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Compatibility/Stability Issues in the Use of Nitride Kernels in LWR TRISO Fuel

January 25, 2012

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UT-BATTELLE

ORNL-27 (4-00)

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ORNL/TM-2012/30

Materials Science and Technology Division

COMPATIBILITY/STABILITY ISSUES IN THE USE OF NITRIDE KERNELS IN LWR TRISO FUEL

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January 24, 2012

Prepared by
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managed by
UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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ACKNOWLEDGEMENTS

The authors would like to thank the following Oak Ridge National Laboratory staff for their contribution to this report: R. A. Lowden and D. F. Wilson for their comments, J. J. Henry, Jr. for the heat treatment of the particles, S. B. Waters for the microscopy, R. A. Meisner for the x-ray diffraction, and H. M. Meyer for the XPS. This research was supported by the US Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program.

1. INTRODUCTION

Tristructural isotropic (TRISO) fuel particles embedded in a silicon carbide (SiC) or metal matrix are the basis of fully ceramic microencapsulated (FCM) fuel or metal matrix fuel, respectively.[1,2] A TRISO particle starts as a spherical fuel kernel that is subsequently coated with successive layers of porous carbon (buffer layer), a dense inner pyrocarbon (IPyC), SiC, and an outer pyrocarbon (OPyC) layer. The TRISO technology has been utilized successfully for many years using uranium oxide or oxide-carbide kernels. Recent interest in the fuel for light water reactor (LWR) applications may require the use of uranium nitride kernels to obtain sufficient actinide loading. There has been concern expressed, however, regarding nitridation of the SiC TRISO layer by nitrogen released from the fuel. Specifically, the concerns are in regard to the free nitrogen produced during fission that could attack the SiC layer. This would possibly jeopardize the stability of the SiC layer with the potential conversion into Si_3N_4 or Si(C,N).

The stability of the SiC layer in the presence of free nitrogen will be dependent upon the operating temperatures and resulting nitrogen pressures whether it is at High Temperature Gas-Cooled Reactor (HTGR) temperatures of 1000-1400°C (coolant design dependent) or LWR temperatures that range from 500-700°C. Due to the high FCM thermal conductivity in comparison to UO_2, the fuel temperature will be at most 100-200°C above the 1200°C loss of coolant accident (LOCA) condition, which will endure no more than 30 seconds. Although nitrogen released in fissioning will form fission product nitrides, there will remain an overpressure of nitrogen of some magnitude. The nitrogen can be speculated to transport through the inner pyrolytic carbon layer and contact the SiC layer. The SiC layer may be envisioned to fail due to resulting nitridation at the elevated temperatures. However, it is believed that these issues are particularly avoided in the LWR application. Lower temperatures will result in significantly lower nitrogen pressures. Lower temperatures will also substantially reduce nitrogen diffusion rates through the layers and nitriding kinetics. Kinetics calculations were performed using an expression for nitriding silicon. In order to further address these concerns, experiments were run with surrogate fuel particles under simulated operating conditions to determine the resulting phase formation at 700 and 1400°C.

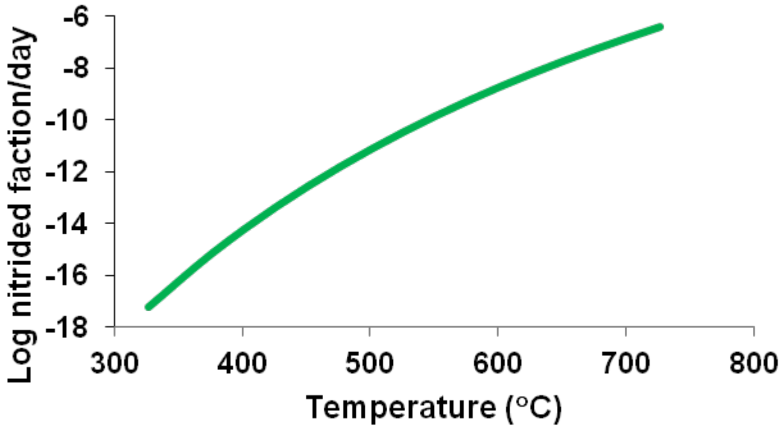
2. NITRIDING KINETICS CALCULATIONS

A review of the literature revealed very limited publications on nitriding of SiC. Rosner and Allendorf [3] investigated oxidation and nitridation of SiC in dissociated gases using a fast flow vacuum technique. Thus their measurements related to removal of SiC and thus the kinetics are not instructive for TRISO fuel. Lichko et al. [4] looked at the effects of temperature and nitrogen pressure on the transformation of SiC to Si_3N_4, although they did not determine kinetics relationships. In both studies, however, there was minimal to no nitridation observed below 1480 and 1550°C, respectively. There is, however, considerable literature on nitriding of silicon, mostly for producing silicon nitride components. For purposes of assessing the issue of nitriding SiC in a TRISO particle the use of relations for nitriding silicon would be a conservative assumption as elemental silicon would be more reactive. Maalmi and Varma [5] obtained an intrinsic kinetics expression for nitriding silicon powder. They determined a relation, Eq. 1, which was entirely chemical kinetic limited and had no influence of mass transport, and thus found the intrinsic nitridation kinetics.

$$r = 2.5 \cdot 10^{4} \exp\left[\frac{-317\ (\mathrm{kJ/mol})}{\mathrm{RT}}\right] \times (C_{\mathrm{N}_2})^{0.92}(S_a)^{0.84}\ \mathrm{mol\ Si/g\ Si\text{-}s} \qquad (1)$$

where R is the ideal gas law constant, T is temperature, C_{N2} is the nitrogen concentration (mol/m^3), and S_a is the SiC specific surface area (m^2/g). Note that hydrogen was present with the nitrogen in the experiments described by Eq. 1.[5]

Equation 1 was used with a set of very conservative assumptions to determine the possible nitriding rate in the SiC layer in a TRISO particle with a UN kernel. Whereas Eq. 1 was derived for a powder, it was assumed in the calculations for a TRISO particle that the SiC grains in a 35 μm thick layer were 3 μm in diameter and treated as a powder. The overall nitrogen pressure was taken as 5 bar, which is well above what is likely to be experienced. The resulting plot for Eq. 1 for estimating the fraction of the 35μm SiC layer nitride per day as a function of temperature is seen in Fig. 1.



Fig, 1. Fraction of a 35 μm SiC layer nitrided per day in reactor as a function of fuel temperature computed from the relations of Maalmi and Varma.[5]

3. EXPERIMENTAL PROCEDURE

A modified TRISO particle composed of a zirconia kernel with successive layers of carbon and an outer layer of SiC was used for this study (no OPyc). The modified particles were placed in either an unglazed Coors 988 high alumina crucible or a Poco graphite crucible and exposed to two heat treatments in a graphite element, controlled environment furnace (Brew). The particles were pretreated at 1200°C at a heating rate of 5°C/min in argon with a balance of 4% hydrogen gas (300 ccm) to remove the native silica surface layer. For the lower temperature exposures they were held for 24 hours at these initial conditions and then the temperature was reduced at 5°C/min to the exposure temperature of 700°C. Once at 700°C, the gas environment was switched to 60 ccm argon with a balance of 4% hydrogen plus 240 ccm of ultra high purity (UHP) nitrogen. The particles were held at these conditions for 168 hours, and then cooled to room temperature at 5°C/min. The 1400°C particle exposures were held at 1200°C for 14 hours before the gas was switched to 60 ccm argon with a balance of 4% hydrogen plus 240 ccm of UHP nitrogen and held at 1200°C for an additional 4 hours. After the 4 hours, the particles were heated at 5°C/min to the final exposure condition of 1400°C and held for 24 hours. Once the exposure was complete, the particles were cooled to room temperature at a rate of 5°C/min. Hydrogen was included in all the experiments as literature on nitriding silicon indicates enhanced kinetics when hydrogen is present.[3]

The resulting exposed particles were characterized using x-ray diffraction (XRD) on a Panalytical Xpert Diffractometer, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) on Hitachi microscopes models 3400 and 4800, and Thermo Scientific K-Alpha X-ray Photoelectron Spectroscopy (XPS) using a Thermo Scientific K-Alpha. Continuous Θ-2Θ scans were performed on the Panalytical Xpert diffractometer from nominally 5 to 80° 2Θ in under 60 min. using slits that adjust to 3mm sample width for all 2-theta values and CuKa radiation (1=1.5405981 Å) with the X'Celerator detector. A search match was conducted using the “Jade” software and the ICDD database. The XPS uses monochromatic Al k-alpha x-rays focused to a 400 μm diameter spot. Photoemitted electrons are dispersed through a double-focusing hemispherical energy analyzer onto a 128-channel detector. Wide energy range survey spectra was collected at 200 eV pass energy at a resolution of 1 ev/step, while narrow energy region core level spectra was collected at 50 eV pass energy at a resolution of .1 eV/step. Data was collected and analyzed using the Avantage Data System version 4.61.

4. RESULTS AND DISCUSSION

The resulting exposed particles were sectioned, mounted and examined using the SEM and are shown in Figures 2 and 3. Figures 2a, 2b, and 2c show increasing magnification of a particle exposed to nitriding conditions at 700°C for 168 hours. In Figure 2a, the top or outer layer is SiC, the middle layer is carbon, and the core or bottom layer is ZrO_2. Figure 2b shows just the outer SiC layer and middle carbon layer, and Figure 2c is a close-up image of just the outer SiC surface. A change in the morphology of the outer layer is visible on the very outer surface indicating that there is some change in the SiC phase under these conditions.

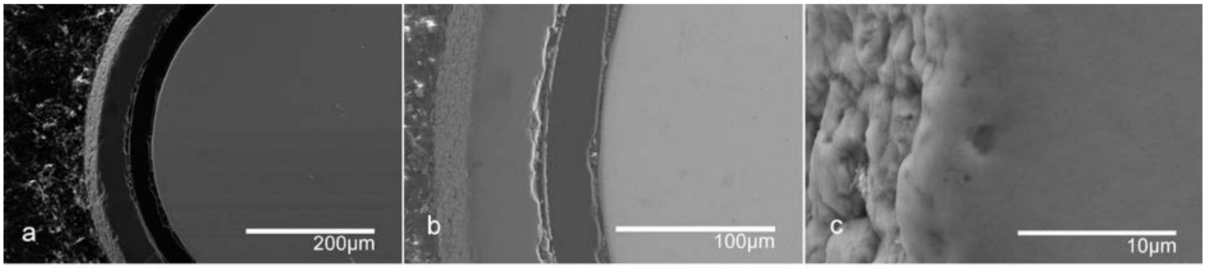


Fig 2. Scanning electron microscopy images of a particle exposed to nitriding conditions at 700°C for 168 hours.

To better elucidate what phase has formed and if any nitrogen containing compounds such as a nitride formed, EDS analysis was also completed on this sample. This elemental analysis of the particle exposed at 700°C for 168 hours is depicted graphically using color mapping in Fig. 3. Red represents carbon, green represents oxygen, blue represents silicon, and yellow represents zirconium. Relatively, the brighter the color shown, the more the element is present. Note there is not a color representing nitrogen as no nitrogen was detected. Also note that the intensity of the carbon present in the outer silicon layer is minimal due to the contrast with the adjacent carbon layer.

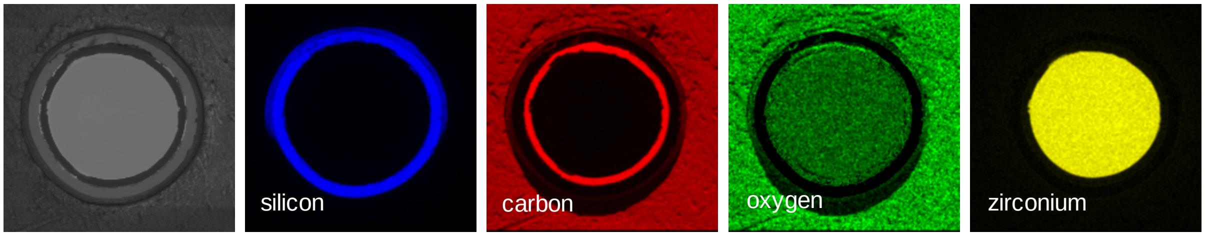


Fig. 3. Backscatter image and energy dispersive spectroscopy maps of a particle exposed to nitriding conditions at 700°C for 168 hours. The image and corresponding maps shown from left to right are backscattered, carbon, oxygen, silicon and zirconium.

Elemental mapping indicated that there was silicon loss in the SiC layer that occurred over the long exposure times. The explanation for this loss is believed to originate from oxygen that was still present in the furnace during this run, which would react with the H_2 to form water. The water then reacted with the SiC to form SiO_2 and/or $Si(OH)_4$ which is removed as a gaseous product in the given conditions. Figure 4 and Table 1 shows the image and the corresponding mapping results indicating the outer layer (area 1) is carbon rich and the layer immediately underneath (area 2) is closer to stoichiometric SiC. Again, no nitrogen was detected using this technique so no nitride was evident.

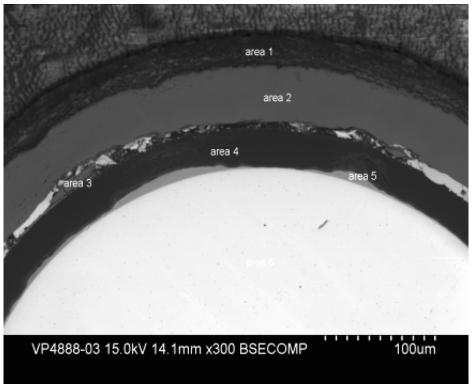


Fig.4. Scanning electron microscopy image of particle exposed to nitriding conditions at 700°C for 168 hours and used for energy dispersive spectroscopy of areas 1 and 2.

Table 1. Elemental mapping of outer surface of a particle exposed to nitriding conditions at 700°C for 168 hours

ELEMENT	AREA 1		AREA 2	
	WEIGHT %	ATOMIC %	WEIGHT %	ATOMIC %
C K	71.40	85.45	45.05	66.76
O K	2.09	1.87	0	0
Si K	24.00	12.28	51.33	32.53
Zr L	2.52	0.40	3.63	0.71
Total	100.0	100.0	100.0	100.0

The particles exposed to nitriding conditions at 1400°C for 24 hours are shown in Fig. 5. As at 700°C, Fig. 5a shows the top or outer layer is SiC, the middle layer is carbon, and the core or bottom layer is ZrO_2. Figure 5b shows just the outer SiC layer and middle carbon layer, and Fig. 5c is a higher magnification image of just the outer SiC surface. At the higher temperature condition, no change in the morphology of the outer layer is visible. This would also indicate, based on the previous results, that there is no nitride formation on the outer surface even at the higher temperature.

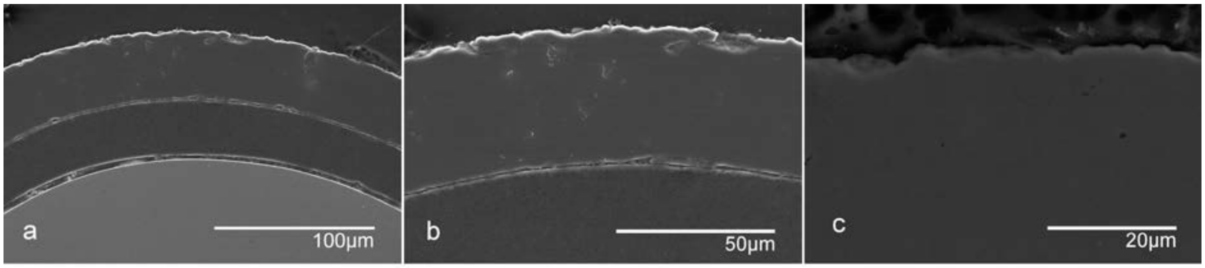


Fig 5. Scanning electron microscopy images of a particle exposed to nitriding conditions at 1400°C for 24 hours.

To again determine if any other phase has formed and if any nitrogen containing compounds such as a nitride are present, EDS analysis was performed on this sample. The EDS map of the particle exposed at 1400°C for 24 hours is shown in Figure 6. Like the 700°C particle there is not a color representing nitrogen as no nitrogen was detected, and the intensity of the carbon present in the outer silicon layer appears minimal due to the contrast with the adjacent carbon layer.

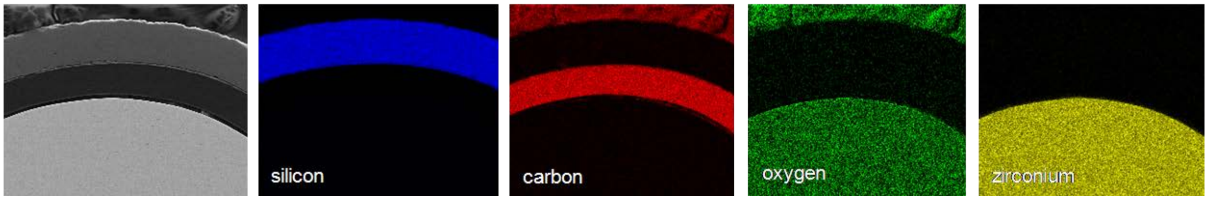


Fig. 6. Backscatter image and energy dispersive spectroscopy maps of a particle exposed to nitriding conditions at 1400°C for 24 hours. The image and corresponding maps shown from left to right are backscatter, carbon, oxygen, silicon and zirconium.

Elemental mapping indicated that there that the SiC layer was unaffected (Fig. 7 and Table 2). Again, no nitrogen was detected using this technique so no nitride was evident.

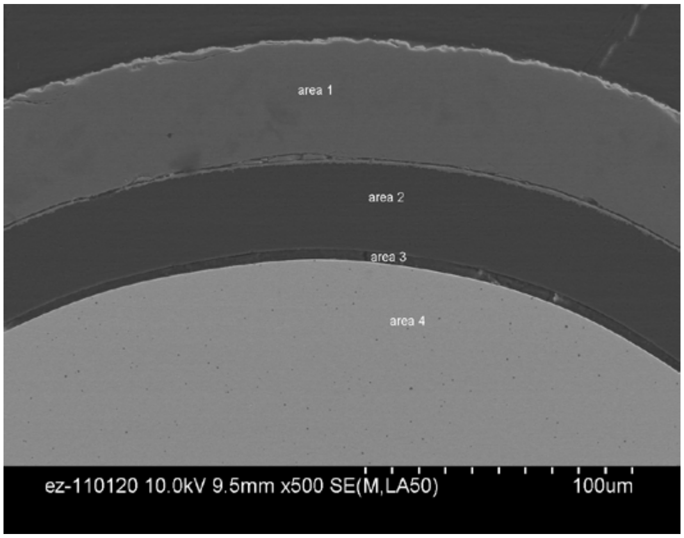


Fig. 7. Scanning electron microscopy image of particle exposed to nitriding conditions at 1400°C for 24 hours and used for energy dispersive spectroscopy of areas 1 and 2.

Table 2. Elemental mapping of outer surface of a particle exposed to nitriding conditions at 1400°C for 24 hours

ELEMENT	**AREA 1**		**AREA 2**	
	WEIGHT %	**ATOMIC %**	**WEIGHT %**	**ATOMIC %**
C K	23.17	41.35	96.71	97.51
Si K	76.83	58.65	0	0
O K	0	0	3.29	2.49
Total	100.0	100.0	100.0	100.0

In order to fully confirm that nitride was indeed not present in either set of samples, both XRD and XPS techniques were utilized. Figure 8 shows the x-ray diffractograms for both the 700°C and 1400°C exposed particles. A non-preferred orientation of SiC is most likely present in the 700°C exposed particle.

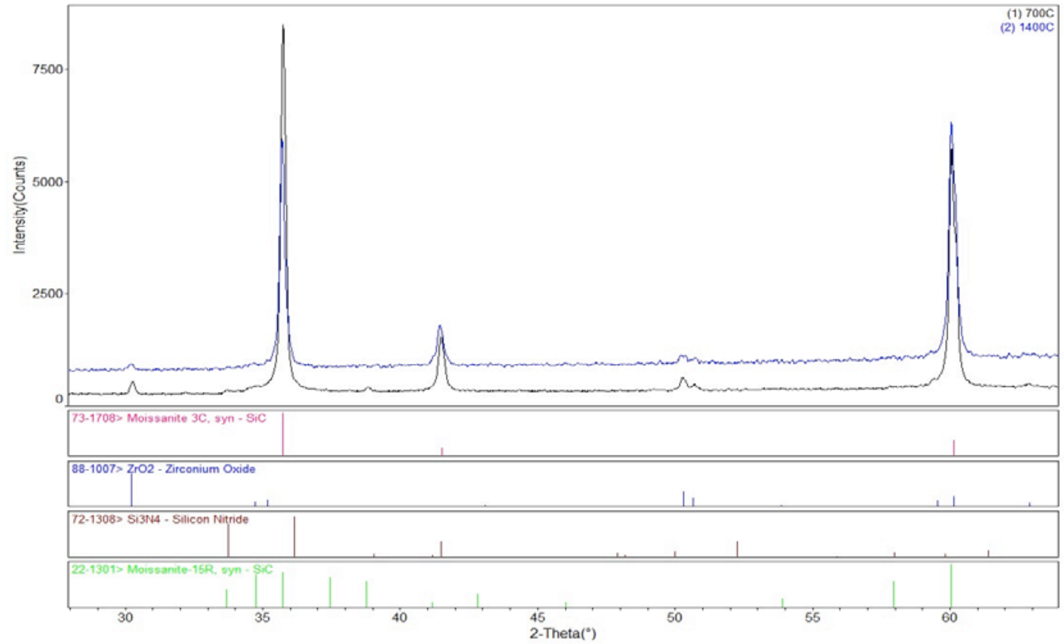


Fig. 8. X-ray diffraction patterns for particles exposed to nitriding conditions at 700°C for 168 and at 1400°C for 24 hours.

As XRD averages composition into the depth of a material, another surface composition analysis technique was also utilized. XPS, however, also did not show any surface silicon nitride formation for either the 700°C and 1400°C exposed particles, although it did show formation of a very thin layer of AlN in the 1400°C condition (Fig. 9). The formation of the AlN is attributed to contamination from alumina present in the furnace.

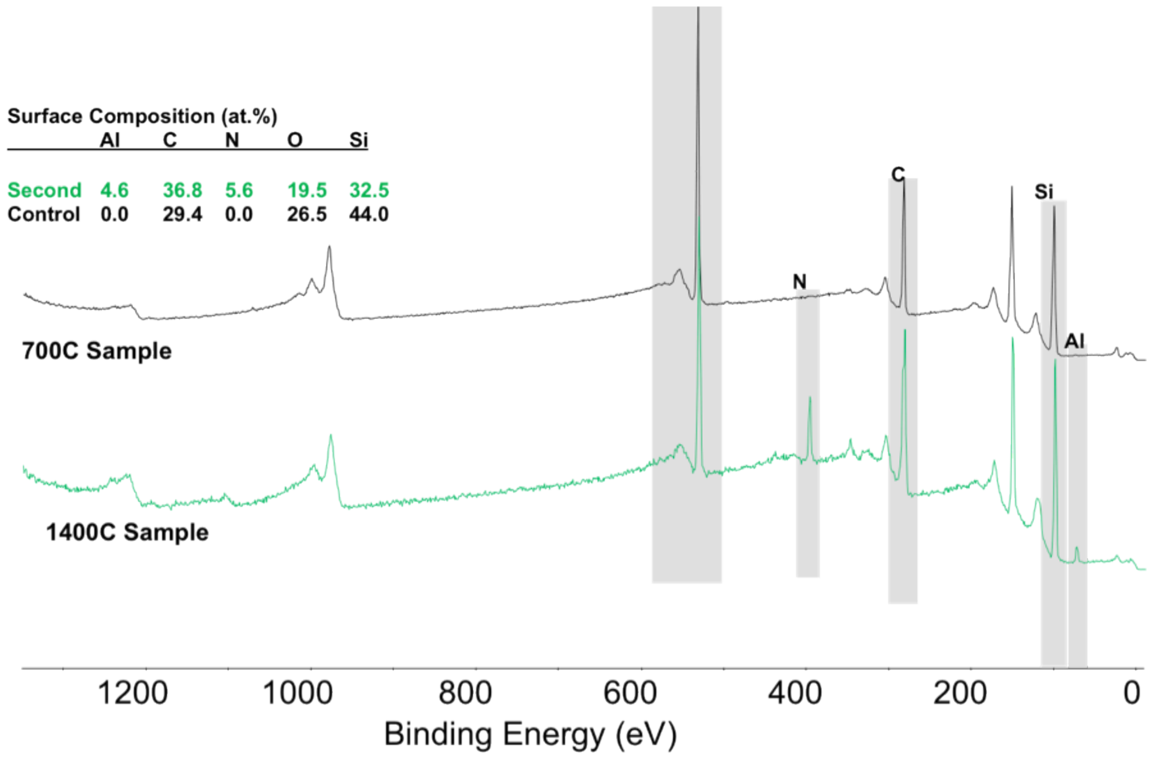


Fig. 9. XPS patterns for particles exposed to nitriding conditions at 700°C for 168 and at 1400°C for 24 hours.

5. CONCLUSIONS

Previous reports and very conservative calculations based on nitriding silicon both indicate that a nitride will not form at the operating conditions within FCM TRISO particles with UN kernels. As the FCM fuel thermal conductivity is significantly higher than that of UO_2 it is expected that operating conditions will not exceed a 700°C maximum fuel temperature. In transient events the fuel temperature will be at most 100-200°C above the 1200°C LOCA condition, which will endure no more than 30 sec. For the purpose of our calculations an assumed a ramp to 1400°C for an extended period is very conservative. In the experimental efforts at 700°C and 1400°C and the respective 168 h and 24 h nitriding times, there was no evidence of silicon nitride formation. There is evidence, however, of compositional changes in the outer SiC layer due to reaction with hydrogen and tramp oxygen.

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