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Dr. K. McCarthy
Director, TIO for LWR Sustainability
Idaho National Laboratory
2525 Fremont Avenue
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Subject: Completion of LWRs Level 3 Milestone (M3LW-13IN0502045) “Document out-of-pile testing to assess chemical interaction of fresh UO₂ fuel with candidate SiC clad materials”, due 7/1/2013.

Dear Madam;

This letter is to document the completion of the LWRs Advanced Fuels program report, “Evaluation of CVD and CVC SiC Reactivity towards UO₂”. The attached document reports the results from the initial experiment that attempted to examine the fundamental chemical compatibility between UO₂ and SiC and to determine the potential difference in the compatibility with UO₂ between two types of SiC, namely an ultra-high purity chemically vapor-deposited (CVD) SiC and TREX CVC™ SiC. The results indicated that either CVD or CVC SiC do not show any detectable chemical reactions at 500°C, the temperature anticipatedly higher than the UO₂-SiC interface temperature during the normal operation of SiC-cladded LWR fuels. At 1500°C, as expected, both type SiC exhibited substantial reactions with the embedding medium UO₂. The reaction phases produced at 1500°C were identified to include UC_x, USi₂, and U₃Si₂. The CVC SiC exhibited significantly higher reactivity than CVD SiC with the UO₂ at this temperature. It is suggested that the current results are considered upon planning of the examination of the fueled SiC composite rodlets that had been irradiated in High Flux Isotope Reactor with an inner layer of CVC SiC.

My thanks to Chinthaka Silva and Yutai Katoh for their work here.

If you have any comments or questions, please contact me. Thank you.

Sincerely,



Dr. Jeremy T. Busby
Senior Research Scientist
Oak Ridge National Laboratory

CC: L. Snead, ORNL

Evaluation of CVD and CVC SiC Reactivity towards UO_2

Chinthaka M. Silva, Stewart L. Voit, Yutai Katoh

Summary

With objectives to advance understanding of chemical compatibility between UO_2 and SiC and to determine potential difference in the compatibility with UO_2 between two types of SiC, namely an ultra-high purity chemically vapor-deposited (CVD) SiC and TREX CVC™ SiC, coupons of these materials were subjected for chemical reactivity tests with UO_2 at elevated temperatures. The initial sets of experiments indicated that both CVD and CVC SiC undergo substantial chemical reactions with the embedding medium UO_2 at 1500°C , whereas they both do not react at 500°C up to 96 hours of heating. The reaction phases produced at 1500°C were identified to include UC_x , USi_2 , and U_3Si_2 . The CVC SiC exhibited significantly higher reactivity than CVD SiC with the UO_2 at this temperature.

1.0 Introduction

This study was performed to evaluate the chemical compatibility of silicon carbide (SiC) with UO_2 under specific test conditions. Two types of SiC synthesized using different chemical processes, Chemical Vapor Deposition (CVD) and proprietary Chemical Vapor Composite (CVC), were tested here. The different deposition methods likely create microstructures with dissimilar properties such as crystal structure, residual strain, grain size, grain boundary types, and surface orientations, and these properties may affect compatibility with UO_2 . As a preliminary attempt, CVD and CVC SiC incorporated UO_2 pellets were heat treated up to 1500°C , and microstructural studies were carried out using optical and electron microscopy.

2.0 Materials and Test Method

The CVD material used in this research was the 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 is commonly used as the 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 of 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.

3.0 Results and Discussion

The first pellet, which was heat treated at 500°C for 24 hours did not survive after the heating. A 2nd pellet was heat treated at 500°C for 96 hours under high purity argon atmosphere. The pellet was broken, at SiC/ UO_2 boundaries, after the heat treatment process. The cracking could be due to one or more of the following reasons: the incompatible hardness of the raw UO_2 and silicon carbides, poor sintering of UO_2 , or early-stage non-uniform shrinkage of the UO_2 . Optical microscopy or SEM studies on the later sample did not reveal any reaction of both CVD and CVC SiC with UO_2 .

A 3rd pellet of UO₂/CVD-CVC SiC was heat treated at 1500°C for 4 hrs under Ar atmosphere. Densification of the UO₂ at 1500°C resulted in cracks around the boundaries of the CVD and CVC SiC pieces. Optical images of the sample before and after the heat treatment at 1500°C are shown in Figure 1. During the heat treatment, the dimensions of the pellet decreased from 0.441 cm to 0.369 cm in height and from 1.2394 cm to 1.0449 cm in diameter. Approximate densities were calculated to be 5.0 and 8.2 g/cm³ before and after heat treatment, respectively. The CVC SiC piece has been displaced with bulk UO₂ when it shrank, but CVD SiC was stationary or its displacement was small compared to CVC SiC. The two CVC and CVD SiC pieces have also moved close to each other (gaps of before and after heat treatment are 595 and 462 μm, respectively) after the heat treatment. Also, slightly different texture of about ~500 μm thickness can be seen in UO₂ around the CVC SiC. Only a slight (thickness of up to 80 μm) area with similar texture can be observed around the CVD SiC piece.

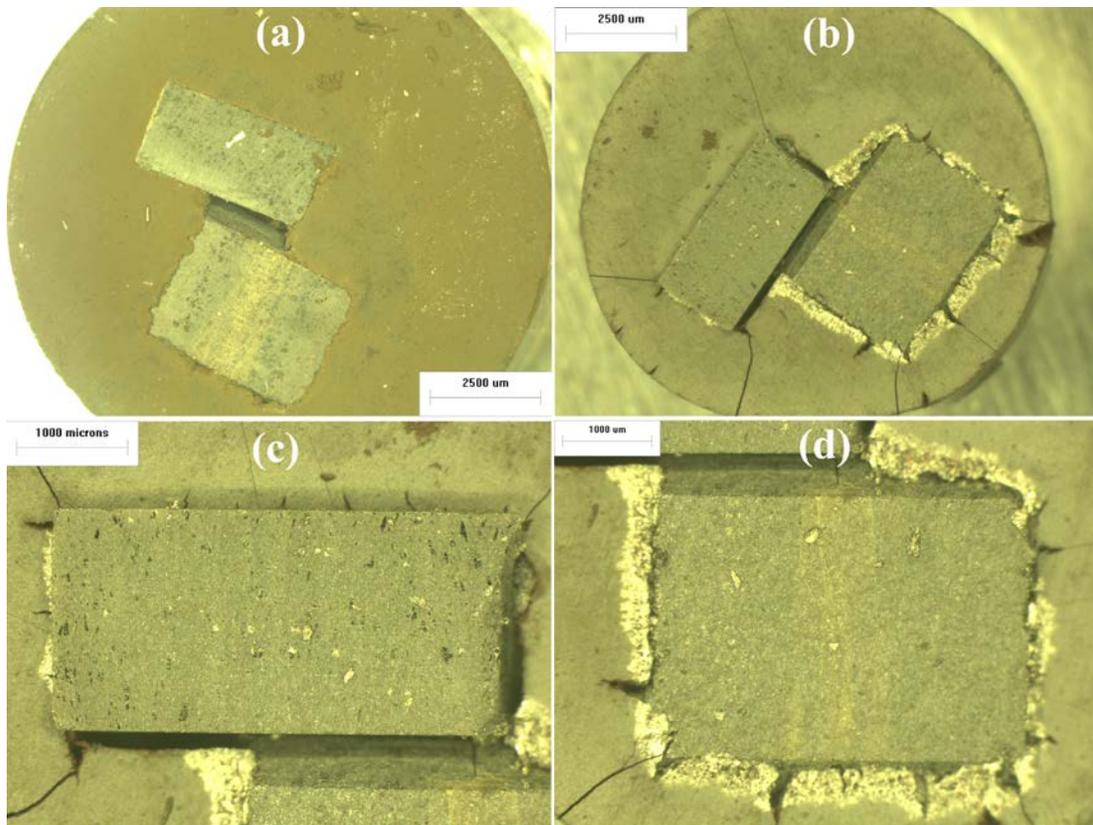


Figure 1. CVD and CVC SiC embedded UO₂ pellet before (a) and after (b) heating at 1500°C in Ar for 4 hrs. (c) CVD SiC and (d) CVC SiC pieces in the heat treated sample.

Figure 2 shows the secondary electron (SE) and the backscattered electron (BSE) SEM images of a selected area of CVD SiC and UO₂ sample. The bulk UO₂ did not show any indication of the presence of SiC or Si-based chemical phases, but the UO₂ edge areas where the CVD SiC interacts with it showed some contrast-based differences in the BSE SEM micrographs (highlighted by arrows in Figure 2a through 2d). Further investigation of these thin areas on UO₂ indicated the presence of chemical phases that are different from UO₂ or SiC, which are the

starting chemical phases. The BSE SEM image and EDS elemental maps of a selected area of the CVD SiC embedded UO_2 highlighted by a box in Figure 2 SE image 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 UO_2 . Si rich areas in the UO_2 side also contain U (highlighted by arrows in U and Si maps in Figure 2) but deficient of C or O, indicating the presence of U-Si based chemical phases.

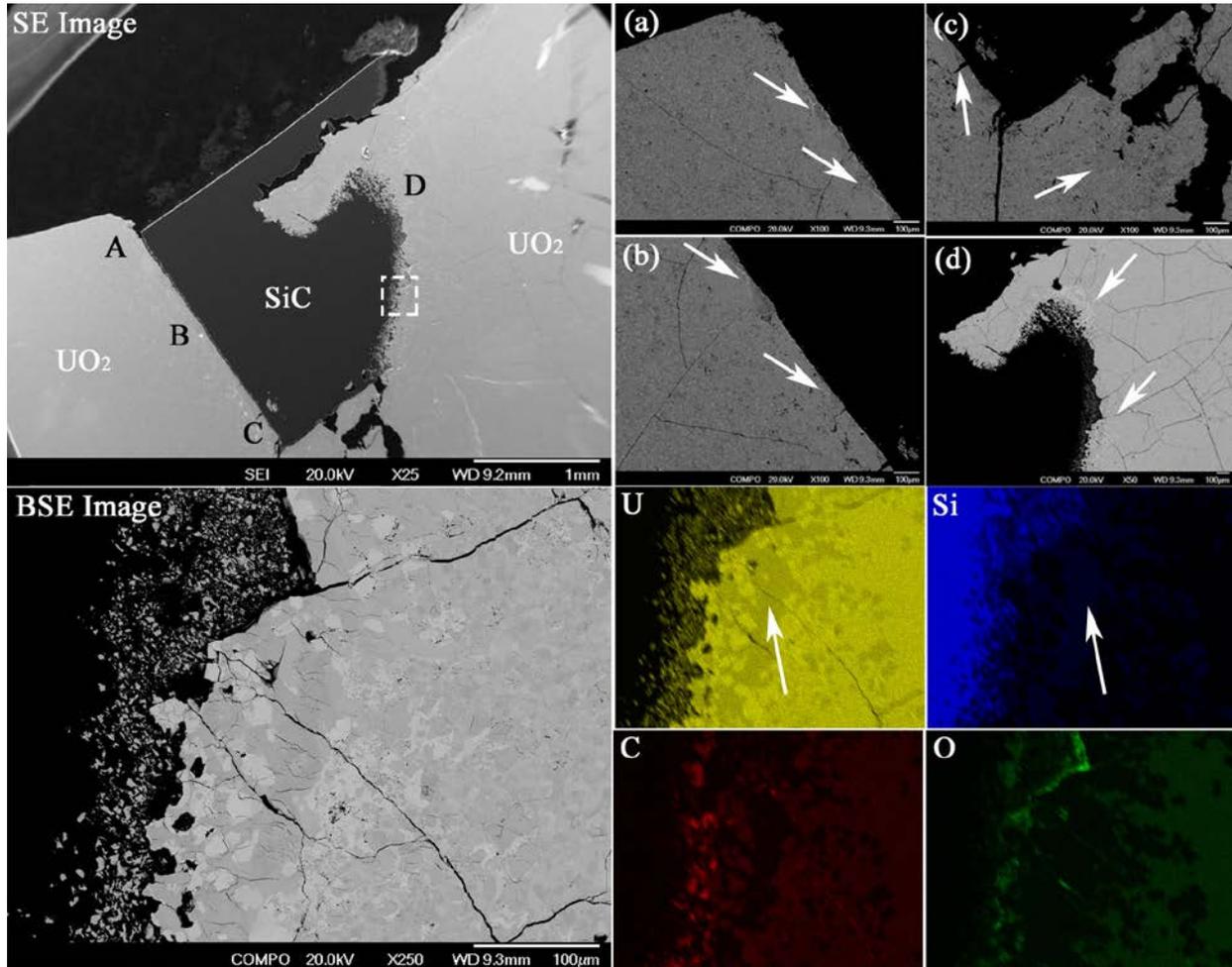


Figure 2. SE (top left) and BSE mode SEM images of selected areas of CVD SiC embedded UO_2 piece. The BSE images (a), (b), (c), and (d) to the right indicated the selected areas highlighted by letters A, B, C, and D, respectively in SE image. The area defined by a box in SE image is selected for EDS elemental maps and the BSE image at the bottom.

As in the CVD SiC embedded UO_2 areas, the CVC SiC embedded UO_2 also showed to form thin layers of new chemical phases on UO_2 (highlighted by arrows in Figure 3a and 3b). These areas on CVC SiC embedded UO_2 sample (100 to 300 μm wide) as shown in Figure 3a and 3b seem to be larger than that of the CVD SiC embedded UO_2 sample area (20 to 50 μm wide) as shown in Figure 2a through 2d. This is in conformation with what was seen in Figure 1. One selected area of the CVC SiC embedded UO_2 sample is shown in Figure 3c together with the corresponding EDS elemental maps to the right of Figure 3c. The high contrast areas in the BSE image

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 UO_2 due to its reaction with SiC at 1500°C .

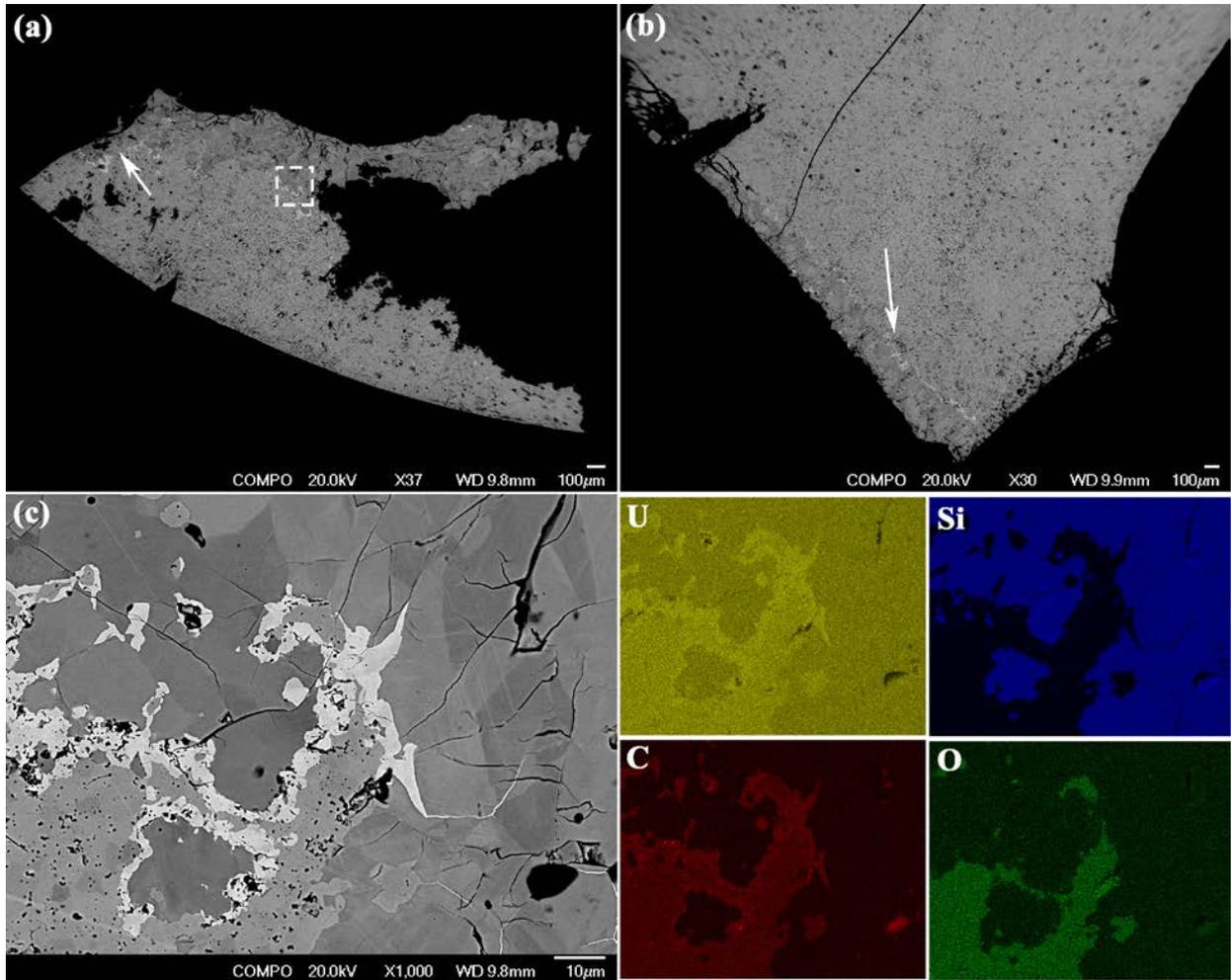


Figure 3. (a)-(b) BSE SEM images of CVC SiC + UO_2 sample area. (c) BSE image of a selected area highlighted by a square in (a) and the corresponding EDS elemental maps to the right.

The EBSD phase maps of two selected areas of the above CVD SiC and CVC SiC embedded UO_2 are shown in Figure 4. The first attempt to incorporate several possible chemical phases, UO_2 , USi_2 , U_3Si_2 , UC_2 , and $\text{U}_3\text{Si}_2\text{C}_2$ including SiC in the data acquisition was not successful due to complications of phases with respect to their crystallography or similar crystallographic orientations. Therefore, SiC was removed in obtaining the CVD SiC embedded UO_2 sample area as shown in left side of the Figure 4. This is the reason why the phase map in the SiC side of the sample had noises. In the UO_2 side of the sample area though had better phase maps correspond to UO_2 , USi_2 , and U_3Si_2 . Phase map for UC_2 also showed decent result up to a certain level. 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 4 (right side). The diffraction patterns of UO_2 , USi_2 , and U_3Si_2 chemical phases that

correspond to phase rich areas in the CVC SiC embedded UO_2 sample area are shown at the bottom of Figure 4.

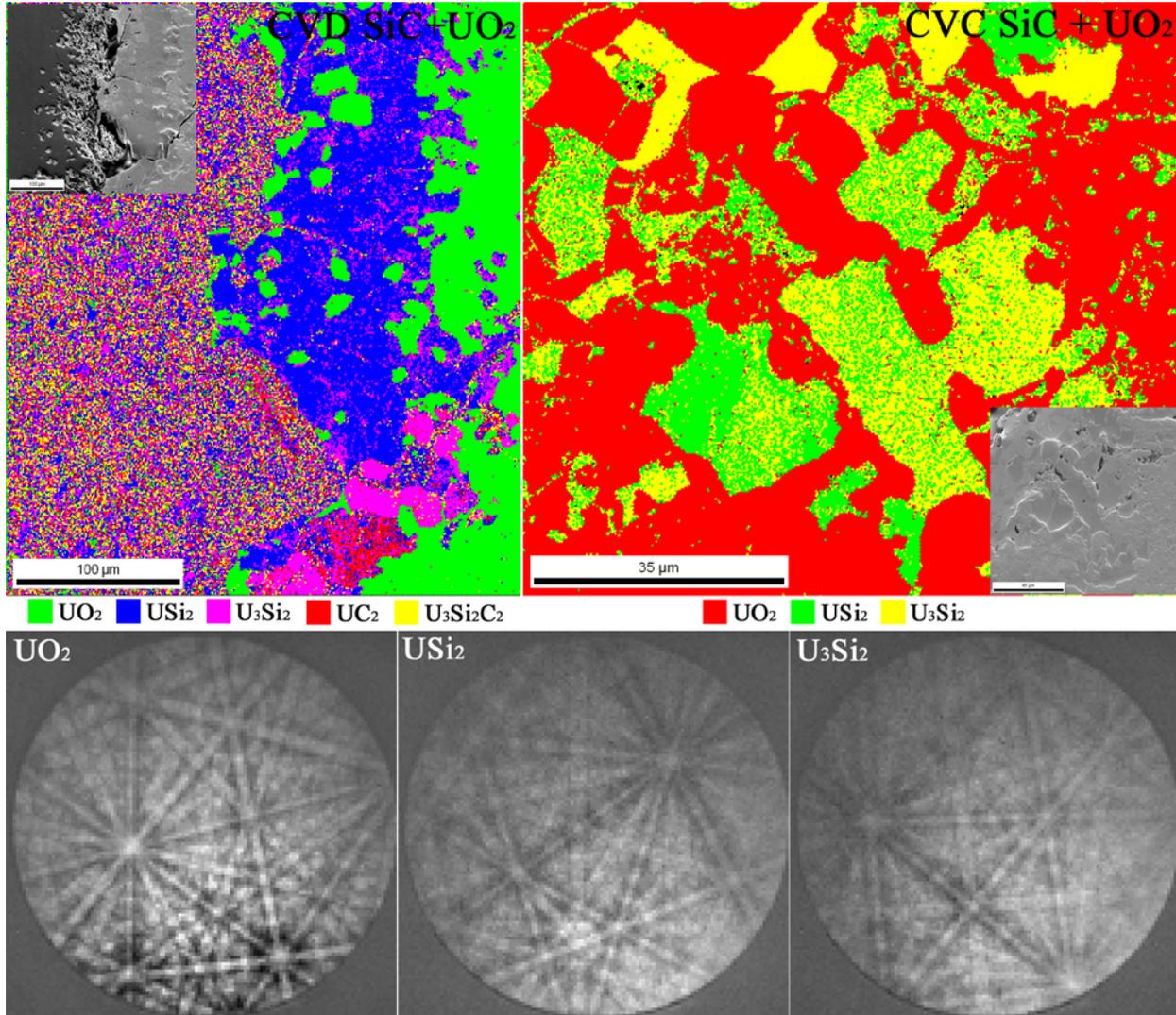


Figure 4. EBSD Phase maps of selected areas of CVD SiC and CVC SiC embedded UO_2 . The insets are SEM images of the corresponding sample areas. SiC side in the left side phase map has noises since SiC was not included in the phase identification. Bottom are the diffraction patterns of UO_2 , USi_2 , and U_3Si_2 chemical phases that correspond to phase rich areas in the CVC SiC embedded UO_2 sample area.

4.0 Preliminary Conclusion

Preliminary results showed that the CVC or CVD SiC did not have any reactions with the embedding medium UO_2 at 500°C up to 96 hrs of heating, whereas they both underwent substantial chemical reactions with UO_2 at 1500°C . With respect to the varied contrast near the SiC/ UO_2 boundaries, the CVC-SiC showed significantly higher reactivity than CVD SiC towards the UO_2 at that temperature. This variation in the contrast was later identified as due to the formation of new chemical phases such as UC_x , USi_2 , and U_3Si_2 .

5.0 Future studies:

- 1). Characterize microstructural differences between the two SiC materials.
- 2). Evaluate few other heat treatment temperatures between 500 and 1500°C such as 700, 900, 1100, 1300, and 1400°C to further investigate the reactivity of the two different SiCs with UO₂.