of silver through the inner SiC coating as confirmed by EDX analysis (not shown). These results provide evidence that silver can diffuse in stoichiometric SiC, thus refuting the idea that silver diffuses due the presence of excess Si (except SiC-PR which...
contained excess carbon, the other sample was stoichiometric. Figure 2(b) shows silver distributed in parallel columns in a feather-like structure due to the presence of large columnar grains (Fig. 2(f)). This parallel arrangement suggests that silver is located at the grain boundaries. High-magnification SEM images also show the presence of silver at the grain boundaries at the diffusion front (Fig. 2(c)). Although silver could 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 silver diffusion.\(^5\) Bulk diffusion would only give a diffusion rate \(\frac{10^{-20}}{10^{-18}} \text{m}^2/\text{s}\) (at 1300°C), at least four orders of magnitude lower than those measured in coated particles.\(^1\) Furthermore, theoretical work have suggested that bulk diffusion would only dominate the diffusion process at large grain sizes (>10 \(\mu\)m) and much higher temperatures (>1600°C).\(^10\) Due to these reasons, it is likely that the silver detected at the grain boundaries is the result of a diffusion process partially controlled by grain-boundary diffusion and even triple junctions.\(^10\) Interestingly, as can be seen in Figs. 2(a) and (e), silver diffusion also had a laminar pattern. A similar laminar pattern was observed after chemical etching (Fig. 2(d)). This pattern has been attributed to the presence of discontinuities in the structure (i.e., possibly nanoporosity, amorphous phases, lattice mismatch, etc.) produced by the interruption in the deposition of SiC as it cycles in and out of the gas stream where most of the deposition occurs.\(^1\) Silver was observed around 8 \(\mu\)m inside the inner SiC even before any heat treatment due to the large concentration of porosity in this section of the coating. At 950°C, 1150°C, and 1500°C, silver was clearly detected on average at 1.7, 3.7, and 50.9 \(\mu\)m, respectively, beyond the initial position of silver inside the coating (Figs. 2(a) and (e)). An estimate of the diffusion coefficients can be calculated with\(^12\):

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D = \frac{X^2}{2t}\quad (1)
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where \(D\) is the diffusion coefficient \((\text{m}^2/\text{s})\), \(X\) is the diffusion distance \((\text{m})\), and \(t\) is the time under heat treatment \((\text{s})\). The diffusion coefficients calculated are \(3.46 \times 10^{-16} \text{m}^2/\text{s}\) for 950°C, \(1.55 \times 10^{-17} \text{m}^2/\text{s}\) for 1150°C, and \(2.99 \times 10^{-15} \text{m}^2/\text{s}\) for 1500°C. These diffusion coefficients are within the range of values recently calculated as best estimates for silver diffusion in SiC using the results of the German HTR program.\(^1\) The presence of defects (i.e., porosity) will no doubt enhanced the diffusion process, however it is likely that these diffusion coefficients are obtained from a sequence of grain-boundary diffusion—defects—grain-boundary diffusion, etc. because these defects are in a parallel arrangement and generally separated by at least one grain (Figs. 2(c) and (f)). Therefore, despite the presence of defects, grain-boundary diffusion will play a very important role in the diffusion of silver.

Figure 3(a) shows that the coating SiC-PR, although deposited at the same temperature with a slight change in composition of the precursor compared with the deposition of SiC-LT (Fig. 2), did not show any clear presence of silver inside the SiC as that found in Fig. 2. This would suggest that SiC-PR was more impervious to silver diffusion. Figure 3(b) shows that this coating also developed laminar features after chemical etching, similar to that found in Fig. 2(d), therefore the existence of this laminar character cannot be directly accountable for the diffusion of silver detected in SiC-LT (Fig. 2). Figure 4 shows TEM images of two SiC samples with high and low diffusion rates of Ag. Neither has shown clear evidence of the presence of porosity. Interestingly, the sample SiC-LT with clear diffusion of silver had smooth grain boundaries (arrows in Fig. 4(a)), whereas the coating SiC-PR with the lowest diffusion of silver had very rough and tortuous grain boundaries. Although this result could agree with previous observations suggesting that columnar grains with smooth grain boundaries enhance the diffusion of silver.
fission products, by possibly providing a more direct diffusion path,\textsuperscript{13} it does not agree with the idea that rough grain boundaries generally have higher grain-boundary diffusivities\textsuperscript{14} due to a higher free energy and concentration of defects. Further work is currently underway to characterize into detail the differences between these two microstructures that could help us elucidate this variation in diffusion behavior.

Although the existence of nanocracks cannot be totally disregarded at the moment, the idea of nanocracks formed by the stress developed due to differences in the coefficients of thermal expansion between PyC and SiC after deposition as suggested by MacLean\textsuperscript{15} is not supported by our results. By this simple reasoning, between sample SiC-LT and SiC-PR, both deposited at the same temperature (1300 °C), we would expect that sample SiC-PR would develop a higher intrinsic stress\textsuperscript{16} due to a higher coating rate (0.5 and 1 \( \mu \)m/min, respectively), thus being more prone to crack formation and a higher silver diffusion. However as it was shown in Fig. 3(a) this was not the case. It is more likely that defects enhancing silver diffusion (Fig. 2(a)) are produced due to the intrinsic lack of uniform deposition conditions in fluidized bed CVD (substrate fluctuates in and out of areas with different residence times, precursor concentrations, and even temperature due to temperature gradients in the coater). Although the presence of these defects could greatly enhance silver diffusion, our results do not support the idea that they dominate this process as suggested by MacLean et al.\textsuperscript{4} Silver in sample SiC-LT (Fig. 2(a)) is arranged in a laminar pattern (Fig. 2(a)) where defects are located (Fig. 2(d)). Although sample SiC-PR had similar pattern (Fig. 3(b)) silver did not diffuse into SiC (Fig. 3(a)), suggesting that the characteristics of the grain boundary (Fig. 4) are possibly the dominant factor.

Interestingly, a recent report\textsuperscript{17} has shown that the SiC coatings of TRISO particles, deposited at 1400 °C have a high concentration of high-angle grain boundaries and that the strains detected in the microstructure increase with coating thickness. These types of characteristics could be very important because it has been observed that a higher concentration of high-angle/ high-energy grain boundaries can greatly enhance diffusivity.\textsuperscript{18} For instance it has been observed that even among high-angle grain boundaries there could be differences in their diffusion coefficients of the order of several orders of magnitude.\textsuperscript{19} Some of these types of high-energy grain boundaries have shown to be able to enhance diffusion by reducing the energy necessary for vacancy formation.\textsuperscript{20,21} Likewise, it has been suggested that the presence of strains in the microstructure may increase the diffusion by introducing a lattice dilation.\textsuperscript{22} It is likely that different deposition conditions will have different effects on the texture, grain size, and grain-boundary characteristics. Therefore, the presence of high-angle grain boundaries, strains in the microstructure, the presence of amorphous phases, nanoporosity, and other microstructural features (defects) need to be considered as possible controlling factors of the release of silver. Here lies the importance of characterizing the SiC used in TRISO particles rather than SiC wafers or even SiC on flat substrates because

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**Fig. 3.** Silicon carbide (SiC)-PR coating heat treated at 1150 °C for 240 h. (a) SiC-PR coating showing no clear diffusion of silver; (b) Chemically etched surface of SiC-PR.

**Fig. 4.** TEM images showing the differences in grain-boundary tortuosity between samples with (a) high silver diffusion and (b) low silver diffusion.
they do not produce the same characteristics as those found in the coated particles.

IV. Conclusions

In summary, we have provided a novel method to trap Ag inside the SiC coatings of TRISO particles, which allows us to study the effect of the SiC microstructure on the diffusion of silver in coated fuel particles for the first time. After decades of speculation we have shown that silver can diffuse in stoichiometric SiC. Despite some speculations it has been confirmed that the SiC microstructure has a big impact on the release of silver. Contrary to a more recent theory, our results do not support the idea of silver diffusing due to the presence of nanocracks. Our results show that despite the presence of defect in a laminar pattern, the diffusion of silver is strongly affected by grain-boundary diffusion, 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 silver diffusion. Our results also suggest that it is possible to greatly reduce silver diffusion by carefully controlling the microstructure of SiC.

References