Chemical reactivity of CVC and CVD SiC with UO_2 at high temperatures^{**}

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Abstract

Two types of silicon carbide (SiC) synthesized using two different vapor deposition processes were embedded in UO_2 pellets and evaluated for their potential chemical reaction with UO_2 . While minor reactivity between chemical-vapor-composited (CVC) SiC and UO_2 was observed at comparatively low temperatures of 1100 and 1300°C, chemical-vapor-deposited (CVD) SiC did not show any such reactivity. However, both CVD and CVC SiCs showed some reaction with UO_2 at a higher temperature (1500°C). Elemental maps supported by phase maps obtained using electron backscatter diffraction indicated that CVC SiC was more reactive than CVD SiC at 1500°C. Furthermore, this investigation indicated the formation of uranium carbides and uranium silicide chemical phases such as UC, USi_2 , and U_3Si_2 as a result of SiC reaction with UO_2 .

** This manuscript has been authored by the Oak Ridge National Laboratory, managed by UT-Battelle LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for U.S. Government purposes.

Keywords: Uranium dioxide, chemical vapor composite, chemical vapor deposition, silicon carbide, SiC, chemical reactivity

1. Introduction

Silicon carbide (SiC) is one of the advanced materials that have many uses. It is important in biomedical applications [1], for the development of nanocrystals that can be used in high temperature applications [2] and in next generation quantum sensing and nanophotonics [3], in microelectronic devices as a semiconductor interface [4], as a hydrogen storage medium [5], to increase plasticity of films in engineering materials [6]. SiC has chemical, physical, and mechanical properties that make it suitable for use as a fuel cladding material, and for this reason, its properties have been studied and reported in the literature in detail [7,8]. It is also the primary coating layer, in the form of chemical-vapor-deposited (CVD) SiC, in tri-structural isotropic (TRISO) coated particle fuels used for advanced gas-cooled reactors (AGR) to contain any breached uranium or irradiation-induced radioisotopes during fuel irradiations [9]. The most recent interests in SiC include its possible application for high-fissile-density uranium mononitride (UN) as an accident-tolerant fuel in the form of TRISO-coated particles. Silicon carbide has also been tested as a fuel encapsulation medium (SiC ceramic matrix) to embed TRISO particle fuel for light water reactors (LWRs). The fuel type is called FCM, or fully ceramic microencapsulated fuel, and has been discussed in detail elsewhere [10]. Because of its extensive use, in the form of nanoparticles or single crystals, SiC and its chemical reactivity with other materials such as Zircaloy (a cladding material) or the nuclear fuel UO_2 under various experimental conditions are of great interest. Reactivity between SiC and ZrC has been reported at temperatures $>900^\circ\text{C}$ [11], and in another study, SiC nanoparticles embedded in UO_2 kernels were found to react with the kernels at very high temperatures [12].

The current study involves further investigation of SiC/ UO_2 interaction at different process temperatures using two SiC pellets that were synthesized via two different methods—chemical vapor deposition and a proprietary chemical vapor composite process. Because the different methods of SiC synthesis are likely to create microstructures with dissimilar properties such as differences in crystal structure, residual strain, grain size, grain boundary types, surface orientations, etc., the two types of SiC are expected to possibly behave differently with respect to their reactivity in UO_2 bulk medium. In this study, UO_2 pellets that were incorporated with CVD and CVC SiC were heat treated at three different temperatures up to 1500°C , and microstructural studies were carried out using optical and electron microscopy.

2. Experimental Details

The CVD material used in this research was ultra-high-purity and high-resistivity-grade SC-003 CVD SiC produced by Rohm & Haas Advanced Materials (presently Dow Chemical, Woburn, MA). CVD SiC of this particular grade with >99.9995% purity is commonly used as the de facto standard material for ultra-high-purity polycrystalline beta-phase SiC. The CVC™ SiC material was produced by TREX Enterprises (Lihue, HI). The CVC process, according to the U.S. patent application publication US 2006/0057287 A1, produces a composite article comprising a CVD matrix with the solid particles dispersed within it. The manufacturer claims that the CVC SiC is of ultra-high purity and nearly as polishable as high-quality CVD SiC, while achieving a significantly faster growth rate over conventional CVD processes.

In this study, test pellet samples of UO_2 powder were prepared in direct contact with the CVD and CVC SiC. The UO_2 powder (AREVA 99.7% U-238) with embedded cut samples of SiC was cold-pressed at a pressure of 70.8 MPa with a 5 minute holding time using a 1.2360 cm (manufacturer specification) diameter die. Three pelletized samples were then thermally treated at 1100°C (8 h), 1300°C (8 h), and 1500°C (4 h). Flowing argon (ultra-high purity) was used as the cover gas. A SiC crystalline chemical phase in both CVC and CVD SiCs was identified using powder X-ray diffractometry (XRD); a Scintag XRD instrument using 40 kV and 40 mA with Cu k- α radiation was used. The microsphere particles were powdered and mounted on a zero-background XRD sample mount, which was sealed using a Kapton tape, to acquire XRD powder patterns. An internal standard Si SRM640b was used with the samples for lattice parameter refinements. Full profile fits of the XRD patterns were performed using GSAS [13]. Mean crystallite sizes were determined using full width half maximum (FWHM) of the fitted XRD peaks, their reflection positions, and assuming spherical shape. The pellets before and after the heat treatments were visually inspected using optical microscopy (OM), and further characterization was done using scanning electron microscopy (SEM) and related techniques such as energy dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD).

3. Results and Discussion

Cut pieces of the two types of SiC pellets were first characterized using X-ray diffraction. Analysis of the XRD patterns indicated both CVC and CVD SiCs to consist of a ZnS (CF8)-type SiC structure, commonly known as 3C (Moissanite 3C). Minor second phases included SiC of type 6H. Fitted XRD patterns of both samples are shown in Figure 1. The refined lattice

parameter of CVC SiC (4.3683(1) Å) is slightly larger than that of CVD SiC (4.3622(1) Å), and both are greater than that of a reported value of 4.348(5) Å for 3C SiC (ICSD #24217). The diffraction profile of the CVD SiC sample did not have any asymmetry. However, the diffraction profile of the CVC SiC sample did exhibit asymmetry; because of this asymmetry, peaks at low angles, particularly the (111) and (200) reflections, had a peak shift toward the low angle direction, as shown in the XRD patterns shown in Figure 1. It can also be noted that the (111) peak for the Si internal standard does not have any significant asymmetry. Therefore, it can be concluded that the asymmetry observed in the SiC XRD profile is not due to instrument effects. That is, depth gradients in composition or strain of the CVC SiC sample are likely the major causes for such asymmetry of the diffraction profile.

In X-ray diffraction, the angle of incidence (θ) should equal to the Bragg angle, so that all scattering will be in phase and would result in constructing a diffraction line. However, if θ is closer to Bragg angle (not equal to it) and the subjected specimen has small enough crystals ($\bullet 1 \mu\text{m}$), scattering will result in broad diffraction peaks (particle size broadening). Such peak broadening can be used to determine sizes of small crystallites using the following Scherrer equation:

$$\tau = \frac{K}{\lambda} \frac{1}{\beta} \cos \theta,$$

where τ is the mean crystallite dimension, K is shape factor (usually ~ 0.9 and 0.94 for spherical shape), λ is the wavelength of the incidence X-ray beam, β is the crystallite size broadening (FWHM), and θ is the incidence angle. Using this equation and the extracted data of the reflections that correspond to 3C SiC phase of the fitted XRD pattern, the mean crystallite sizes were calculated to be 40.1 and 40.4 nm for CVC and CVD SiC, respectively.

Figure 1. XRD patterns of CVC (a) and CVD (b) SiC pellets fitted with 3C cubic SiC. Arrows indicate a minor peak due to hexagonal 6H SiC (101 reflection). Red and black tick marks correspond to Si SRM 640b internal standard and 3C SiC, respectively. Pink pattern at the bottom in (a) and (b) is the residual between the experimental and calculated patterns. Goodness of fit (χ^2) for (a) and (b) are 1.9 and 1.0, respectively. Four figures at the bottom show single peaks for Si (111) reflection and the first three peaks of the CVC SiC XRD pattern. Vertical dotted lines are used to indicate the peak shifts, especially for SiC (111) and (200) reflections.

Figure 2 (a–c) shows SEM micrograph, EBSD image quality (IQ), and inverse pole figure (IPF) maps of a sample area of the as-received CVC SiC, respectively. The bulk area of the sample contains large columnar grains (max diameter 17 μm) along the growth direction, while some areas contain grains as small as 0.6 μm . Rohm & Haas (RH) CVD SiC used in this study also indicated similar microstructural properties though with a comparatively smaller number of larger grains of size $\sim 10 \mu\text{m}$ and many small grains $< 1 \mu\text{m}$, as reported elsewhere [14]. Furthermore, CVC SiC consists of high angle grain boundaries compared to that of CVD SiC. The calculated 001, 111, or 101 pole figures (PFs) corresponding to the IPF maps of CVC SiC

did not show any significant texture (only reaches $\sim 2\times$ random), as shown in Figure 2d. This observation was in agreement with XRD results (Figure 1) in which no substantial texture (preferred orientations) was identified. This was also identical to that observed in the CVD SiC used in this study [14].

Figure 2. SEM micrograph (a), EBSD image quality (b), corresponding IPF maps (c), and PFs for 3C SiC (d) of CVC SiC.

Figure 3 shows the three pellets of UO_2 embedded with CVC and CVD SiCs after being heat treated at 1100, 1300, and 1500°C. As expected, the pellets shrank as a result of the heat treatment, with shrinkage increasing from 13.5% to 15.7% as the temperature rose from 1100°C to 1500°C. The SiC pellets also moved with the bulk UO_2 pellet, and this displacement was greater for CVC SiC pellets (large pellet), especially in the pellet heat treated at 1500°C, compared to that of CVD SiC pellets. The degree of discoloration of UO_2 near CVC SiC is

slightly greater than that near CVD SiC in the pellet heat treated at 1100°C, indicating comparatively higher reactivity of CVC SiC with UO_2 at this temperature. Even though these discolorations of UO_2 near CVC and CVD SiCs are similar in the 1300°C pellet, the overall reaction estimated by surface recession depth on bulk UO_2 pellet looks more significant for CVC than for CVD.

For the third pellet (1500°C), approximate densities were calculated to be 5.0 and 8.2 g/cm³ before and after heat treatment, respectively. The CVC SiC piece was displaced by the bulk UO_2 , but the CVD SiC was stationary or its displacement was small compared to CVC SiC. The two CVC and CVD SiC pieces also moved closer to each other (gaps before and after heat treatment were 595 and 462 μm , respectively) after the heat treatment. Also, slightly different discoloration on the side of UO_2 (~500 μm thickness) around the CVC SiC can be seen. Only a small area (thickness of up to 80 μm) with similar discoloration can be observed around the CVD SiC pellet. These observations indicate that the reaction of SiCs with UO_2 is less at 1100°C and 1300°C compared to at 1500°C, and CVC SiC has a higher tendency to react with UO_2 than CVD SiC.

Figure 3. Optical microscopic images of three UO_2/SiC pellets heat treated at three different temperatures: (a–b) 1100°C, (c–d) 1300°C, and (e–f) 1500°C. Larger of the two SiC pieces is the CVC SiC.

The backscatter electron (BSE) SEM micrographs of CVC SiC from the pellet heat treated at 1100°C showed the presence of high-contrast thin layers on the surface of some part of the SiC pellet.

Figure 4 (a and b) shows these high-contrast areas. A composite image of the EDS elemental maps (Figure 4d) on one of these areas (Figure 4c) indicated that the high contrast comes from high-Z uranium-bearing UO_2 . These elemental maps also showed that the high-contrast U-bearing layer had penetrated into the SiC, indicating a reaction of between UO_2 and CVC SiC. As shown in Figure 4c, the reaction between CVC SiC and UO_2 is uneven indicating preferred reaction in the nano-crystalline domains. As shown in Figure 4(e–f), a UO_2 layer was also observed on the CVD SiC. However, significant penetration of high-contrast U-bearing materials into the CVD SiC pellet [Figure 4 (g and h)] was not observed as in CVC SiC, other than the presence of a thin layer of UO_2 that has been split from the bulk UO_2 either during cooling or handling the pellets, indicating that no significant reaction between UO_2 and CVD SiC occurred during the heat treatment at 1100°C.

Figure 4. SEM micrographs of CVC SiC/ UO_2 (top) and CVD SiC/ UO_2 (bottom) heat treated at 1100°C for 8 h. (a–b) BSE SEM micrographs of CVC SiC/ UO_2 . (c) Field of view of a magnified CVC SiC/ UO_2 area. (d) Composite image of corresponding U (red) and Si (green) EDS maps. (e–f) BSE SEM micrographs of CVD SiC/ UO_2 . (g) Field of view of a magnified CVD SiC/ UO_2 area. (h) Composite image of corresponding U and Si EDS maps.

As depicted in Figure 5(a–c), CVC SiC in the UO_2 pellet heated at 1300°C also showed some reaction of SiC with UO_2 , as was observed in the pellet heat treated at 1100°C. CVD SiC did not show any such reaction with UO_2 [Figure 5(d–f)].

Figure 5. SEM micrographs of CVC SiC/UiO₂ (top) and CVD SiC/UiO₂ (bottom) heat treated at 1300°C for 8 h. (a–b) BSE SEM micrographs of CVC SiC/UiO₂. (c) Composite image of corresponding U (red) and Si (green) EDS maps. (d–e) BSE SEM micrographs of CVD SiC/UiO₂. (f) Composite image of corresponding U and Si EDS maps.

Since the pellet heat treated at 1500°C exhibited more evidence of interaction between the SiC samples and UiO₂, a thorough microscopic evaluation was done on the UiO₂/SiC sample areas of this pellet. Microstructures of CVD SiC, UiO₂, and CVD SiC/UiO₂ boundary together with the EDS elemental maps of a selected sample area are shown in Figure 6. BSE imaging or elemental mapping did not show any evidence of the presence of SiC or Si-based chemical phases in the bulk UiO₂, but the UiO₂ edge areas where the CVD SiC interacts with it showed some contrast-based differences in the BSE SEM micrographs (highlighted by arrows in Figure 6a through 6d). Further investigation of these thin areas on UiO₂ indicated the presence of chemical phases that are different from UiO₂ or SiC, which are the starting chemical phases of the material. The BSE SEM image and EDS elemental maps of a selected area of the CVD SiC embedded UiO₂ highlighted by a box in Figure 6 SE micrograph (top left) are also shown at the bottom of the figure. Some high-contrast areas in the BSE image correspond to U- and C-rich areas, as shown in the elemental maps. This suggests the presence of UC_x chemical phases in the UiO₂. Silicon-rich areas in the UiO₂ side of the pellet also contain U (highlighted by arrows in U and Si maps in Figure 6) but deficient in C or O, indicating the presence of U-Si-based chemical phases.

Figure 6. Top left is the secondary electron (SE) and bottom left is the BSE SEM micrographs of selected areas of CVD SiC embedded UO_2 piece of the sample heat treated at 1500°C . The BSE images (a), (b), (c), and (d) to the right indicated the selected areas highlighted by letters A, B, C, and D, respectively, in the SE image. The area defined by a box in the SE image is selected for the EDS elemental maps and the BSE image at the bottom.

As in the CVD SiC embedded UO_2 areas, the CVC SiC embedded UO_2 areas also showed the formation of thin layers of new chemical phases on UO_2 , as highlighted by arrows in Figure 7(a and b). These areas on the CVC SiC embedded UO_2 sample (100 to $300\ \mu\text{m}$ wide) shown in Figure 7(a and b) are larger than those on the CVD SiC embedded UO_2 sample area (20 to $50\ \mu\text{m}$ wide) shown in Figure 6(a–d). Figures 6 and 7 confirm what was seen in Figure 3. One selected area of the CVC SiC embedded UO_2 sample is shown in Figure 7c, together with the corresponding EDS elemental maps to the right of Figure 7c. The high-contrast areas in the BSE micrograph correspond to U- and C-rich grain areas, as observed in CVD SiC embedded UO_2 , and in these areas Si and O are deficient. This indicates the formation of UC_x chemical phases on

UO₂ due to its reaction with SiC at 1500°C. The oxygen rich areas sitting on silicon rich side can also be found in these images. This suggests the presence of thin layers of SiO₂ in these oxygen and silicon rich areas.

Figure 7. (a–b) BSE SEM micrographs of CVC SiC + UO₂ sample area of the sample heat treated to 1500°C. (c) BSE SEM micrograph of a selected area highlighted by a square in (a) and the corresponding EDS elemental maps to the right.

Figure 8 shows the EBSD phase maps of two selected areas of CVD SiC and CVC SiC embedded UO₂ of the sample heat treated at 1500°C, shown in Figures 6 and 7, respectively. The first attempt to incorporate several possible chemical phases—UO₂, USi₂, U₃Si₂, UC₂, and U₃Si₂C₂ including SiC in the data acquisition—was not successful due to complications associated with phases with respect to their crystallography or similar crystallographic orientations. Therefore, SiC was removed in obtaining the phase maps for the CVD SiC embedded UO₂ sample area, as

shown on the left in Figure 8, and is why the phase map on the SiC side of the sample had noises. However, the UO_2 side of the sample area had better phase maps, corresponding to UO_2 , USi_2 , and U_3Si_2 . The phase map for UC_2 was also better but with comparatively significant noise possibly due to complications that arose from similar crystallographic orientations between the UC_2 and U_3Si_2 phases. Only these three phases, UO_2 , USi_2 , and U_3Si_2 , were included in the CVC SiC embedded UO_2 sample area for this reason. The results indicate the presence of the phases, as shown in the phase map in Figure 8 (right side). The diffraction patterns of the UO_2 , USi_2 , and U_3Si_2 chemical phases that correspond to the phase-rich areas in the CVC SiC embedded UO_2 sample area are shown at the bottom of Figure 8.

Figure 8. EBSD phase maps of selected areas of CVD SiC and CVC SiC embedded UO_2 sample heat treated to 1500°C . The insets are SEM micrographs of the corresponding sample areas. SiC side in the left side phase map had noises since SiC was not included in the phase identification.

At the bottom are the diffraction patterns of UO_2 , USi_2 , and U_3Si_2 chemical phases that correspond to the phase-rich areas in the CVC SiC embedded UO_2 sample area.

It is generally accepted that SiC oxidation is inhibited by a SiO₂ layer on its surface, as is suggested its presence in Figure 7. The following reaction (1) is suggested in some of the literature [15, 16]. The Gibbs free energy (ΔG) for this reaction at standard state (25°C and 1 atm) is 1337.6 kJ/mol and therefore requires a considerable amount of energy (endothermic). However, it is assumed that this reaction is feasible at higher temperatures and produce free carbon (at 1100°, 1300°, and 1500°C the ΔG is 775.1, 670.5, and 565.9 kJ/mol, respectively).

This free carbon could react with bulk UO₂ forming UC_x phases (ΔG at 1500°C is 134.6 kJ/mol):

Such UC_x chemical phases were not observed in the samples that heat treated at 1100° and 1300°C, probably because not enough energy was introduced to the system to undergo reaction (1) at these experimental conditions. However, CVC SiC showed minor reactivity with UO₂ at 1100° and 1300°C forming some U- and Si-based chemical phases, especially close to SiC/UO₂ interfaces (Figure 4 and Figure 5). Since USi₂ and U₃Si₂ were the main chemical phases identified using EBSD for these SiC samples (Figure 8), the following two direct reactions can be suggested for CVC SiC and UO₂ at these two lower temperatures as well:

Other than reactions (3) and (4), SiC samples could also undergo the following reactions in the samples heat treated at 1500°C because of the available free carbon:

4. Conclusions

Two types of silicon carbides (CVC and CVD SiC samples) fabricated using two different chemical processes were embedded in UO_2 pellets and evaluated for their potential reaction with UO_2 at three different temperatures: 1100, 1300, and 1500°C. These comparatively high temperatures were used in order to supply enough energy to the pellets to initiate any possible reaction of the SiC samples with UO_2 . While some reaction between the SiC samples and UO_2 was observed at 1100 and 1300°C, higher reactivity was seen in CVC SiC compared to that of CVD SiC. Both CVC and CVD SiC samples embedded in the third UO_2 pellet heat treated at 1500°C showed substantially higher chemical reactivity with UO_2 compared to the reaction of SiC samples in the pellets heat treated at 1100 and 1300°C. SEM, EDS, and EBSD studies indicated both types of SiC samples reacted with UO_2 at 1500°C, forming a few different chemical phases, including UC_x , USi_2 , and U_3Si_2 . Moreover, CVC SiC also showed significantly higher reactivity with UO_2 compared to CVD SiC at 1500°C. This difference in reactivity could be explained due to the presence of smaller grains accompanied by high angle grain boundaries in CVC SiC compared to CVD SiC.

Acknowledgements

This research work was sponsored by the U.S. Department of Energy through the Office of Nuclear Energy, Science and Technology's Fuel Cycle Research and Development Program under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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