

Wet-Chemical Dissolution of TRISO-Coated Simulated High-Temperature-Reactor Fuel Particles

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Abstract

Chemical etching with different mixtures of acidic solutions has been investigated to disintegrate the two outermost coatings from tri-structural isotropic coated particles containing zirconia kernels, which are used in simulated particles instead of uranium dioxide. A scanning electron microscope (SEM) was used to study the morphology of the particles after the first etching step as well as at different stages of the second etching step. SEM examination shows that the outer carbon layer can be readily removed with a $\text{CrO}_3\text{-HNO}_3/\text{H}_2\text{SO}_4$ solution. This finding was verified by energy dispersive spectroscopy (EDS) analysis. Etching of the silicon carbide layer in a hydrofluoric-nitric solution yielded partial removal of the coating and localized attack of the underlying coating layers. The SEM results provide evidence that the etching of the silicon carbide layer is strongly influenced by its microstructure.

Keywords: TRISO coated fuel particles; Silicon carbide; Pyrolytic carbon; Chemical etching; Scanning electron microscope

1. Introduction

TRISO particles used in high temperature reactors (HTRs) consist of fissionable uranium dioxide (UO_2) fuel kernels. The kernels are individually enclosed with four distinct coating layers, starting from the inside a porous carbon buffer, then an inner pyrolytic carbon (IPyC) layer, followed by a layer of ceramic silicon carbide (SiC) and finally an outer pyrolytic carbon layer (OPyC) [1]. Collectively, the coating layers provide the primary barrier that prevents release of fission products generated during burn up in the UO_2 fuel kernel [2]. Among the coating layers, silicon carbide is the most important and essential of the barrier coatings. It acts as the main fission product barrier and provides mechanical support and structural rigidity to the coated particle [3].

During fission of uranium, heat is generated along with a large number of fission products. Oxygen atoms are also liberated during the fission reaction. The kernel constitutes the first barrier to the release of the fission products. The released oxygen in the kernel binds with rare earth products to form immobile oxides, thereby controlling their migration potential to the coating layers, while fission products that do not form stable oxides are released from the kernel through a diffusion process and are contained to a very high extent by the SiC layer [4]. Fission products such as palladium may chemically interact with the silicon carbide, resulting in corrosion and thinning of the coating layer [5]. Hence, it is crucial to understand the distribution and behaviour of fission products in the coating layers. The information obtained from the distribution can provide insight into the underlying physical and chemical mechanisms responsible for coated particle failure.

One way to ascertain the distribution and migration of fission products in coating layers of the coated particles is by separating the layers in sequence. Removal of the coating layers has been studied by several authors using ion sputtering [6], chemical dissolution with chrome oxide in sulphuric acid and hydrofluoric acid at 140 °C [7], and the disintegration of carbon layers at 600 °C and 800 °C by thermal oxidation followed by crushing of the silicon carbide layer [8-10]. The removal of the silicon carbide layer by molten salts has been studied by Fukuda and Iwamoto [11].

Layer by layer removal of the coatings of the TRISO particle is considered difficult regardless of the method employed. This is due to the chemical properties and strength of the coatings, in particular the silicon carbide layer, which is rigid and is known to react poorly with acids and bases [12]. The small particle size, diameter of ~ 1 mm, has an impact on the method chosen. The removal by ion sputtering technique does not produce uniform removal of the layers [6], and the removal of the silicon carbide layer by molten salts at 800 °C affects the distribution of fission products in the layer [11]. The carbon layers can be readily removed by thermal oxidation [8-10]. However, EDS studies [8] show that the removal of the carbon layers at 600 °C cause partial oxidation of the SiC layer. The main focus in these studies was the determination of fission products in the removed contents of irradiated fuel particle coatings.

In the present work, results are presented for the selective removal of coating layers by more facile wet chemical methods in order to obtain optimum etching conditions for irradiated TRISO coated particles.

2. Material and Experimental Methods

2.1 Samples

The samples used in this study were simulated coated fuel particles with normal SiC/PyC multilayer coatings produced by chemical vapour deposition processes. The kernels consist of zirconium dioxide (ZrO_2) substituting for the actual UO_2 (Figure 1). The following gases at various temperatures were used to deposit each coating layer: acetylene (C_2H_2) for the porous buffer (95 μm), a mixture of acetylene and propylene (C_2H_2/C_3H_6) for the IPyC (40 μm) and OPyC (40 μm) layers, and methyltrichlorosilane (CH_3SiCl_3) for the SiC layer (35 μm). In all the pyrolytic carbon layers, argon was used as a carrier gas, while hydrogen was used for the SiC layer. Exact preparation conditions were not the same for the ZrO_2 ; these were altered so that the kernels experience same: fluidizing conditions and temperatures of deposition. SEM observed structure and appearance seemed to be the same as for UO_2 coated particles used, for fuel [John Barry, private communication].

2.2 Reagents

All etching reagents used were obtained from Merck: 16 molar (M) nitric acid; 18 molar (M) sulphuric acid; 22 molar (M) hydrofluoric acid and chromium trioxide.

2.3 Chemical Etching of the Outer Pyrolytic Carbon

The etching solutions were prepared using an acidic mixture consisting of 18M sulphuric acid (H_2SO_4), 16 M nitric acid (HNO_3) and chromium trioxide (CrO_3). The pre-weighed samples, about 0.5 g of coated particles, were added to a glass vessel (25 ml) containing the mixture prepared by dissolving 0.5 g of CrO_3 with equal amounts (6 ml) of H_2SO_4 and HNO_3 . After heating it to no more than 140 °C for 15 to 30 minutes, the solution obtained was cooled, diluted with water and decanted. The particles were then washed with de-ionised water (~25 ml), followed by ethanol, to remove any residue that remained on the surfaces. The surface appearance of the particles was examined to determine whether the layer had

dissolved completely and if not, the etching process was repeated with a fresh etching solution until full dissolution of the layer had been achieved.

2.4 Chemical Etching of the Silicon Carbide Layer

Chemical etching of the silicon carbide layer was carried out in a microwave-assisted reactor system (MARS 5) with a power setting of 500 W at 2450 MHz. The microwave heating technique has been used previously for dissolution of UO_2 fuel particles in a nitric acid medium [13] and for decomposition of carbide compounds [14]. This heating technique was chosen because the reaction time is faster than conventional heating [15].

The MARS 5 system is equipped with 12 PTFE vessels, which contain the solution and samples. The vessels may be used simultaneously with one control vessel for monitoring temperature and pressure. The control vessel is connected to a fibre optic temperature sensor that penetrates into the vessel and a pressure sensor, which is attached to the lid. It is assumed that the temperature and pressure inside the control vessel are representative of all the samples that are digested simultaneously.

The sample used to study the etching of the silicon carbide layer consisted of particles of which the kernels were only coated up to the silicon carbide layer, without application of the outer pyrolytic carbon layer. Two etching solutions were prepared: one solution consisting of equal amounts of 18 M H_2SO_4 , 16 M HNO_3 and 22 M hydrofluoric acid (HF); the other prepared with equal amounts of HNO_3 and (HF). The volume of the solution that could be used in each vessel is limited to 8 mL.

A sample weighing between 0.5 to 1.0 g was introduced into each vessel and 6 mL of the etching solution was then added. The vessels were closed and clamped in accordance with the manufacturer's procedure and placed in the microwave oven. The heating system consisted of a three-stage power setting with pre-set temperature and pressure. The heating program started with a 10-minute period where the temperature was ramped to 200 °C and held for 60 minutes. After elapse of the hold time, a cooling step was applied for 10 minutes until 60 °C was reached. The vessels were then removed from the MARS 5 and cooled for a further 15 minutes. When cooled, they were uncapped, the solution diluted with distilled water (20 mL), and the retrieved samples were washed extensively using de-ionised water (15 mL), followed by boric acid (10 mL) and then dried.

A surface examination was conducted on these etched samples and when applicable some were etched again using a fresh solution every 60 minutes for up to 3 hours.

2.5 Analytical Techniques

The surfaces of the coated particles, prior and after etching were first investigated with a NIKON SMZ800 stereoscopic zoom microscope and then with a high resolution ZEISS ULTRA PLUS SEM to examine the morphology and microstructure features of the particles. The elemental analysis of the coated particle surface after chemical etching was done using a SEM model FEI Quanta 200 3D, equipped with an EDS system.

3. Results and Discussions

3.1. Outer Pyrolytic Carbon Etching

3.1.1. SEM Examination

The outer pyrolytic carbon surface of the particles prior to chemical etching, Figure 2(a), shows densely packed material with globular features and interspatial voids. To investigate how pyrolytic carbon decomposes under the chemical treatment of $\text{CrO}_3\text{-HNO}_3/\text{H}_2\text{SO}_4$ solution a coated particle sample was partially etched for 10 minutes. SEM examination of the surface, Figure 2(b), reveals a structure, which is dominated by more distinctly globular features and voids that are more prominent and linked together. It is evident that the chemical etchant penetrates between the carbon globules resulting in disintegration of the layer.

After completion of the chemical treatment to remove the OPyC layer, SEM examinations showed that the globular amorphous features visible in Figure 2 on the untreated as well as the partially etched sample are no longer visible. The microstructure, Figure 3, is now dominated by SiC crystalline grains of varying sizes. The image was taken at a lower magnification than that of the particle morphology prior to chemical treatment, Figure 2, to allow more precise identification of carbon remnants. The results confirm that the OPyC layer had been completely removed with no indication of physical damage caused by the etching solution to the silicon carbide surface.

3.1.2. EDS analysis

The EDS quantitative analysis (Table 2) indicates the presence of silicon and carbon, which corresponds to the calculated weight percentage of the chemical compound with formula SiC (silicon carbide). This analysis confirms that the observed microstructure after chemical etching is silicon carbide. A further conclusion is that the outer pyrolytic carbon layer, previously covering the SiC layer, is completely removed by the chemical treatment. The EDS result mentioned is one measurement but other few measurements were done on other areas as well to see if the values are representative, which it was.

3.2. Silicon Carbide Microwave-Assisted Etching

3.2.1. Sample Treated with $\text{HF}/\text{HNO}_3\text{-H}_2\text{SO}_4$ Solution

The etched surfaces were investigated initially under an optical stereomicroscope and then with a high resolution SEM. Figure 4 displays the optical microscope images of samples before and after chemical etching. The outer surfaces of particles before etching had a shiny metallic grey appearance with a smooth texture. After etching for 2 hours with the $\text{HF}/\text{HNO}_3\text{-H}_2\text{SO}_4$ solution under the same conditions (Figure 4b and 4c), the surface appearance changed from a metallic grey surface observed before etching to a yellow-coloured grainy structure. A few particles show an irregular etching pattern, Figure 4(b), and resulting in partial removal of the layer. Figure 4(c) shows a black particle where the black colour represents the inner pyrolytic carbon layer with the SiC layer completely removed; some of the other particles do not show any signs of attack, while the silicon carbide layer of several particles disintegrated into pieces due to the reaction with chemical etchants.

Some of the challenges experienced were variations of the results from etched surfaces. The shards obtained after etching imply that the layer had separated from the rest of the particle. However, the manner in which this layer has been removed is not fully understood. Another disadvantage of this process is that after 3 hours of etching, the inner carbon layer was attacked by the etchant, resulting in the undesired dissolution of the carbon layer.

The samples etched for 60 minutes were investigated further using a high resolution SEM. The micrographs Figure 5(a) and 5(b) represent the same region of the sample under investigation but at different magnifications. The etched surface now consists of separated grain clusters. The smooth microstructure observed before etching is now attacked and separated by the etchant. The conclusion at this point was that etching under these conditions was producing undesirable results.

3.2.2. Samples treated with HF/HNO₃ solution

A SEM micrograph of the samples treated in the microwave system with a HF/HNO₃ solution for 60 minutes at a temperature of 200 °C is shown in Figure 6. The examination shows that the etchant initially attacks the grains along grain boundaries and to a lesser extent, the planar faults that are revealed by somewhat rounded dislocation etch pits. Figure 7 shows the etched surface of a sample treated for 2 hours under similar conditions as the sample discussed in Figure 6. In this sample, the etchant seems to severely attack the grain boundaries thus separating individual grains. The planar faults revealed through etching are again noticeable but a slightly lower magnification was used to clearly indicate the grain separations. The reason for this phenomenon is not fully understood, but it is possible that these effects are due to chemical attack on slip planes in the silicon carbide crystal. Higher magnification (Figure 8) shows severely etched strained regions, due to slip in compressed crystals, consisting of jagged contours. At prolonged time, 3 hours of etching at 200 °C (Figure 9), the etched sample disintegrated into single crystals with needle like appearance and maximum size of 8 μm. This phenomenon shows that SiC can be etched to some extent but that the reaction also vigorously attacks the inner carbon layer.

4. Conclusion

In this study two different mixtures of acidic solutions were employed to etch away the two outermost coatings from single zirconia TRISO coated particles. The particle surface was studied by scanning electron microscopy after the first etch step removing the outer pyrolytic carbon layer, and at different stages of the second step that etched the SiC layer. It was established that the outer pyrolytic carbon layer can be readily removed using a solution of CrO₃-HNO₃/H₂SO₄ in the temperature range 130 - 140 °C, leaving the SiC layer exposed. This result was verified by EDS analysis.

The MW-assisted chemical etching studies on the silicon carbide layer indicates that attack starts at grain boundaries and progresses to the intragranular features. Partial removal of this layer was observed together with localized attack of the underlying inner pyrolytic carbon layer.

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5. References

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Authors Biography

- 1) ***Kholiswa Patricia Skolo*** (figure 10a): Holds a BSc honours degree in Materials Science. She is currently working for the South African Nuclear Energy Corporation (Necsa) as a scientist.
- 2) ***Professor Philip Crouse*** (figure 10b): Is a physical chemist with more than two decades experience in the nuclear and related industries. He is the current Fluoro-materials, Chair holder at the department of Chemical Engineering, at the University of Pretoria. The South African Department of Science and Technology, and Fluorine Expansion Initiative fund his chair.
- 3) ***Wouter Klopper*** (figure 10c): Is currently a project manager at Necsa for post irradiation examination of PBMR Fuel elements. He has 10 years of experience as a scientist on Laser Isotope Separation at AEC and 7 years as a group leader and later business area manager for laser materials processing.
- 4) ***Johan Venter*** (figure 10d): is a physicist with more than forty years experience in the nuclear industry in South Africa, first in the LWR field and later in the HTR field, specializing in HTR fuel. He is currently a consultant for Necsa and PBMR (Pty) Ltd in the field of HTR fuel development and qualification.
- 5) ***Trudy Jacobs*** (figure 10e): Has a Diploma in Physical Metallurgy with 10 years experience in scanning electron microscopy. She is currently employed as a technical consultant at Necsa

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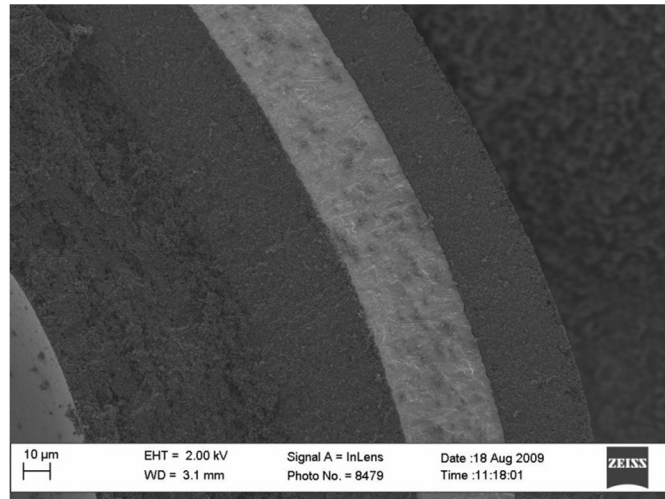


Fig. 1. SEM image of a transverse section of a Zirconia TRISO coated particle.

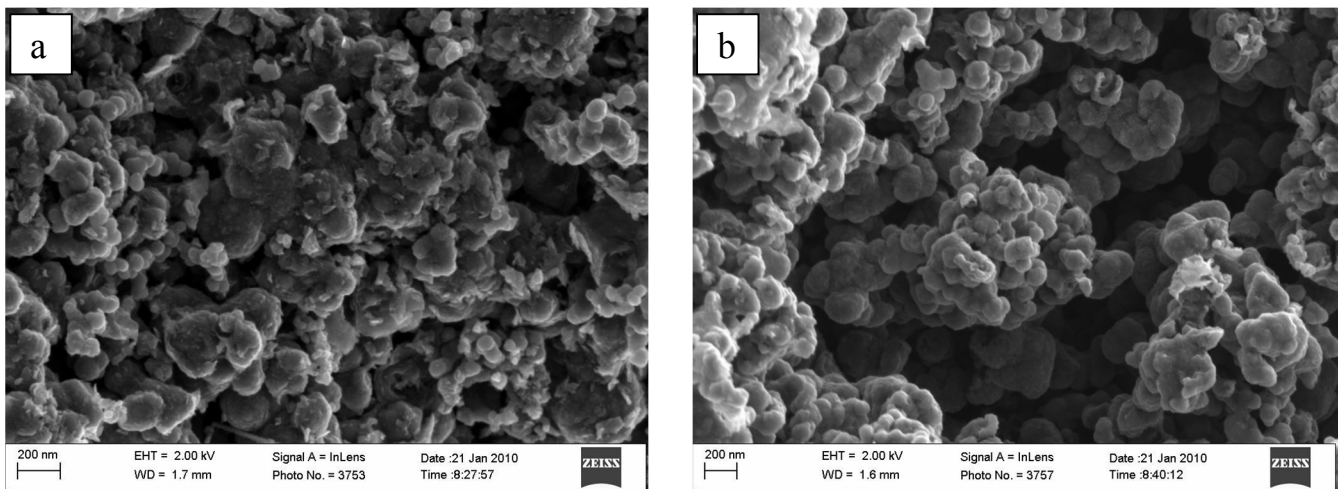


Fig. 2. SEM micrographs of OPyC surface (a) prior to $\text{CrO}_3\text{-HNO}_3/\text{H}_2\text{SO}_4$ etching (b) after 10 minutes of etching.

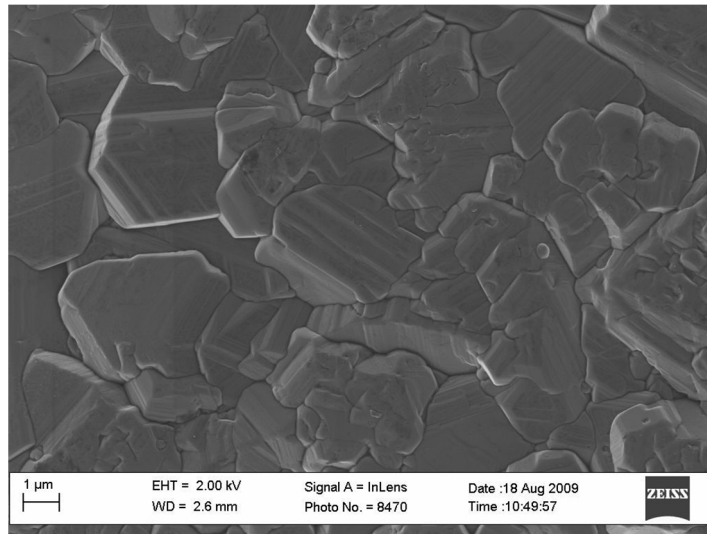


Fig.3. SEM micrograph of SiC surface after removal of OPyC.

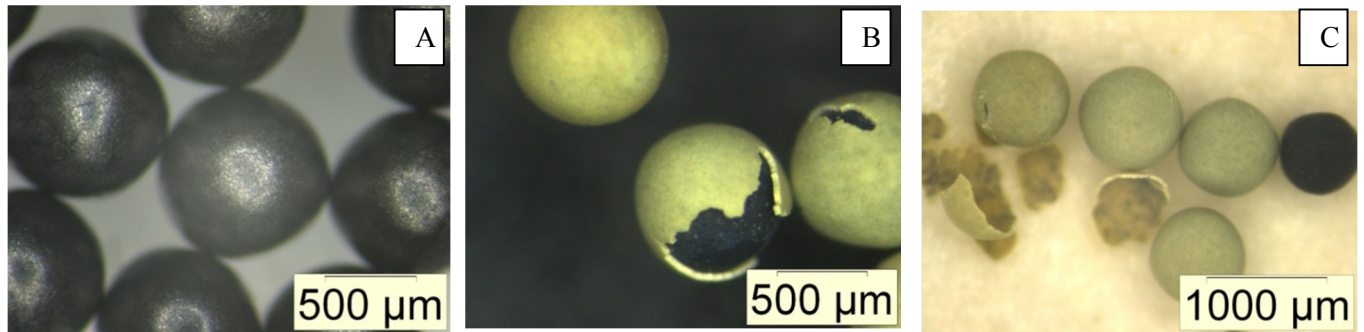


Fig. 4. Optical light microscopy images of samples before (a) and after MW HF/HNO₃/H₂SO₄ treatment (b) and (c).

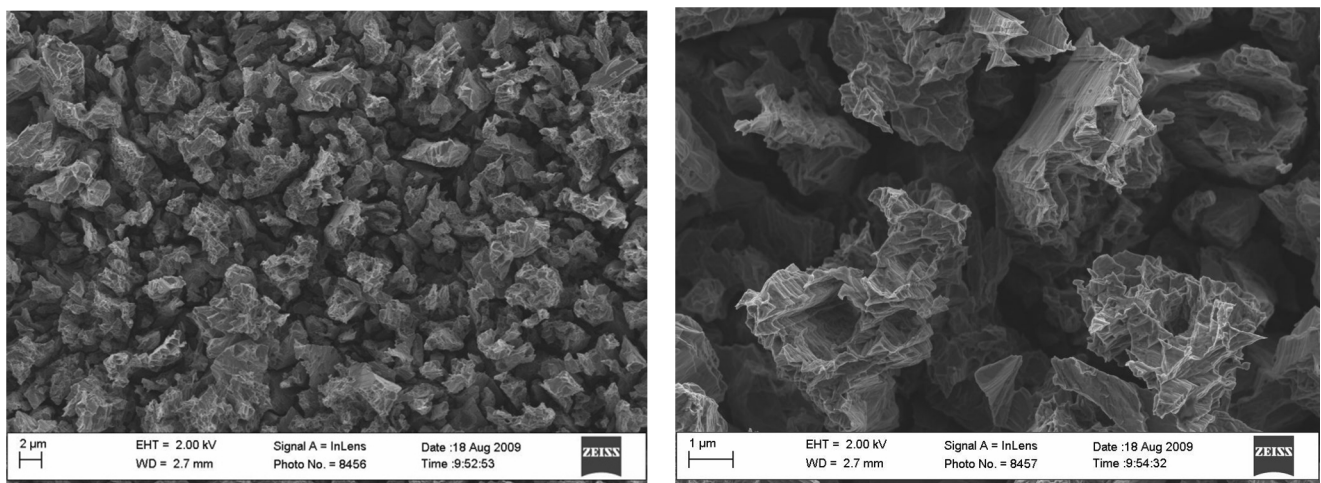


Fig. 5. Silicon carbide surface etched for 60 minutes in HF/HNO₃/H₂SO₄.

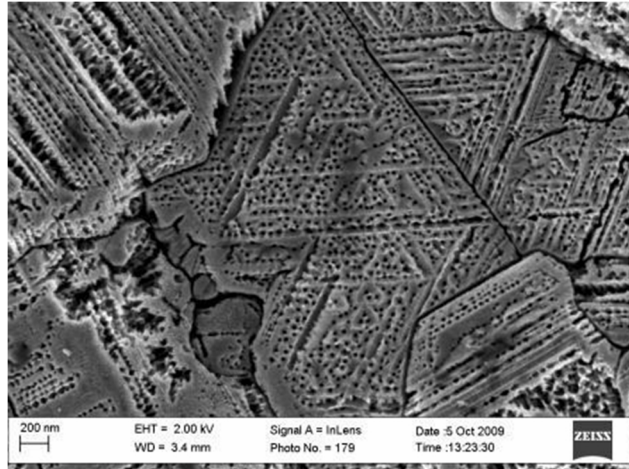


Fig.6. SiC surface HF/HNO₃/H₂SO₄ etched for 60 minutes

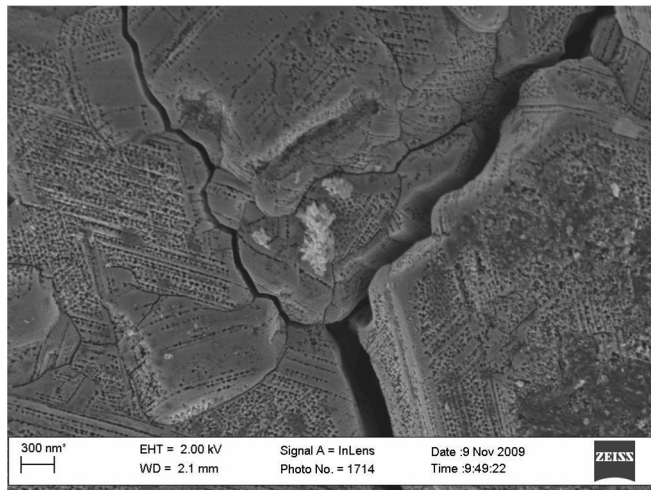


Fig.7. SEM image of SiC grain structure after HF/HNO₃/H₂SO₄ etching for 2 hours

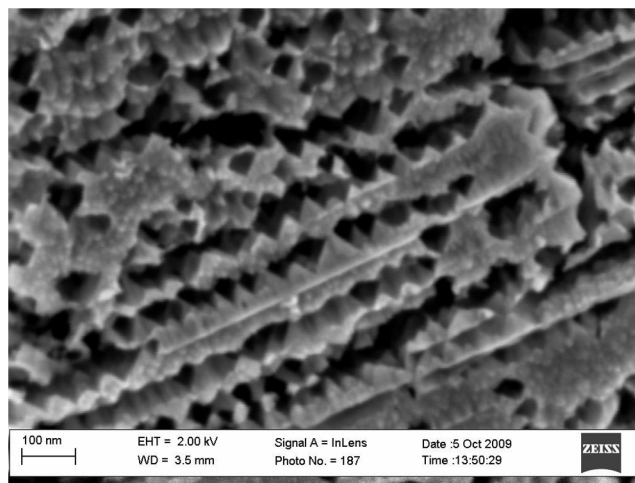


Fig.8. SEM micrograph of SiC slips planes after 2 hours of HF/HNO₃/H₂SO₄ etching

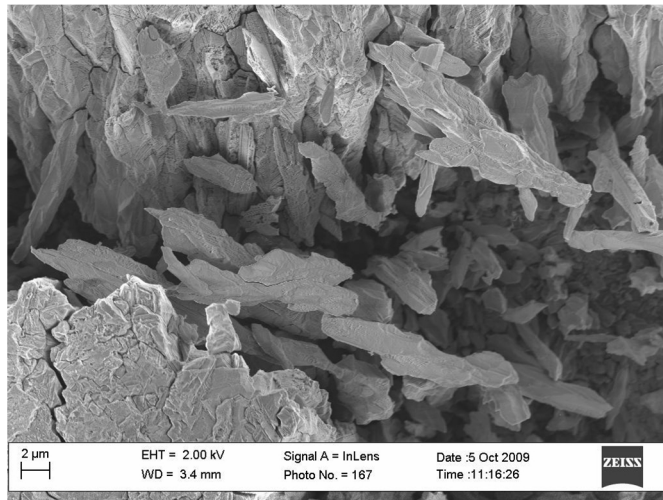


Fig.9. SEM micrograph revealing single SiC crystals after 3 hours HF/HNO₃/H₂SO₄ etching.



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(b) Prof Philip L. Crouse



(b) Mr. Wouter Klopper



(c) Dr Johan H. Venter



(d) Ms. Trudy Jacobs

Fig.10: Images of the Authors

Table 1

Nominal layer thicknesses of a coated fuel particle.

Coating layer	Thickness (μm)
Porous buffer layer	95
IPyC	40
SiC	35
OPyC	40

Table 2

EDS Analysis of SiC surface after removal of the OPyC layer.

Element	Quantity (wt %)
Carbon	30.35
Silicon	69.65
Total	100.00