The Effect of High Temperature Annealing on the Grain Size of CVD-grown SiC and Experimental PBMR TRISO Coated Particles

S M Mokoduwe[1], I J van Rooyen[1,2,3], J H Neethling [2], A Janse van Vuuren[2], E J Olivier[2]

PBMR, Fuel Design
1279 Mike Crawford Avenue, Centurion, 0046, South Africa
phone: +27-72-7449015, ivrooyen@csir.co.za

[1]*Fuel Design, PBMR, 1279 Mike Crawford Avenue, Centurion, 0046, South Africa*

[2]*Department of Physics, Nelson Mandela Metropolitan University, PO Box 77000, Port Elizabeth, 6031, South Africa.*

[3]*National Laser Centre, CSIR, P.O. Box 395, Pretoria 0001, South Africa.*

Abstract – *Recent research and development activities of the PBMR Fuel Characterization and Optimization Programme focused on the high temperature characteristics of the PBMR fuel and more specifically on the SiC layer. PBMR fuel consists of Tri-Isotropic (TRISO) Coated Particles (CPs) in a graphite matrix with the SiC layer being the main barrier to fission and transmutation products. The integrity of the CP three layer system namely, Inner Pyrolytic Carbon- Silicon carbide- Outer Pyrolytic Carbon (IPyC-SiC-OPyC) has a direct impact on fission product release. Grain boundary diffusion is identified as a possible mechanism by which ^{110m}Ag, one of the activation products, might be released through intact SiC layer. Temperature is evidently one of the factors/parameters amongst others known to influence the grain size of SiC and therefore it is important to investigate the effect of high temperature annealing on the SiC grain size. The ASTM E112 method as well as EBSD was used to determine the grain size of various commercial SiC samples and the SiC layer in experimental PBMR CPs after annealing at temperatures ranging from 1600 to 2100 ^{o}C. The high standard deviation results obtained for CVD-grown SiC are discussed and explanation for the observations are given.*

I. INTRODUCTION

The main function of the SiC layer of the Pebble Bed Modular Reactor (PBMR) Tri-Isotropic (TRISO) Coated Particles (CPs) (shown in Fig. 1 [1]), is to contain gaseous and metallic fission and activation products within the coated particle. The SiC layer is deposited on the pyrolytic carbon layer (PyC) by the Chemical Vapour Deposition (CVD) process at temperatures of approximately 1450ºC. Although most fission products are retained by the combination of SiC and pyrolytic carbon layers, previous observations of silver release during fuel testing and operations identified the release of silver by so-called intact SiC layers [2, 3]. Nabielek and Brown proposed grain boundary diffusion as a mechanism for ^{110m}Ag release through intact SiC layers [4]. Petti et al. [5] also microscopically compared US manufactured- with German manufactured TRISO CPs and found that the grain size and structure influence the ^{110m}Ag release. It was found that 90% of the ^{110m}Ag was released from the large columnar grained SiC, whereas only 30% was released from the small grained SiC particles.

The main purpose of this work is to investigate the effect of high temperature annealing on the grain size of the SiC layer of PBMR TRISO CPs. The

reason for this investigation is to determine the change in grain size after high temperature annealing as grain size may influence the strength of the CP and further may influence the silver release from the CP during operation. It was decided to initially do grain size evaluation after annealing from 1600 – 2100 ºC on flat commercial 3C-SiC samples, due to the relatively ease of sample handling and preparation. This work was followed by the annealing of two selected experimental PBMR CP batches at temperatures from 1600 – 2000 °C. These very high annealing temperatures were chosen because Snead et al. [6] found that no significant strength degradation of CVD SiC occurs for temperatures up to 1500°C. Long duration annealing (>100h) studies, although important for the effect on SiC strength [7] as it is an indication of how the grain size will be modified during the reactor operation under specific conditions, is not included in this phases of work. Work by Byun et al. [8] also makes reference to the influence of grain size on the SiC strength. This temperature range is also of interest as the fuel sphere manufacturing process make use of a 1h sintering process at 1950ºC and this study will indicate if any grain size changes could be expected due to the sintering operation. This work forms part of a larger experimental programme of the PBMR Fuel Design department to test the design parameters of the CPs for application in very high temperature reactors.
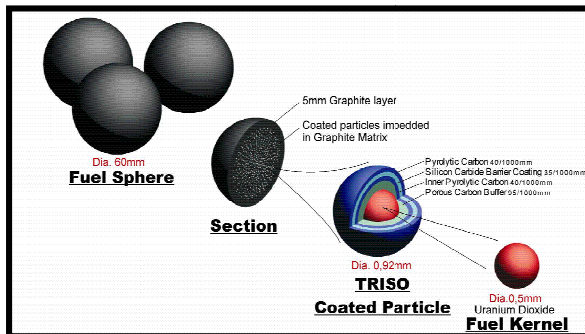

Fig. 1: A diagram illustrating the construction of a PBMR fuel sphere [1].

II. MATERIALS AND METHODS

II.A. Material

The bulk CVD-grown polycrystalline 3C-SiC (flat samples) used for the first phase of this study was prepared by Rohm and Haas, Advanced Materials Co, USA. This commercial available SiC was chosen since it provided similar grain sizes to that used in the PBMR fuel SiC layer. Five small square samples were cut from the original sample received from ORNL and prepared for grain size

determination. Four flat CVD-grown SiC samples were annealed at temperatures 1600 °C, 1700 °C, 2000 °C, 2100 °C in a Webb 89 Vacuum furnace at Nelson Mandela Metropolitan University (NMMU), South Africa, and one sample kept as reference.

The two experimental CP batches used for the second phase of this study were produced by PBMR Fuel Development Laboratories at NECSA during 2007. These two batches were chosen as it gave a range of different manufacturing conditions manufactured in the "Advance Coater Facility" (ACF). Selected manufacturing data are given in Table 1 and it is noted that the SiC deposition temperatures and the SiC thickness are different for these two batches. The SiC thicknesses of the two batches (39 and 32 µm respectively) represent also the highest and the lowest of the SiC thickness specification values. Approximately 1000 TRISO coated particles from the two batches each were annealed in ceramic crucibles in a Webb 89 Vacuum furnace at Nelson Mandela Metropolitan University (NMMU), South Africa, for temperatures of 1600 ˚C, 1800 ˚C and 2000 ˚C, as shown in the Research Project Plan flow diagram in Fig. 2.

Batch	SiC Deposition Temperature (ºC)	SiC Deposition Rate (µm/min)	SiC Thickness (µm)	SiC Density (gcm^{-3})
D	1450	0.23	39	3.2
E	1510	0.24	32	3.2

Table 1: Selected manufacturing data of the two experimental PBMR TRISO coated particle batches.
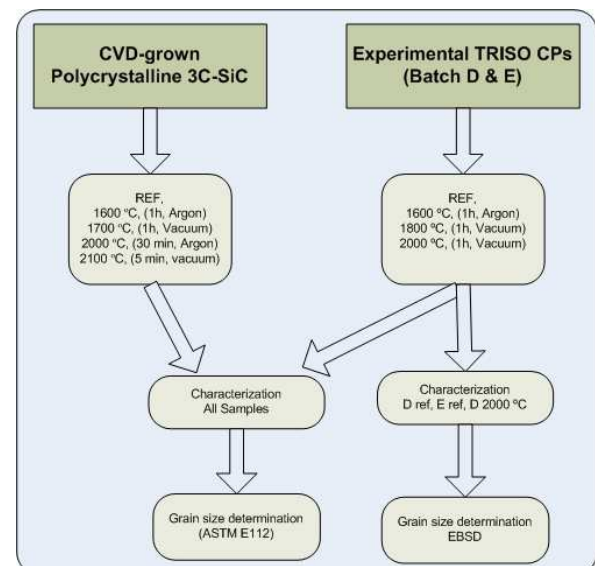

Fig. 2: Experimental Research Plan

The flat SiC samples were polished with 30, 9, 6, 3 and 1 µm polishing cloths to obtain a mirror finish side to be analyzed. The TRISO CPs under

investigation was prepared by grinding the particles to half-way through in order to expose the different layers. The particles were polished with the final polishing done with colloidal silica, containing particles with an average size of 0.05μm. All prepared samples were then etched using a modified Murakami's etchant. The modified Murakami's etchant was prepared by adding 25g of both KOH and NaOH to 100ml of distilled water. After the fore mentioned dissolved and the liquid cleared, 25g of $K_3[Fe(CN)]_6$ (potassium-hexa-ferricyanide) was added to the mixture and stirred while heated until it dissolved. The reagent was kept at approximately 200°C throughout the etching process. The CPs were then added and left in the etchant for approximately 1 hour and separately, the CVD-grown samples were etched for 30 minutes. The samples were then removed from the etchant and rinsed repeatedly in distilled water containing KOH and then in distilled water only. Finally the samples were placed in an ultrasonic bath for a few minutes and then mounted and placed in the SEM for investigation of the grains and grain boundaries.

Grain size determination was carried out using two methods namely the Heyn Lineal Intercept procedure in accordance with ASTM E112-96 (2004) [9] and electron back scatter diffraction (EBSD) analysis [10, 11].

II.B. Grain Size Determination using Heyn Lineal Intercept Method

The average grain size of the flat CVD SiC samples and the two batches CPs were determined using the Heyn Lineal Intercept method on ten SEM micrographs for each sample and it was calculated as follows:

Every micrograph has a demonstration line at the bottom with the size of the line, S_D, given in microns. The length of the demonstration line, L_D can be measured in cm. Draw 15 test lines on the micrograph, see example in Fig. 3, measure the length of one test line, L_T in cm (the measurement will apply to all the test lines). Now, the size of the test lines, S_T can be calculated using the following expression:

$$S_T = \frac{S_D L_T}{L_D} \qquad \text{(eq. 1)}$$

Grain size, G, is therefore the size of the line, S_T, divided by the number of grains cut by the test line, N, and mathematically it is expressed as:
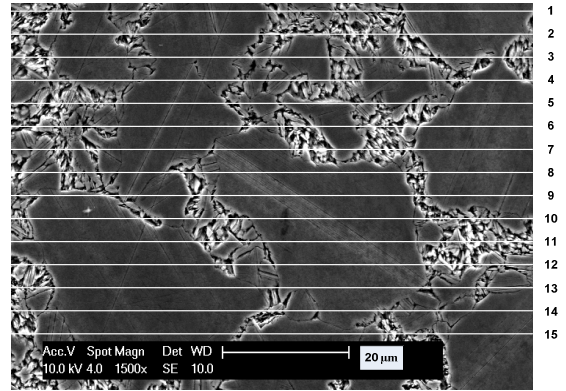
$$G = \frac{S_T}{N} \qquad \text{(eq. 2)}$$

Fig. 3: Example of a SEM micrograph used for grain size determination.

Follow the same procedure for all ten micrographs and for every test line drawn on each micrograph and take the average grain size. The % relative accuracy (RA) as determined according to ASTM E112 [9] is in all cases calculated to be lower than 10% and is considered to be acceptable precision. However, the grain size of the SiC layer of the TRISO CPs are not equiaxed in shape and therefore the grain sizes determined in this study, should be clearly indicate the measurement direction for comparison purposes with results from other researchers.

II.C. Grain Size Determination using EBSD

The coated particles containing the SiC layers were embedded in an epoxy resin and mechanically thinned and polished using a Buehler-Beta grinder polisher down to a 0.05 μm colloidal silica finish.

The analysis of the prepared samples was done using a HKL electron backscattered detector coupled to a JEOL 7001F scanning electron microscope. The sample was tilted to 70 ° within the chamber with fine calibration of the detector geometry done using the crystal structure for 3C-SiC, the expected SiC polytype to be present. The area for the EBSD analysis was selected with a step size of 0.1 μm for the mapping chosen. The scan duration was typically between 9 to 11 hr for each scan. In addition the crystal structure for the 6H-SiC phase was also included during the analysis to check if any grains of this structure were present.

III. RESULTS AND DISCUSSION

III.A. Grain Size Determination using Heyn Lineal Intercept Method

The grain size measurement of the annealed bulk CVD 3C-SiC results indicates that the grain size

increases with increasing annealing temperature. This can be seen in Fig. 4, which shows the micrographs of etched grains and in Fig. 5. The average grain size increases from 7.6 µm for the unannealed sample to 10.1 µm for the sample annealed at 2100°C. The observation made from these results is that the average grain size seems to reach an upper limit after annealing at 2000°C. This however needs to be confirmed with more samples to increase the statistical confidence. Further examination reveals that the shape of the grains also change significantly from elongated in the unannealed sample, to more spherical grains after annealing as shown in Fig. 4. The high concentration of twins and stacking faults present in the SiC grains contributes to the difficulty to differentiate between grain boundaries and this is partly responsible for the relatively large standard deviations obtained for the measured grain sizes. Another possible reason for the large deviation in measured grain sizes is most probably due to the fact that the samples were only prepared in one direction (perpendicular to the plane of deposition), therefore the shape factor is not taken into account.

The results of grain size determination of the SiC layer of the two experimental PBMR TRISO CP batches are presented in Fig. 6 and although the results suggest also a slight increase in grain size within experimental error, after high temperature annealing, the increase in grain size is smaller than that reported in Fig. 4 for the flat SiC samples. It should be noted however, that the grain size in the flat SiC samples exhibited a definite distribution of large and small grains which is most likely the reason for the larger increase in average grain size upon annealing measured in these samples. From the data shown in Fig. 6 it is clear that the average grain size of batch D is larger than that of batch E for temperatures up to 1600 °C. For annealing temperatures above 1600 °C the average grain sizes seems to remain the same. This phenomenon is in agreement with the findings by Van Rooyen et al. [7] where the strength measurements of CPs showed also that no significant difference in strength values of these two batches exists at 2000 °C. Fig. 7 shows a typical etched structure used for the grain size determination of the SiC layer of the TRISO CP. This figure also illustrates the difficulty to identify the grain boundaries due to the presence of high density stacking faults which also are accentuated during the etching process.
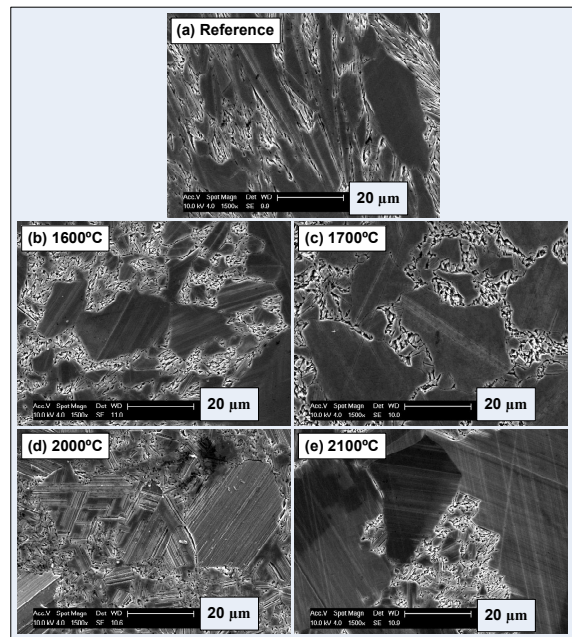

Fig. 4: Example of a SEM micrograph used for grain size determination
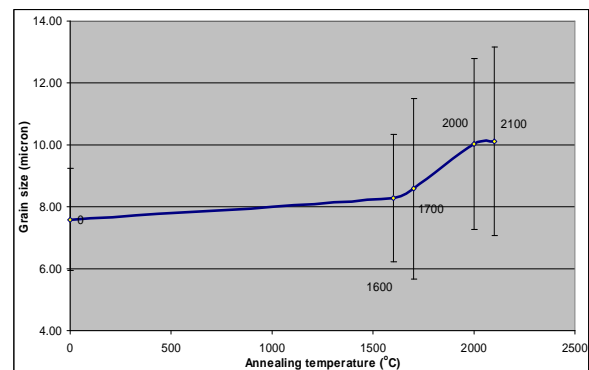

Fig. 5: Influence of high temperature annealing on the CVD ORNL polycrystalline 3 C-SiC.
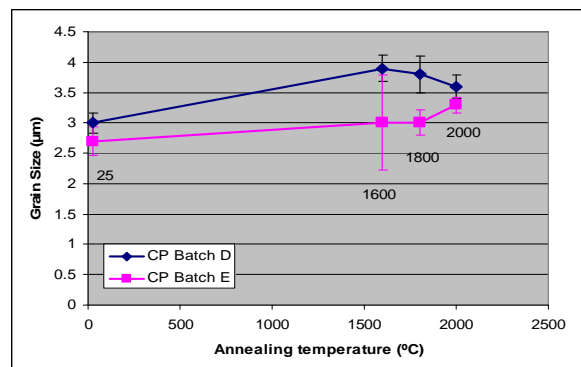

Fig. 6: Influence of high temperature annealing on the polycrystalline 3 C-SiC layer of PBMR TRISO CP batches D and E.
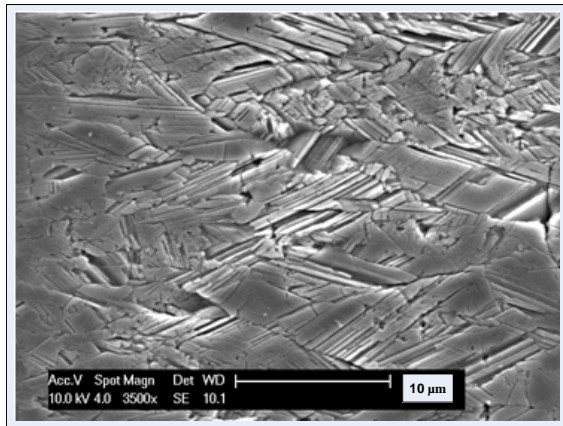
Fig. 7: Micrograph showing a typical etched image of the SiC layer of the CP batch D after annealing at 2000 °C with an average grain diameter of 3.7 µm (Heyn Lineal Intercept Method). The etching process also accentuated the high density of stacking faults.

III.B. Grain Size determination using EBSD

Fig. 8 shows an example of an IPF coloured crystal orientation map of the 3C-SiC structure across the layer of the reference sample of CP batch D. No 6H-SiC areas could be detected during the mapping of any of the layers investigated. In all the cases studied the grain sizes across the layer progressively varied from being sub-micron at the inner-PyC and SiC interface to being several micrometers in size at the outer PyC and SiC interface. Fig. 9 shows a histogram of grain size distribution and Table 2 the grain size statistics of the analyzed region.
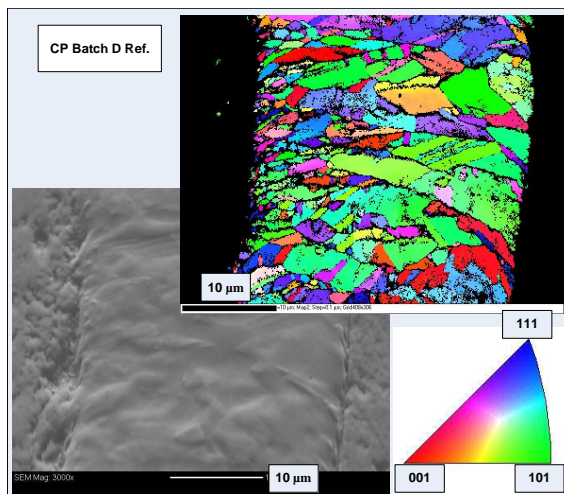

Fig. 8: An example of an IPF coloured orientation map of the 3C-SiC structure across the layer of the reference sample of CP batch D. The grain sizes across the layer progressively varied from being sub-micron at the inner-PyC and SiC interface to being

several micrometers in size at the outer PyC and SiC interface.
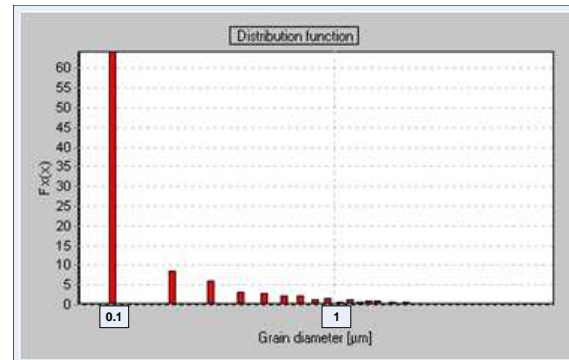

Fig. 9: A histogram of grain size distribution and grain size statistics of the analyzed region of the reference sample of CP batch D.

The grain size statistics for D-REF show an average grain diameter of 0.368 µm, however if the histogram of grain size distribution is considered, a large contribution towards the grain size statistics originate from grains smaller in size or close to 0.1 µm in diameter which is comparable to the step size used. Thus these grains cannot be considered for the analysis. Setting a threshold grain diameter value of at least 0.4 µm to be included for the analysis and removing all the grains less than this would remove any uncertainty. Thus choosing a minimum grain size of 0.4 µm (two adjacent indexed spots in the x and y directions) would minimize the incorrect statistical evaluation. Removing these grains form the data set for the case under discussion, the size is being reduced from 1533 grains to 355. The recalculated grain size statistics is shown in Table 2 with the re-plotted histogram in Fig. 10.
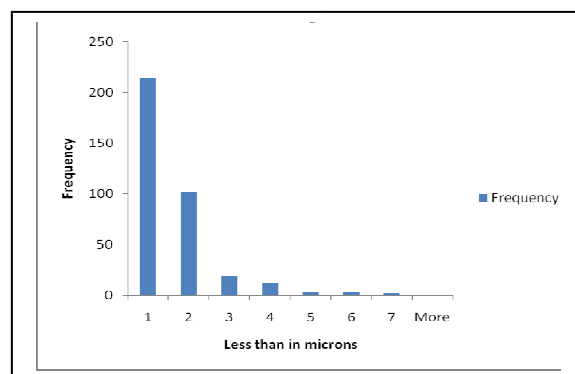

Fig. 10: This histogram showed the recalculated grain size statistics of the reference sample of CP batch D after removing the grains with a minimum grain size of 0.4 µm (two adjacent indexed spots in the x and y directions) which would minimize the incorrect statistical evaluation.

Measurement	D-REF	D-2000 °C	E-REF	D-REF re-calculated
Average, expectation (EX) µm	0.368 (3,0)**	0.307 (3.6)**	0.343 (2.7)**	1.158
Variance, dispersion (D²X)	0.340	0.276	0.279	*
Standard deviation (s)	0.583	0.525	0.528	0.928
Coefficient of variation (s/EX)	1.587	1.710	1.539	*
Minimum value (Xmin) µm	0.113	0.113	0.113	0.407
Maximum value (Xmax) µm	6.502	10.466	6.651	6.502
Size of the data set (N)	1533	2786	1564	355

* Not Available ** Determined ASTM E 112

Table 2: EBSD grain size statistics of the analysed region of the SiC layer of the CP batches D and E.

IV. CONCLUSIONS

The average grain size determined on the flat CVD SiC samples, suggests an increase from 7.6 µm for the unannealed sample to 10.1 µm for the sample annealed at 2100°C. An interesting observation made from these results is that the average grain size seems to level off after annealing at 2000°C. Further examination reveals that the shape of the grains also change significantly from elongated in the unannealed sample, to more spherical grains after annealing.

The increase of average grain size of the SiC layer of the two experimental PBMR TRISO CP batches with increasing annealing temperature is smaller than that determined for the flat CVD 3C-SiC. Although there is a difference in grain size noted between the two batches after annealing at 1600 ℃ (3.9 and 3.0 respectively), the average grain size of the two batches levels off at temperatures above 1600 ℃. This result is in agreement with the findings by Van Rooyen et al. [7] where the compression strength measurements of CPs showed this same trend.

The average grain size values from EBSD are approximately 10% lower than those measured by the Heyn Lineal Intercept method and this is most likely a consequence of the different approximations used for the quantification schemes.

V. RECOMMENDATIONS

The observed grain size increase with increasing annealing temperature for both the flat SiC and SiC layer of the CPs needs to be verified with a larger statistical sample. Furthermore, it is important to include the shape factor in these determinations by doing a qualification measurement test on different oriented sections with regards to the growth direction.

As no grain size specification for SiC layers for TRISO CPs is documented, it is recommended that a statistical sample of CPs per batch needs to be investigated with the following in mind:
- o the grain size of actual CPs are investigated with specific reference to long duration (>100h) annealing as a function of temperature to relate the grain size modification with specific reactor operational requirements
- o the grain size and strength correlation be determined
- o the influence of grain size on the Ag transport rate be determined

It is also recommended that the EBSD results be further interpreted with regards to the grain boundary orientation. The EBSD map could also give valuable information with regards to the orientation with respect to the growth direction and needs to be evaluated further to do comparisons between the two batches and the influence of this orientation on the strength of the CP.

ACKNOWLEDGEMENTS

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