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Controlled etching of the SiC layer in TRISO coated particles using CF_4 in a non-thermal plasma

Authors:
Renier Koen[a]
Izak J van der Walt[a]
Arnold A Jansen[a,b]
Philippus L Crouse[b]

Affiliations:
[a]The South African Nuclear Energy Corporation Ltd (Necsa)
PO Box 582, Pretoria 0001, South Africa
[b]Department of Chemical Engineering, University of Pretoria, Lynnwood Road, Pretoria 0001, South Africa

Corresponding author:
Renier Koen
E-mail:
koen.renier87@gmail.com

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The fluorine radicals generated in a CF_4 non-equilibrium RF plasma readily react with silicon carbide (SiC) forming volatile SiF_4 and CF_4. In a spouted-bed configuration this enables the complete removal of the SiC layer of TRISO coated particles in 14–15 h with excellent control of the process for analysis and quality control of the coatings.The process kinetics is mass-transfer controlled.

Beheerde etsing van die SiC-laag in TRISO-bedekte partikels in 'n nie-termiese CF_4 plasma: Die fluoorradikale wat in 'n nie-termiese CF_4-radiofrekwensieplasma (glimontladingsplasma) opgewek word, reageer geredelik met silikoonkarbied (SiC) met die vorming van vlugtige SiF_4 en CF_4. In 'n spuitbedopstelling wat hier gebruik word, bewerkstellig dit binne 14 tot 15 h die volledige verwydering van die SiC-deklaag vanaf TRISO-partikels, met uitstekende beheer oor die proses vir analitiese en kwaliteitsbeheerdoeleindes. Die proseskinetika word deur massa-oordrag beheer.

Background

It has been well-documented that the successful operation of modular high temperature gas-cooled reactors (HTRs), depends on the performance and structural stability of TRISO-coated fuel particles (Gulol et al. 2006, Seibert et al. 2019, Verfondern et al. 2007). The term TRISO refers to a TRi-structural ISOtropic particle that commonly consists of a ~0.5 µm, fissile UO_2 kernel encapsulated by a series of four functional layers deposited by means of a standardised chemical vapour deposition (CVD) process (Del Cul et al. 2003). These four layers represent three types of structures, namely UO_2, carbon and SiO_2. The inner porous carbon layer acts as a buffer layer for gaseous fission products and is protected by a high density pyrolytic carbon layer (IPyC). A β silicon-carbide (β-SiC) layer encapsulates the two carbon layers. Several of these coated particles are grouped together, to eventually form a fuel pebble. To improve binding between the coated particles and the amorphous carbon of the pebble, an additional pyrolytic carbon layer (OPyC) is deposited around the SiC layer. A schematic representation of the general structure of a TRISO fuel particle is presented in Figure 1.

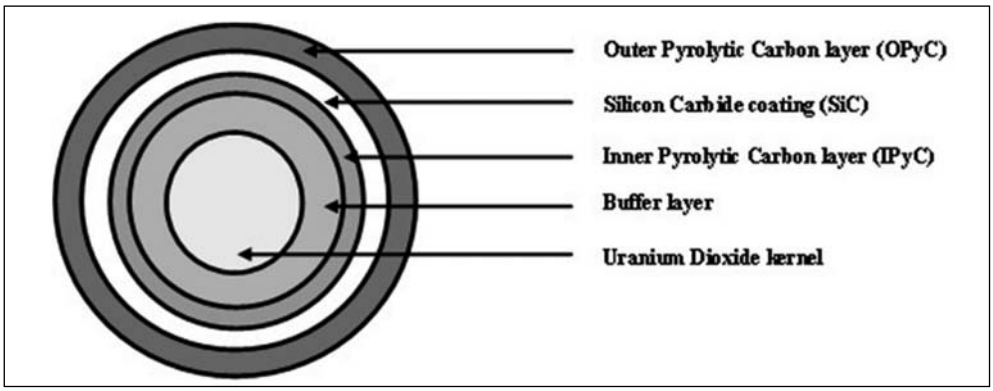

FIGURE 1: Schematic representation of the layer composition of a UO_2 type TRISO coated particle (Gulol et al. 2006, Verfondern et al. 2007)

The SiC coating (Figure 1) functions as the main pressure vessel against internal forces generated by gaseous fission products, while also providing a stout diffusion barrier for hazardous metallic fission products in irradiated particles (Fukuda et al. 1991). It is therefore imperative that the SiC coating remains intact, even after being exposed to high radiation doses and high internal pressures caused by fission products originating from the UO_2 kernel (Gulol 2006). In order to minimise the possibility of fuel particle failure under irradiation and postulated accident conditions, well-defined SiC specifications are accordingly required to enforce limits on key structural attributes. To this end, fuel performance testing is always required to develop these specifications and determine critical limits for material characteristics.

This quality control (QC) method requires process development that dove-tails into a robust performance testing practice. Therefore, this study serves as proof-of-concept to test the effectiveness of a spouted-bed configuration (using a low-temperature CF_4 plasma), to induce uniform etching of the SiC layer from TRISO particles. If proven successful, it is postulated that the quality of the SiC layer and original CVD process may be evaluated by controlled erosion of the SiC layer in post-irradiated particles. This will be accomplished by analysing the degree of fission product seepage at constant intervals during the etching process. Any noticeable increase in the fission product concentration, compared to previously qualified specifications, will indicate a flawed SiC coating. Subsequently the particle, or batch particles will be deemed to be off-specification and corrective actions taken.

The proposed technique reported here is a modification based on previous work by Van der Walt et al. (2011) in which an alternative recovery method for UO_2 kernels from off-specification TRISO particles was investigated. These substandard particles were noted to have inadequate structural integrity due to a defective CVD layering procedure, requiring the UO_2 kernels to be liberated for recoating. It was shown that the SiC layer could be completely removed by the active fluorine species present in an inductively coupled radiofrequency CF_4 glow-discharge plasma. However, the etching was not uniform due to the particles being in a stationary-bed configuration. Although this method was developed for kernel recovery, the opportunity was identified to develop a uniform SiC layer removal method for evaluating this layer`s integrity after irradiation.

In this study, a spouted-bed configuration was employed with the advantage of uniform etching of the SiC layer as well as control over the etch rate. This experimental configuration affords a more chaotic and random particle motion, increasing the circulation of the particles which allows for uniform contact of the fluorine radicals with the SiC layer (Flamant 1994, Duarte et al. 2008). This investigation therefore evaluates the effectiveness of the proposed spouted-bed experimental setup on the etching uniformity of the SiC layer and subsequently serving as a proof-of-concept for further QC protocol development, highlighting the structural-activity relationships within these materials.

Structural considerations

The structure of SiC can be described as a highly covalent assembly formed by conformational tetrahedra centred around either carbon or silicon atoms (Zhang 2012). This arrangement establishes a close-packed framework with half of the available tetrahedral lattice sites being filled. These SiC bilayers may display different stacking modes within the structural lattice giving rise to extensive range of polytypes which are dependent on the assembling arrangements along the c-axis (Knippenberg 1963). The most common phases are the hexagonal 2H, 4H, 6H, and 15R (referred also as α-SiC) and the cubic 3C (or β-SiC). However, only the cubic polymorph of SiC (β-SiC) is desirable for nuclear applications due to its superior dimensional stability under irradiation (Lopez-Honorato et al. 2008).

Some of the β-SiC layers deposited during TRISO particle manufacturing may not conform to the specified structural requirements mainly due to compositional defects such as impurities in the β-phase and/or stacking faults which may induce further undesirable phase transformations. In addition to this, intrinsic defects such as vacancies, interstitials and anti-sites, known to be common in the SiC structure, may hamper the mechanical properties of the macro-structure (Käckell et al. 1998).

The aforementioned stacking faults have been described as mainly responsible for the structural failure of the SiC layer in TRISO particles (Zhang 2012, Jiang et al. 2016). These deformities can be defined as disordered sections of the overarching ordered sequence within an fcc-type lattice and are categorised as either intrinsic (ISF) or as extrinsic stacking faults (ESF) (Käckell et al. 1998). In the case of ISF a double layer is removed from the ordered system (ABC) with the resultant sequence being (ABC)(A\\C)(ABC)…, whereas for an ESF, a double layer is incorporated into the systematic structure, resulting in a (ABC)(A//C//BC)(ABC)… type arrangement (Figure 2). These deformities may promote the glide of partial dislocations when exposed to excessive internal pressure from within the IPyC layer, resulting in a potential escape pathway for volatile fission products. Compared with dislocations and vacancies, no formal bonds are broken by stacking faults, leading to a small energy difference between faulty and perfect structures.

As it pertains to this investigation, the aforementioned stacking faults and β-phase impurities may cause noteworthy structural deficiencies within the SiC layer of the TRISO particles and may lead to additional stresses

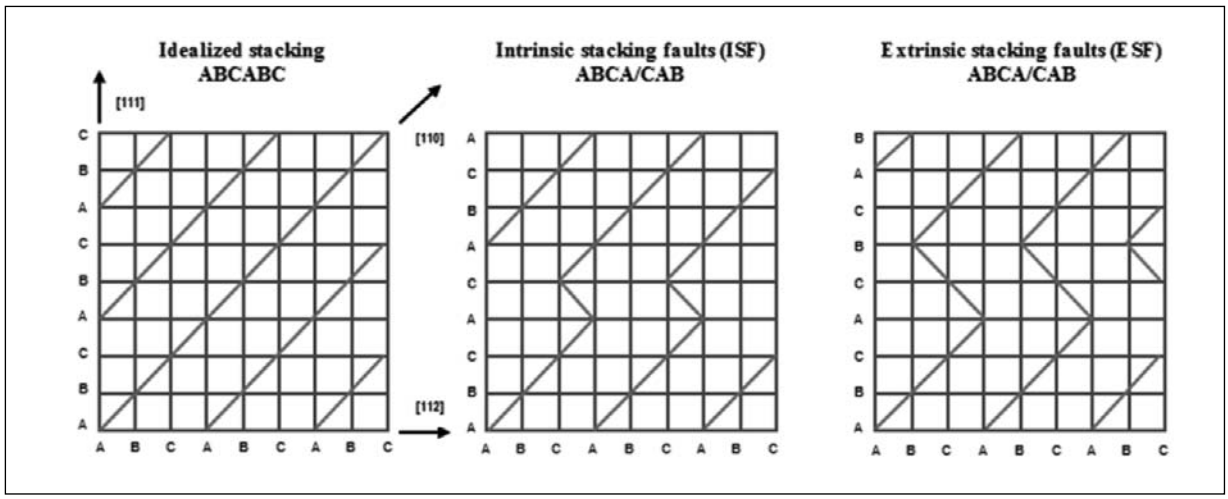

FIGURE 2: Stacking sequences for (a) Idealised, (b) ISF and (c) ESF stacking sequences for fcc-type conformations, adapted from Zhang (2012)

in the matrix crystal structure, affecting stability, SiC robustness and lead to the development of potential escape pathways for hazardous volatile fission products.

Experimental

Process modification for optimised SiC etching

In previous work (Van der Walt et al. 2011), etching was carried out in a stationary bed experimental setup, and non-uniform removal of the SiC layer was observed on the TRISO particle surfaces exposed to the downward-flowing gas. Although this was adequate for UO_2 kernel recovery, a uniform SiC etching process is required for SiC layer quality control purposes. The work reported here involves a spouted-bed experimental setup (Figure 3) to attempt even exposure of the particle surfaces to the etch gas in a CF_4 glow discharge plasma by the random nature of particle movement.

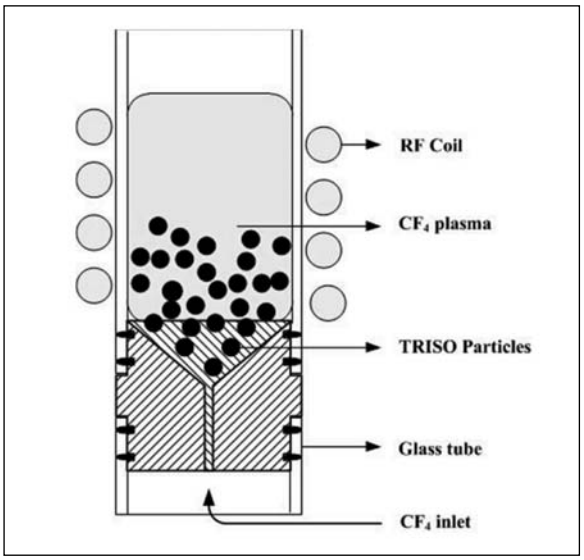

FIGURE 3: A schematic representation of a spouted-bed reactor setup

Spouted-bed plasma reactors are known for their superior mixing in the solid phase and excellent heat- and mass-transfer between the solid and plasma phases. This technique is usually applied when stable fluidisation is difficult to achieve (Duarte et al. 2008). Previous investigations have noted that knowledge and control of the plasma and particle dynamics in a spouted-bed reactor are important for evaluation of particle circulation rate and plasma-solid contact efficiency (Flamant et al. 1994). Some of the predominant parameters that require consideration for spouted-bed type experiments are: 1) the minimum spouting velocity; 2) the maximum spoutable bed height; 3) spouting stability; and 4) pressure drop.

Empirical tests were performed prior to the plasma etching experimentation in order to determine the minimum parameters for the spouted-bed to operate effectively under vacuum conditions, and in a non-thermal plasma. Using the experimental setup described in the following section, a bed of 5 mm deep, consisting of 30 particles, required a minimum spouting velocity of $2 \cdot 10^{-4}$ m/s under these conditions. The pressure drop was not measurable and the spouting action was stable.

In this investigation TRISO coated zirconium oxide (ZrO_2) kernels were used as surrogate High Temperature Reactor (HTR) fuel particle analogues. The relevant physical properties of particles were: diameter (d_p) = 0.858 mm; particle density (ρ_s) = 5 890 kg/m^3; bulk density (ρ_b) = 3 534 kg/m^3.

Equipment and experimental conditions

The experimental configuration used during this investigation (Figure 4), is similar to the setup described previously (Van der Walt et al. 2011), except for the use of a spouted-bed configuration. The spouting gas (CF_4), which also acts as plasma gas, enters a quartz tube from below via

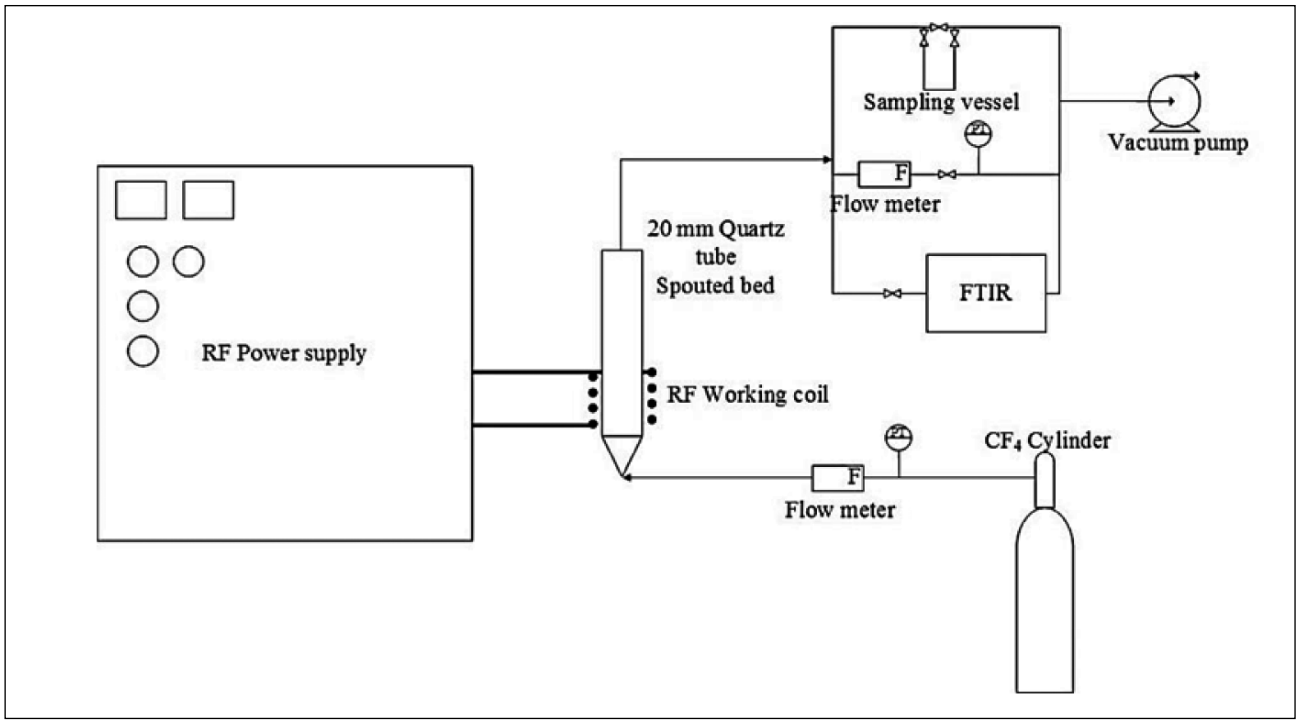

FIGURE 4: Schematic representation of the modified experimental setup

a conical nozzle with a 0.8 mm inlet, resulting in a random spouting movement of the particles as described in the previous section.

The 20 mm diameter quartz tube was fitted with a 60° PTFE spouting nozzle with an inlet diameter of 0.8 mm to prevent the TRISO particles from falling through when the spouting gas is not flowing. The non-thermal CF_4 glow discharge plasma was generated by a 1.5 kW RF power supply operating at 13.56 MHz. The mean CF_4 gas flow was $7.33 \cdot 10^{-3}$ kg·h^{-1} and effective power input (plate power) to the plasma was 0.3 kW, resulting in a plasma enthalpy of 147.3 MJ kg^{-1}. The system pressure was maintained at within a range of 1 to 6 kPa (abs) by a vacuum pump exhausting through a scrubber.

General experimental procedure

The analyte particles were pre-treated by heating overnight in air at 1000 °C to remove the OPyC layer, thereby exposing the SiC layer of the kernel for subsequent plasma etching. In this series of experiments, an aliquot of 30 pre-treated particles was progressively exposed to the plasma for 1 h per run-up to a total of 6 h reaction time. The feed rate of CF_4 gas and power input were maintained at constant values throughout a run. These conditions were utilised throughout the experiments reported herein.

The total sample (30 particles) was weighed before and after each hour of exposure. After each run five particles were removed from the analyte sample and the thickness of the residual SiC layer calculated by weight loss measurement. The remaining sample was again weighed and returned to the reactor for the ensuing run. It is important to note that the total (aggregate) exposed area of the sample decreased not only due to SiC etching, but also due to the sampling process (removal of 5 particles). It must however be noted that no attempt was made to limit the plasma gas/spouting gas to a stoichiometric amount. In order to reach the minimum spouting velocity while still maintaining the plasma, a significant excess of CF_4 was used.

Results and discussion

A SEM image of a TRISO particle presenting the uniform etching of the SiC layer after 7 hours of exposure in a non-thermal CF_4 glow discharge plasma, is shown in Figure 5.

The specific mass loss rate during the etching process was calculated by the particle surface area from the diameter and original layer thickness (obtained from SEM analysis), the density and the number of particles obtained from sample mass.

A plot of SiC layer thickness as a function of time is given in Figure 6 below, and the linear fit on the data clearly shows some scatter of data points ($R^2 = 0.9707$). The estimated time (t_f), for full removal of the SiC overcoat as calculated from the trend line is about 15 h, which would be acceptable for industrial application.

Two kinetic models for a shrinking particle were fitted to the data, *viz*., chemical reaction control and stagnant gas-film (diffusion) control. The expressions for these are respectively given in Eqs. 1 and 2 below (Levenspiel, 1999):

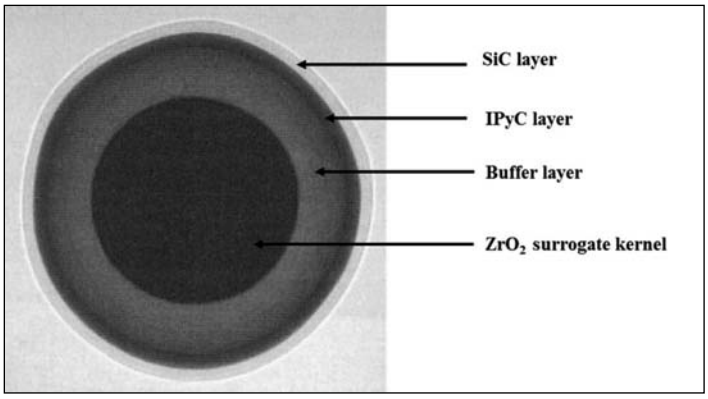

FIGURE 5: Illustration of the uniform etching of the SiC layer of a TRISO particle after 7 hours of exposure

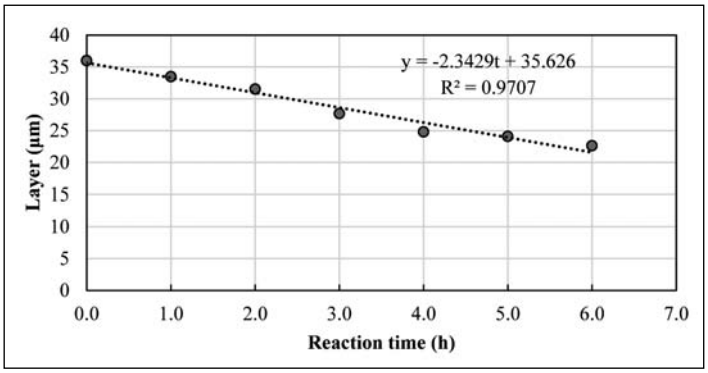

FIGURE 6: Plot of SiC layer thickness vs reaction time

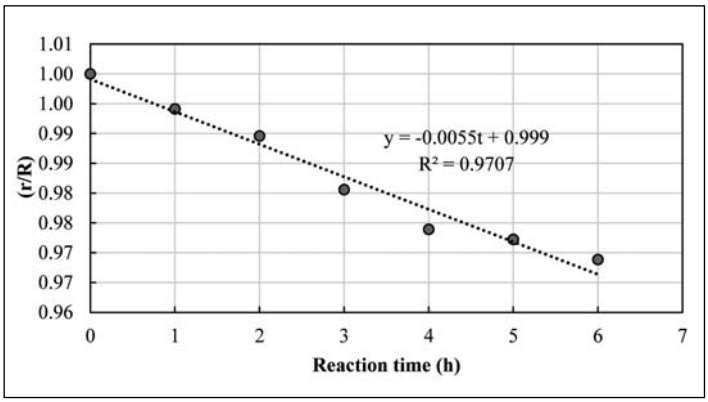

FIGURE 7: Ratio of particle radii vs reaction time

$$\frac{t}{\tau} = 1 - \left(\frac{r}{R}\right) = 1 - (1 - X_B)^{1/3} \quad (1)$$

Eq. 1 is identical to the expression for particles of unchanging size in Eq. 2.

$$\frac{t}{\tau} = 1 - \left(\frac{r}{R}\right)^2 = 1 - (1 - X_B)^{2/3} \quad (2)$$

Here, t is reaction time, τ is time to complete disappearance of a hypothetical SiC particle, which is assumed here for modelling purposes. R is the initial (outer) diameter of the particle at time $t = 0$, and r is the particle radius at time (t) during etching. At time t_f the SiC layer in question has been completely stripped away and the particle radius has reached the inner diameter of the SiC layer and the ratio (r/R) = 0.916. Assuming that the original particle under examination consisted purely of SiC, the extent of the reaction is denoted by X_B ($0 \leq X_B \leq 1$). The ratio of particle radii (r/R) *vs*. time as plotted in Figure 7, was used to model the reaction rate and stagnant gas layer-controlled cases represented by Eq. (1) and Eq. (2), illustrated in Figure 8 (a) and (b) below. The fitted equations for the linearised plots and their R^2 values are shown on the plot areas.

The estimated t_f for complete removal of the SiC layer calculated from the line fit slope in Figure 7 was 15.1 h, which compares favourably with that calculated from the data in Figure 6.

The t_f values calculated from the τ values obtained from Figure 8(a) and (b), i.e. for the reaction control and diffusion control models, yield (r/R) = 0.916-values of 14.9 h and 14.4 h respectively. Since the two R^2 values are practically identical, and the two predicted t_f values are accurate within the margin of error for the relatively short time required for complete stripping of the SiC, no real distinction can be made between the two possible controlling mechanisms from the above.

If the data for the previously reported (Van der Walt et al. 2011) packed-bed configuration are analysed in the same way as above, the total reaction time (t_f) for the

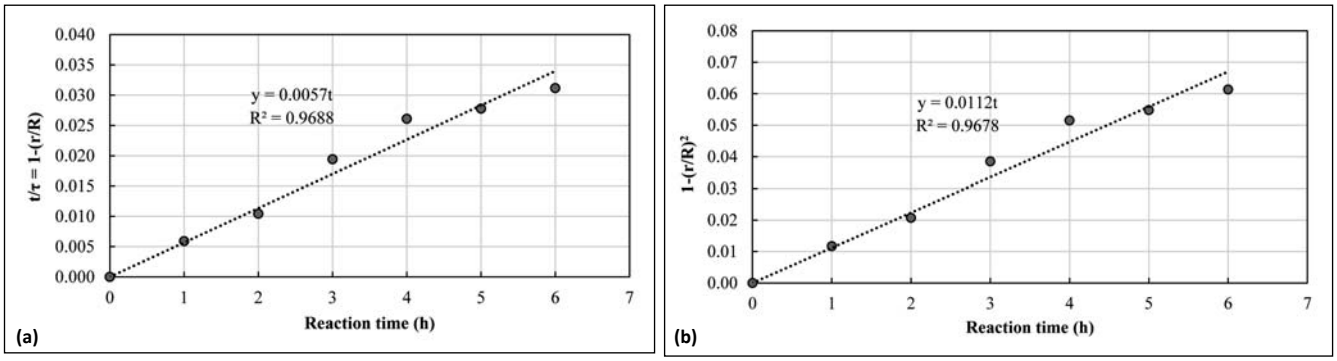

FIGURE 8. (a): Chemical reaction control model according to Eq. (1); **(b)** Gas layer diffusion control model according to Eq. (2)

packed bed is significantly shorter. This may be explained by considering, among others, the relative plasma gas velocities in the two cases. In the packed bed, assuming a bed void volume of 35%, with other factors being equal, the plasma gas velocity flowing downward through the bed in this case, is roughly three times higher than in the case of the spouted-bed set-up. In addition to this, the particles in the spouted-bed are levitated into the plasma region so that the gas velocity relative to the particles is expected to be lower than indicated by its freeboard velocity in the vicinity of the plasma. These effects suggest that a mass-transfer controlling mechanism, not obvious from the data presented above, may be rate limiting, and that Eqn (2) is preferred.

As was noted in the previous investigation, various resultant species; (CF_4, SiF_4, C_3F_6, C_4F_8 and CO_2), were detected in the post-etching off-gas stream. In addition, sodium aluminium fluoride was observed as a flaky white solid on the inner wall of the borosilicate glass containment tube due to the fluorination of the reactor wall and is to be expected for this setup.

Conclusions

The results presented complement previously reported data, obtained in a packed bed. The uniform etching of the extremely inert SiC layer, used as containment mechanism in TRISO particles, is demonstrated. The fluorine radicals generated in a CF_4 non-equilibrium RF plasma reacts readily with silicon carbide (SiC) forming volatile SiF_4 and CF_4. In a spouted-bed configuration the removal of the 36 µm coating takes 14 to 15 h, enabling excellent control of the process for analysis and quality control of the coatings. In this set-up the kinetics of the process is controlled by diffusion of the fluorine radicals through the stagnant film surrounding the particles. This contrasts with a packed-bed configuration where the etching is quicker, but less uniform, and the kinetics are controlled by the chemical reaction itself.

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