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The diffusion of cesium, strontium, and europium in silicon carbide

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ABSTRACT

A novel multi-layer diffusion couple was used to isolate the diffusion of strontium, europium and cesium in SiC without introducing radiation damage to SiC and at concentrations below the solubility limit for the fission products in SiC. Diffusion occurred by both bulk and grain boundary pathways for all three fission products between 900° C and 1,300° C. Cesium was the fastest diffuser below 1,100° C and the slowest above this temperature. Strontium and europium diffusion tracked very closely as a function of temperature for both bulk and grain boundary diffusion. Migration energies ranged from 1.0 eV to 5.7 eV for bulk diffusion and between 2.2 eV and 4.7 eV for grain boundary diffusion. These constitute the first measurements of diffusion of cesium, europium, and strontium in silicon carbide, and the magnitude of the cesium diffusion coefficient supports the premise that high quality TRISO fuel should have minimal cesium release.

1. Introduction

Tri-isotropic (TRISO) coated fuel is the fuel form of choice for the Next Generation Nuclear Plant (NGNP) program that will demonstrate the technologies for fuel fabrication and qualification on an industrial scale. The fuel particles consist of kernels of uranium oxycarbide (UCO) or uranium oxide (UO_2) that are then coated with a porous carbon buffer, a pyrolytic carbon layer (PyC), a SiC layer, and a final PyC layer, to produce a nominally 1 mm diameter particle. These fuel particles are able to survive extreme environments of 900° C-1,300° C under normal operating conditions and as high as 1,600° C in accident situations [1]. During operation, several fission products (FPs): silver, strontium and europium in particular, have been observed to be released through intact SiC [2]. While significant research efforts have focused on silver release through the SiC [3–6], little is known about other FPs such as europium and strontium. Cesium, europium, and strontium all pose important radiological health concerns if released from reactors [7]. Cesium diffusion has been shown to be negligible in high quality fuel [8], but has not been quantified for kinetics.

Post-irradiation annealing of fuel has shown several features in FP release curves that can't be interpreted without knowing the FP distribution in the fuel a-priori. The low solubility of most FPs and low melting and boiling temperatures compared with the temperatures of interest makes diffusion couples very difficult to construct [4,6]. Several studies have attempted to isolate thermal and radiation enhanced diffusion for FPs with little success. Ion implantation has been used to introduce FPs into SiC, but this creates several complications including the introduction of trapping sites due to radiation damage from the implantation, and the likely change in diffusion mechanisms due to the very high concentrations necessary to measure the diffusion profiles [3,5,9–11]. Spherical diffusion couples made using the same coaters for TRISO particle production have shown that grain boundary diffusion plays an important role in silver diffusion through SiC, but these experiments have been conducted at very high silver concentrations (pure silver at the interface) that are not relevant under fuel operating conditions [6]. The spherical geometry also limits the analytical techniques for concentration profiling to those with poor sensitivity, significantly reducing the accuracy of the measured diffusion coefficients. Recently a novel diffusion couple was developed that maintains a thin film geometry to allow the use of depth profiling techniques, introduces FPs into PyC adjacent to SiC without causing radiation damage in the SiC and at concentrations that would be relevant to TRISO fuel, recreates the PyC/SiC interface, and allows for the isolation of thermal diffusion [12]. This

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design was used to study the thermal diffusion of cesium, strontium, and europium between 900° C and 1,300° C reported here.

2. Experimental method and analysis

2.1. Sample specifications

Polycrystalline high purity high resistivity grade β-SiC was supplied by Rohm and Haas Inc. in the form of 1 cm square substrates 0.6 mm thick with the growth direction normal to the sample surface. Previous electron back scatter diffraction (EBSD) analysis showed large and small columnar grains in the growth direction with an average grain size of 1.5μm with grains as large as 14μm [13].

The microstructure of TRISO SiC depends on the deposition conditions which have been varied over the past 60 years to reduce the dominant fuel failure mode of that test campaign. Four different variants of SiC were tested in the AGR-1 campaign conducted at Idaho National Laboratory [14]. In all four variants, large grains tend to be columnar in the growth direction, while small grains are equiaxed. The grain size ranges from 600 nm to 2μm. Variant 1 is the most similar variant to the SiC used here with grains ranging in size from 500 nm to 8μm, with an average grain size of 2 μm. Grain boundary character determination (GBCD) of TRISO SiC showed a microstructure dominated by random high angle boundaries and a lack of low-Σ grain boundaries as is the case in the material used here [15].

The diffusion couple is a substrate of high purity CVD β-SiC obtained from Rohm and Haas Inc., that was coated with 300 nm of PyC. The FP of interest: cesium, europium, or strontium was then implanted into the PyC. A final coating of plasma-enhanced CVD (PECVD) SiC sealed the diffusion couple to allow the FP to have sufficient residence time at the interface to diffuse into the SiC substrate. For this study, all three FPs were implanted at 400 keV to a total fluence of $10^{16} cm^{-2}$. Table 1 lists the FP implant energy, range, full width half maximum (FWHM), and peak concentration for the three FPs as calculated by SRIM [16] and verified with Rutherford back-scattering spectroscopy (RBS). These settings ensured that the FP remained within the PyC and did not penetrate the SiC substrate, allowing for the calculation of purely thermal diffusion coefficients within the SiC. Details of the novel diffusion couple design were reported in Ref. [12].

2.2. Thermal annealing

All thermal annealing treatments were performed in a high temperature graphite furnace with a custom gas delivery system that allows for PyC deposition or ultra clean annealing. Ultra high purity (UHP) (99.995%) argon was passed through an inert gas purifier to prevent oxygen contamination and is admitted to the furnace via a mass flow controller with an upstream solenoid to allow for vacuum operation. An oil-based rotary vane rough pump is used to create a temporary vacuum and to allow for flushing and backfilling at the beginning of operation. Vacuum is measured using a wide range diaphragm manometer that is sensitive down to 1 mTorr. Argon is introduced through the top port during the furnace flushing operation or a side quartz window port during high temperature annealing. A calibrated boron-graphite thermocouple provides feedback for power control. The calibration is performed at 900° C, 1,100° C, 1,300° C, and 1,500° C using a Type C thermocouple that can be inserted through a top feed-through. A graphite crucible with a cavity positioned at the sight-line of the quartz window is also calibrated for emissivity for use with a pyrometer. During operation the temperature control is from the boron graphite thermocouple, but is validated using the pyrometer. A calibration is performed after every 4 annealing treatments or 2 weeks to ensure the accuracy of the furnace temperature remained at 1% of the measured temperature.

Diffusion couples were cleaned in a sonic cleaner filled with ethanol to remove any surface contaminants and then loaded into a graphite crucible in the furnace. The furnace was then evacuated to 100 mTorr and back-filled with argon once to flush the argon lines and inert gas purifier, followed by a second evacuation to 100 mTorr. Power was slowly applied and the furnace was heated to 400° C in 30 min and then held at this temperature in order to remove water and nitrogen contaminants in the graphite felt insulation. Once the vacuum returned to 100 mTorr, ultra high purity argon was admitted to establish a pressure of 10 Torr within the furnace and held for 15 min to continue to flush contaminants. The vacuum pump is then isolated and the furnace is pressurized to 800 Torr to ensure that air could not leak into the furnace. The furnace is then ramped to operating temperature at ramp rates of 200° C/hr up to 900° C, and then 100° C/hr up to 1,300° C. The furnace temperature is verified at the beginning of the dwell and at the end via the calibrated pyrometer and cavity. Ramp down rates are 100° C/hr above 900° C and 200° C/hr below 900° C. Five annealing conditions were used in this study: 900° C:40hr, 1,066° C:10hr, 1,100° C:10hr, 1,200° C:10hr, and 1,300° C:10hr. The 1,100° C:10hr condition was repeated for strontium to test the repeatability of the results.

2.3. Transmission electron microscopy

Transmission electron microscopy (TEM) samples were prepared via the focused ion beam (FIB) lift out method using a FEI Helios with a final thinning performed using 5 kV Ga^+ ions. Scanning transmission electron microscopy (STEM) analysis was performed on the sample containing strontium and thermally treated at 1,100° C for 10 h using a FEI Titan G2 80–200 with ChemiSTEM technology operated at 200 kV. Bright field diffraction contrast images were used to identify grain boundaries in the SiC substrate. High angle annular dark field images were used to identify areas of build up of strontium along the PyC/SiC interface. Bulk and grain boundary diffusion were profiled using energy dispersive spectrometry (EDS) with a collection solid angle of 0.7 sr. X-ray images were acquired in STEM mode using a sub-nm probe at a current of 2 nA.

2.4. Time of flight secondary ion spectrometry

Time of flight secondary ion mass spectrometry (ToF-SIMS) was used to profile the diffusion of FPs into the SiC. Two separate Ion-

Table 1
FP Implantation range, FWHM, and peak concentration for cesium, europium and strontium in PyC as calculated by SRIM 2013. RBS measured values are in parenthesis.

Fission product	Energy (keV)	Range	FWHM (nm)	Peak concentration (%)
Cesium	400	144 (140)	63 (65)	1.38 (1.37)
Europium	400	118 (115)	45 (48)	1.84 (1.82)
Strontium	400	184 (178)	88 (90)	0.96 (0.95)