SiC Grain Boundary Character and Fission Product Transport in Irradiated TRISO Fuel Particles
Isabella J. van Rooyen and Tom M. Lillo

Background

Post-irradiation examination of tristructural isotropic (TRISO) fuel particles from the first Idaho National Laboratory’s Advanced Gas Reactor (AGR)-1 experiment, using scanning transmission electron microscopy and energy dispersive spectroscopy analysis, identified both intragranular and intergranular fission product precipitates, ranging in size from several microns (predominantly at or close to the silicon carbide [SiC]-inner pyrolytic carbon interface) to nanoscale precipitates as small as about 2 nm through the entire SiC layer thickness [1-5]. During these AGR-1 research activities on various lamellae from coated particles irradiated to levels between $10^4$ to $10^9$°C, it was found that silver (Ag)-containing precipitates are predominantly located at grain boundaries and triple points, with only two sitings within an SiC grain, of which one Ag-containing precipitate was allocated at a stacking fault [6].

The predominant association of Ag-containing precipitates at grain boundaries and triple points in neutron-irradiated SiC layers of the AGR-1 experiment, in addition to various out-of-pile experimental and modeling work [7-10], suggests grain boundary diffusion as a potential transport mechanism for Ag. To determine the influence of grain boundary character on fission-product migration in SiC, it was necessary to employ techniques that can determine misorientation across individual grain boundaries, including grain boundaries that contain and those that do not contain fission products. While scanning electron microscopy-based electron backscattered diffusion and transmission Kikuchi diffraction or t-electron backscattered diffusion can determine grain boundary misorientation, it is not possible to identify the nano-sized fission product precipitates on the grain boundaries or identify the composition of these nano-precipitates. Therefore, precession electron diffraction (PED) (i.e., a transmission electron microscope [TEM]-based technique) was explored [11]. The advantage of PED is that it utilizes a very small electron-beam spot size (i.e., about 5 nm or less) and the interaction volume is on the order of the beam size because the sample is very thin. Both enable a very small step size and high spatial resolution, allowing orientation analysis at the nanolevel. A method using PED on the SiC layer of an unirradiated TRISO fuel particle has been demonstrated [12].

Experimental Samples

Three TEM samples (referred to as inner, center, and outer, respectively) from particle AGR1-632-035 (compact irradiated to 11.4% fissions per initial metal atom to a time-average, volume-average temperature of 1070°C) were prepared by standard focused ion beam methods at the locations in Figure 1 to obtain qualitative information as a function of distance through the thickness of the SiC layer. Individual particle burnup and temperature may have varied considerably from the compact average depending on its location within the compact.

Figure 1. Focused ion beam-prepared TEM samples from particle AGR1-632-035 were taken from the general area indicated in (a), while the specific locations of the TEM samples are indicated in (b): inner (IE), center (Ctr), and outer (OE). The center sample significantly overlaps the IE and OE samples.
Experimental Results: Grain Boundary Data for Grain Boundaries Containing Fission Products

Figure 2 shows one area with fission product precipitates that was analyzed for composition and associated grain boundary information, as an example of the type of information that was obtained from analysis areas. In this particular area, seven grain boundary segments exhibited fission product precipitates. Even though all segments were connected, the fission products present in each segment were not necessarily the same (Table 1). Most segments contained palladium (Pd) with the exception of Boundary Segments 2 and 3, which contain only Ag. In this example, it appears that the grain boundary parameters, which determine grain boundary energy and grain boundary atomic structure, affect which fission products may be present on a particular grain boundary segment. Boundary Segments 1, 2, 3, and 4 in Table 1 are all considered to be random, high-angle grain boundaries; all are expected to be relatively high energy and with no expected specific repeating atomic structure because they are random grain boundaries and yet they exhibit elevated levels of different fission product elements. They must possess unique characteristics, energy, or atomic structures, which allow preferential segregation of certain fission product elements to them. In any case, the specific boundary parameters strongly influence the diffusion of the various fission products.

Table 1. Summary of fission product precipitate information and associated grain boundary information (• indicates the presence of fission product) [13].

<table>
<thead>
<tr>
<th>Grain Boundary Segment</th>
<th>Angle</th>
<th>Axis</th>
<th>CSL designation</th>
<th>Pd</th>
<th>Ag</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.6</td>
<td>20 13-13</td>
<td>—</td>
<td>•</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>45.7</td>
<td>5 13 15</td>
<td>—</td>
<td></td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>54.2</td>
<td>18 2-15</td>
<td>—</td>
<td></td>
<td>•</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>43.6</td>
<td>4 16-19</td>
<td>—</td>
<td>•</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>38.7</td>
<td>1 0 1</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>56.8</td>
<td>20 1-23</td>
<td>—</td>
<td>•</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>13.8</td>
<td>-7 23-18</td>
<td>—</td>
<td>•</td>
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</tr>
</tbody>
</table>
Experimental Results: Summary of Precipitate Composition and Associated Grain Boundary Information

SiC grain boundary precipitates were most prevalent near the IPyC layer (Figure 3, inner sample), which is as expected because this location is nearest the source of the fission products (i.e., the central fuel kernel). The occurrence of specific fission product elements and their combinations revealed interesting trends related to grain boundary type. Precipitates that contain only Pd seem to occur on all types of grain boundaries, with preference for random, high-angle grain boundaries. However, when Pd was found in conjunction with either Ag or uranium (U), low-angle grain boundaries no longer appear to be viable defects for formation of fission product precipitates. Also, Ag by itself was found to only occur on random, high-angle grain boundaries and never on low-angle or coincident site lattice (CSL)-related grain boundaries. The larger atomic radii of Ag or U can potentially increase the strain energy of such precipitates on low energy boundaries to the point where they are no longer energetically favorable. The almost complete lack of solubility of Ag in SiC [16] (i.e., a thermodynamic consideration) may also prevent precipitation on low angle and CSL-related boundaries.

The presence of Ag only precipitates when Pd is close by remains unexplained. Another study [14] also shows that Ag is capable of diffusing through SiC, even when Pd is not present. However, if Pd were available, as in the present study, then one would expect to find only Pd+Ag precipitates due to the complete solubility of Ag in Pd [15] if the precipitates are metallic solid solutions. If a particular boundary possesses a grain boundary energy and structure amenable for Ag-only precipitates (i.e., random, high-angle grain boundaries; Figure 4), then Pd would not be expected to be excluded from also being present on this boundary, because it can precipitate on grain boundaries of all types and energies. Thus, it is not clear what combination of grain boundary energy and structure could allow precipitation of Ag and prevent Pd from also precipitating. However, Pd may actually be present in the Ag-only precipitates, but at levels below the limits of detection for the characterization methods. The same may be said of the Pd-only precipitates, Ag may actually be present but below the limits of detection. If so, then the grain boundary structure and/or energy of random, high-angle grain boundaries somehow determine the ratio of Ag to Pd in the fission products.
product precipitate, again implying that not all random, high-angle grain boundaries should be considered equivalent or even similar when it comes to segregation and transport of fission product elements.

Conversely, if the precipitates are actually silicides, then it might be possible to have Ag in solid solution in a Pd-silicide produce the Pd+Ag precipitates and not have Pd in solid solution in an Ag-silicide to produce the Ag-only precipitates. However, Ag-silicides do not seem to occur [17]. Therefore, the existence of Ag-only precipitates found in this study is unexplained at this time and will require determination of not only the crystal structure of the Ag-only precipitates but also that of the Pd and Pd+U precipitates to fully understand segregation of the fission product elements during (and after) irradiation. A more detailed understanding of the grain boundary energy and grain boundary structure also will be required.

Conclusions

The PED method developed earlier on unirradiated SiC was successfully used to determine the grain boundary misorientation angle and axis in the SiC layer of an irradiated TRISO fuel particle. It was also successfully demonstrated that detailed grain boundary characteristics in the vicinity of fission products could be established and compared to areas without fission products. These results show great promise for revealing the relationship between SiC grain boundary character and fission product migration through the SiC layer of TRISO-coated fuel particles. Specific findings are listed [13] as follows:

- Fission product precipitates were commonly found on random, high-angle grain boundaries and to a lesser degree at low-angle and CSL-related grain boundaries.
- Pd was found at all types of grain boundaries, but most prominently on random, high-angle grain boundaries.
- Pd-U and Pd-Ag precipitates were found on CSL-related and random, high angle grain boundaries, but not on low-angle grain boundaries.
- Precipitates containing only Ag were only found on random, high-angle grain boundaries (i.e., not on either low-angle or CSL-related grain boundaries). The reason for Ag-only precipitates is not known.

This study was expanded to obtain information from more TRISO particles from the AGR-1 experiment to enable comparative datasets. These results are now being analyzed and integrated into the final AGR-1 advanced microscopy report.

It is further recommended that efforts be made to analyze the grain boundary plane in addition to the other grain boundary parameters to fully understand the influence of grain boundaries on fission product migration through the SiC layer of TRISO and, ultimately, fission product release during irradiation.

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References


Isabella J. van Rooyen

Isabella J van Rooyen (Ph.D., 2011, Physics, Nelson Mandela Metropolitan University; M.Sc., 1988, Metallurgy, University of Pretoria; MBA, 2003, Business Administration, North West University; B.Sc., 1981, Metallurgy, University of Pretoria; B.Sc. Honors, 1983, Metallurgy, University of Pretoria) is a Distinguished Staff Scientist at INL where she leads the advanced electron microscopy, and micro-analysis examinations for the Advanced Gas Reactor TRISO fuel development program from 2011. Additionally, she is also the principal investigator (PI) of an additive manufacturing U3Si2 fuel research project, the PI or co-PI of 4 research projects funded by the national scientific users facility as well as a co-PI on a Nuclear Energy University Program research project focusing on SiC-ODS alloy gradient nano composite cladding. Prior to joining INL, Dr. van Rooyen held various technical leadership roles in the nuclear, aerospace and automotive industries in South Africa, with most notable the research at Pebble Bed Modular Reactor (PBMR) Company and NECSA. Dr. van Rooyen has in excess of 30 peer reviewed journal publications, more than 40 conference papers and presentations, over 100 company specific technical/scientific reports, three invention disclosures and one patent application in progress.

Tom Lillo

Thomas Lillo (Ph.D., 1994, Metallurgical Engineering, Michigan Technological University) is a staff scientist in the Department of Materials Science and Engineering with 20+ years of experience in materials characterization of high-temperature metallic alloys, intermetallic alloys, ceramics, and composites for power generation applications. He has expertise in the areas of TEM, SEM, OIM, and x-ray diffraction. Additionally, he is directing a study on the high-temperature creep behavior of alloys for the intermediate heat exchanger of the very high-temperature reactor. Dr. Lillo has in excess of 30 technical publications and has collaborated on six patents.