Neutron Irradiation-Induced Damage and Associated Intragranular Fission Product Transport Mechanisms in SiC Layer of TRISO Fuel Particles

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Background

Certain metallic fission products are found to transport into and through the silicon carbide (SiC) layer of tristructural isotropic (TRISO) nuclear fuel particles, and various studies have been undertaken to understand this transport behavior [1,2]. While the trapping or precipitation of fission products in the form of multi-phased complex compounds at grain boundaries is most probable from a metallurgical perspective [2,3], the intragranular nanoscale precipitation of fission products, mainly Pd silicide, has raised questions regarding their transport mechanisms [1,4]. Moreover, research on neutron irradiation damage tolerance of SiC and its composites, used in TRISO fuel and a candidate accident tolerant fuel cladding for light-water reactors, has neglected the low-temperature irradiation-induced "polymorphism" of SiC. In the post-irradiation advanced microscopy effort at Idaho National Laboratory (INL), a surprising two-step nucleation route has been discovered through which nanoscale distribution of the second phase is achieved by reaction of fission products with neutron irradiation-induced precursors [5]. In the first step, nanoscale α–SiC precipitates in a α–SiC matrix unexpectedly nucleate heterogeneously at structural defects. This occurs at significantly lower temperatures compared with the usual β→α transition temperature. Subsequently, α–SiC precipitate acts as a surrogate template for its structural and compositional transition into a fission product precipitate, Pd silicide. Research on possible influence of the neutron irradiation-induced damage structures on this nucleation process has been carried out.

Experimental Samples

TRISO-coated nuclear fuels were fabricated using a chemical vapor deposition process and subjected to irradiation under the Advanced Gas Reactor (AGR)-1 and AGR-2 experimental programs in the Advanced Test Reactor at INL. Samples for transmission electron microscopy (TEM) were prepared by a dual-beam Quanta three-dimensional focused ion beam instrument. Scanning transmission electron microscopy (STEM) and conventional TEM analysis were conducted on an FEI Tecnai F30 microscope operated at 300 kV, at the Microscopy and Characterization Suite Laboratory at the Center for Advanced Energy Studies.

Experimental Results—A Dual-Step Intragranular Transport Mechanism of Fission Products

Figure 1(a) shows voids and polygonal-shaped precipitates with edge lengths of about 20–30 nm that are mostly observed on Frank loops on {111} planes. The approximate volume fraction of these precipitates is less than one percent of the entire grain of β-SiC under study. Previous TEM results on unirradiated β-SiC samples do not show any Frank loops or polygonal precipitates. Their chemical identities are revealed by the energy dispersive spectroscopy analysis in TEM. While the precipitate indicated by the blue box in Figure 1(b) did not contain any element other than Si and C, a significant amount of Pd (a fission product) was found along with Si and C in the precipitate indicated by the red box in Figure 1(b). The presence of a fission product other than Pd in these precipitates was not observed in this study. The diffraction study confirmed them to be α-SiC (hexagonal 4H or 6H) and $L1_2$ structure Pd_3Si precipitates. The usual transformation of β-SiC into α-SiC takes place at 2,000°C or higher [6]. This unusual behavior can be attributed to accelerated diffusion in Si and C that facilitates reconstructive transformation of β-SiC into α-SiC heterogeneously at linear and planar defects [7]. Unlike the isolated

α-SiC and Pd-rich precipitates presented in Figure 1(b), an interesting feature in Figure 1(c) is a nanoscale region that resides in β-SiC and has varied contrast within its own periphery. The image not only shows the contrast in mass of the two regions confined in the periphery of the precipitate, but also the appearance of different crystallography. From this evidence, it appears that the diffusional transformation of α-SiC into Pd_3Si is aided by the intragranular transport of Pd via linear or planar defects. These results lead to the intriguing puzzle of why Pd reacts with the α variant of SiC only. Interestingly, the presence of nanoscale α–SiC variant avails the readiness of Pd reaction with SiC as compared with that with a single-phase, β-SiC [8]. It can be extrapolated that α-SiC precipitates potentially accelerated the Pd-silicide formation. It is probably energetically expensive for Pd silicide to create new semi-coherent or incoherent interfaces with the β-SiC phase, together with the fact that it has a lower chemical affinity with β-SiC. This allows Pd_3Si precipitates to be metamorphosed upon the surrogate α-SiC phase without movement of any phase boundary.

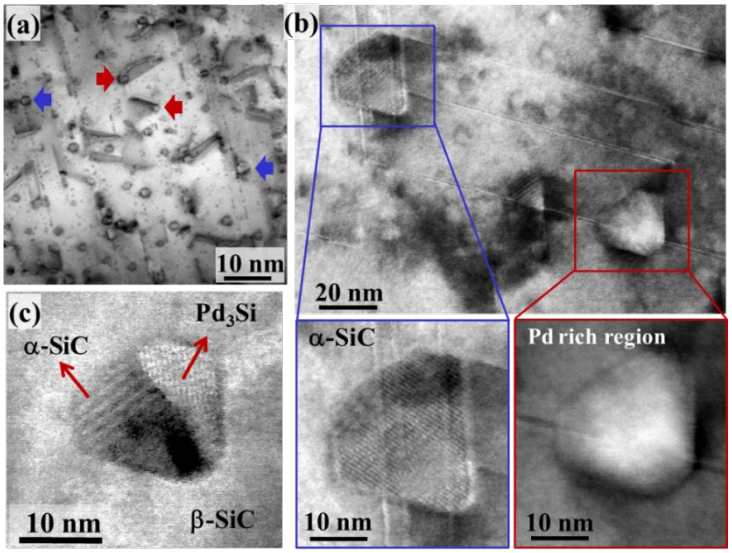

Figure 1: Neutron irradiation-induced microstructural changes in a β-SiC layer of TRISO-coated fuel particle. a) A STEM micrograph of β-SiC along [110] zone axis, reveals Frank loops, stacking faults and damages induced due to irradiation at a fluence of 2.38×10^{21} n/m^2 in a temperature range of 1,000-1,200°C. Red arrows indicate the precipitates at the ends of Frank loops. Blue arrows indicate precipitates along stacking faults. b) A STEM micrograph shows polygonal structures at structural defects with different chemical compositions. Energy dispersive spectrometry in TEM indicates a significant amount of Pd, along with Si and C, in the precipitate labelled by the red box. The precipitate labelled by the blue box contains only Si and C. c) A STEM micrograph along <110> of the β-SiC matrix clearly shows imprinting of Pd silicide into morphological templates of α-SiC precipitates. Different crystallography and mass contrast within the precipitate are clearly visible.

Experimental Results—Irradiation-Induced Damage Structures

In both AGR-1 and AGR-2 experiments, neutron irradiation-induced cavities were observed in TEM, though their distribution and sizes are not homogenous. Figure 2(a) shows preferential formation of cavities at stacking faults, though it is unclear if the migration of cavities took place during post-irradiation cooling or during the duration of the heating while irradiated. While these cavities appear to be black spots with very small size (1-2 nm) in the AGR1-433-001 TRISO particle, they are usually 3-5 nm in size in other TRISO particles with mostly polygonal shape. In Figure 2(b), the β-SiC layer of the AGR2-222-RS36 particle is analyzed along its <011> direction. Two sides of the voids parallel to the [111] and [111] planes, respectively, while the other side is parallel to the $(\bar{2}20)$ direction. The dislocation loops and void are repetitively appeared to be associated with α-SiC or Pd-silicide precipitates, as shown in Figure 2(c-d), only in the TRISO particle that was subjected to post-irradiation heating at 1600°C for 300 h. Further microstructural investigation is recommended to ensure whether these precipitates act as sink sites for cavities during safety-tested thermal treatment or the defects aid the intragranular nucleation at first place.

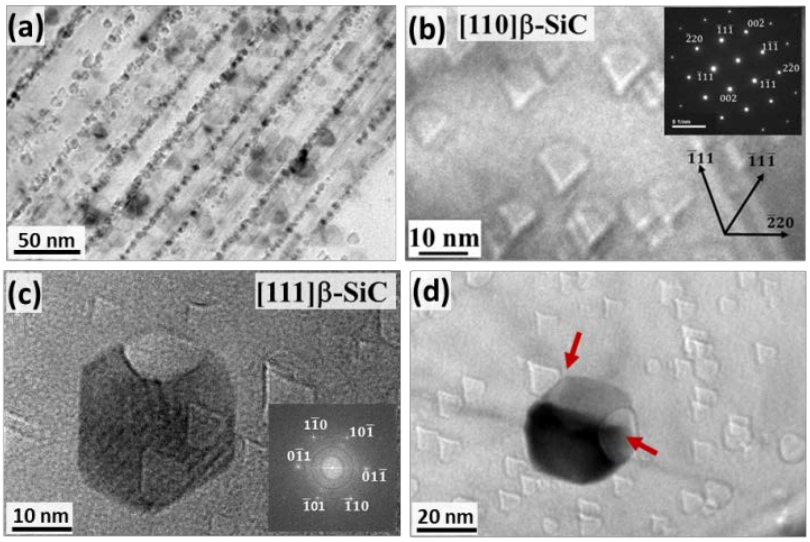

Figure 2: TEM study under kinematical underfocus or overfocus to understand the nature of neutron irradiation-induced defects. (a) A bright field TEM image shows preferential cavity formation/segregation at structural defects such as stacking faults. (b) The polygonal shape of cavities is identified in most of the TRISO particles. (c-d) Dislocation loops and cavities appear to be associated with α-SiC and Pd-silicide precipitates in AGR1-433-001 particle that was subjected to post-irradiation heating at 1600°C for 300 h.

Conclusions

The fission product transport in a SiC layer of TRISO fuel via a heterogeneous nucleation process has been discovered that involves two discrete reconstructive and diffusive transformations in a sequence. Specific findings are listed as follows:

- The low temperature α-SiC formed upon the irradiation-induced reconstructive transformation of β-SiC subsequently acts as a surrogate phase and facilitates its reaction with Pd (a fission product) that is transported in the microstructure via linear and planar defects.
- The Pd-silicide compound adopts the exact morphology of the parent phase (α-SiC) without movement of any phase boundary and does not require the activation energy otherwise required for its nucleation.
- The irradiation defects distribution is inhomogeneous in SiC, and they appear to be associated with intragranular fission products.

The present dual-step nucleation process challenges the conventional wisdom of precipitation in a nuclear reactor environment. The knowledge gained from irradiated fuel analysis could be applied to irradiation engineering for nanostructured SiC that can be useful for electronic or spintronic applications [9, 10].

A future research plan involves atomic-scale structural and compositional analyses along with three-dimensional electron tomography using INL's unique microscopy capability. This approach will lead to better understanding of the role of dislocations and cavities in Pd transport to the α-SiC sites and subsequent precipitation.

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Dr. Subhashish Meher is a Staff Scientist in the Materials Science and Engineering Department at INL. Since joining the research team in 2014, he has studied the extended microstructural stability of high refractory containing nickel-base superalloys using advanced characterization tools such as atom probe tomography and TEM. A component of his work has also relied on his experience in equilibrium and kinetic microstructural modeling. Currently, he is actively involved in advanced characterization of neutron irradiated TRISO-coated nuclear fuel. He has also done a comparative study of coarsening kinetics of gamma prime precipitates in both nickel- and cobalt-base superalloys while pursuing his Ph.D. at the University of North Texas (UNT). Dr. Meher was a recipient of master and doctoral fellowships during his 4 years at UNT and was recognized with an Exceptional Contribution Award at INL in 2015. He has co-authored in excess of 15 peer-reviewed articles and review papers.

Dr. Isabella van Rooyen is a Distinguished Staff Scientist in the Fuel Design and Development Department at INL where she has led advanced electron microscopy and micro-analysis examinations for the Advanced Gas Reactor TRISO Fuel Development Program since 2011. In addition to this role, she is also the principal investigator (PI) of an additive manufacturing U_3Si_2 fuel research project; the PI or co-PI of research projects funded by the National Scientific Users Facilities; and a co-PI of three Nuclear Energy University Program research projects and a Nuclear Energy Enabling Technology research project, focusing on SiC-oxide-dispersion-strengthened alloy gradient nanocomposite cladding, fission product transport in TRISO-coated particles, advanced manufacturing and developing high-temperature in-pile temperature sensors, respectively. Prior to joining INL, Dr. van Rooyen held various technical leadership roles in the nuclear, aerospace, and automotive industries in South Africa, with the most

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Dr. Jhonathan Rosales is a nuclear engineer with experience in fuel performance and fuel fabrication by means of different methodologies including Spark Plasma Sintering (SPS), conventional sintering, and laser synthesis. He has been involved in the High Temperature Gas Reactor fuel development program and contributed with mechanistic studies on the fission product deposition on the SiC layer of TRISO fuel after neutron irradiation. In addition he has supported all characterization activities pertaining the Additive Manufacturing as an Alternate Fabrication Technique for uranium silicide (U_3Si_2) fuel. Prior to joining INL, he was a researcher at the Laboratory for the Development of Advance Nuclear Fuels at the University of Florida developing UO_2 doped fuel (diamond, SiC) fabricated by means of SPS. Dr. Rosales holds a Ph.D. in Nuclear engineering emphasized in nuclear and non-nuclear materials, a MSc. in Nuclear Engineering from the University of Florida, and a B.Sc. in Mathematics with a minor in Physics from the Wisconsin Lutheran College.