Journal of Nuclear Materials 392 (2009) 219–224

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

TRISO coated fuel particles with enhanced SiC properties

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ABSTRACT

The silicon carbide (SiC) layer used for the formation of TRISO coated fuel particles is normally produced at 1500–1650 °C via fluidized bed chemical vapor deposition from methyltrichlorosilane in a hydrogen environment. In this work, we show the deposition of SiC coatings with uniform grain size throughout the coating thickness, as opposed to standard coatings which have larger grain sizes in the outer sections of the coating. Furthermore, the use of argon as the fluidizing gas and propylene as a carbon precursor, in addition to hydrogen and methyltrichlorosilane, allowed the deposition of stoichiometric SiC coatings with refined microstructure at 1400 and 1300 °C. The deposition of SiC at lower deposition temperatures was also advantageous since the reduced heat treatment was not detrimental to the properties of the inner pyrolytic carbon which generally occurs when SiC is deposited at 1500 °C. The use of a chemical vapor deposition coater with four spouts allowed the deposition of uniform and spherical coatings.

1. Introduction

The high temperature reactor (HTR) is considered one of the most promising candidates for the production of nuclear energy due to a series of features which include the enclosure of its fuel kernel with several layers of ceramics [1,2]. This type of fuel, known as TRISO (tristructural isotropic) coated fuel particle, is made of three layers of pyrolytic carbon (buffer, inner pyrolytic carbon and outer pyrolytic carbon) and one of silicon carbide (SiC) (Fig. 1). These coatings are fundamental to the safety of this nuclear reactor since they are responsible for the confinement of all fission products inside this fuel [3–5]. Among these layers, the silicon carbide coating has received particular attention since it provides the mechanical stability to this fuel and is the main diffusion barrier to the release of fission products.

Both pyrolytic carbon (PyC) and silicon carbide are produced by a process known as fluidized bed chemical vapor deposition (FBCVD) [6–8]. Most of the CVD equipment currently used for the production of coated fuel particles consist of a gas distributor of conical shape (Fig. 2(a)), even though some work suggests that a different configuration with a better gas distribution could be beneficial to the properties of these coatings [9].

Silicon carbide is generally deposited by the decomposition of methlyltrichlorosilane (MTS) in a hydrogen environment at around 1500–1650 °C. This range of temperatures is generally selected since it is in this region where stoichiometric cubic SiC (β-SiC) coatings are produced [5,10–16]. The temperature range in which stoichiometric SiC is produced would depend on how and where the temperature is measured, the characteristics of the coater and the particle loading. These variables would ultimately define parameters such as residence time and surface area/volume ratio that will in turn affect the homogeneous and heterogeneous reactions during the deposition of SiC [17,18]. Lower deposition temperatures are not normally used since they would result in the codeposition of excess silicon and the formation of some porosity. A very peculiar feature in the production of this type of coating is that grain size is not constant but grows considerably with thickness [19–21], i.e., it can grow from around 0.8 μm up to 10 μm. Since grain size has an important effect on the diffusion of fission products and on the mechanical properties of ceramic materials, this change in grain size could be detrimental to the properties of SiC [5,22].

Another problem currently faced in the production of coated particles is the effect of heat treatment suffered by the inner pyrolytic carbon due to the deposition of SiC at 1500 °C. It has been reported that the deposition at this temperature results in an increase in coating density and anisotropy [23,24]. This increase in anisotropy could also seriously reduce the performance of these coatings, since higher anisotropies would produce a higher probability of coating failure [25,26].

In this work we show the production of coated fuel particles with a nozzle capable of producing four spout regions, instead of one as obtained with a conical shape nozzle. By doing so, SiC coatings with a more uniform grain size of 0.8 μm across the entire coating thickness were produced. Furthermore, by the addition of propylene and argon we show the possibility to obtain pore free stoichiometric SiC coatings at 1300 or 1400 °C, which should not affect the properties of the inner pyrolytic carbon in comparison with production of SiC at 1500 °C.

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doi:10.1016/j.jnucmat.2009.03.013

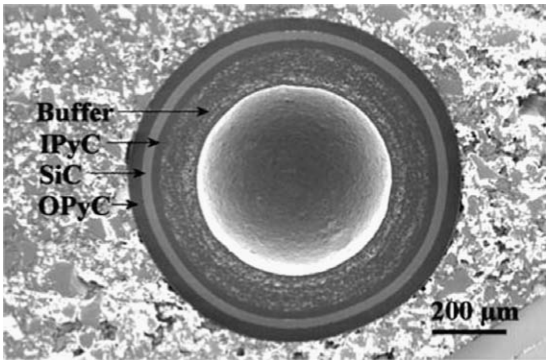

Fig. 1. TRISO coated particle.

2. Experimental

2.1. Sample preparation

The FBCVD coater used consists of a 200 mm long graphite tube with 35 mm inner diameter, heated with a graphite resistance element and a multi-hole nozzle as gas distributor (Fig. 2(b)) [27]. A 30 g load of Al_2O_3 particles 500 µm in diameter was initially fluidized by argon in spouted mode at atmospheric pressure. The buffer layer was produced with 70 vol.% acetylene concentration at 1400 °C for all samples. The inner and outer pyrolytic carbon layers were produced with 25 vol.% acetylene/propylene at 1250 °C. SiC was deposited either at 1400 °C with 1.27 vol.% MTS, together with 50 or 80 vol.% argon as diluent gas or deposited at 1300 °C with 9.1 vol.% MTS and 0.5 vol.% propylene in a complete hydrogen environment.

2.2. Sample characterization

Samples were mounted in copper-loaded resin and ground with successive grades of SiC paper to the cross-section of the sample, and polished down to 0.25 µm diamond paste followed by silica suspension. Samples were characterized using Raman spectroscopy (Renishaw 1000 Raman system with a 514 nm Ar-ion laser source). Raman analysis was performed by single spot measurements of around 1 µm in diameter, using a 50x objective lens. Measurements were generally performed every 10 µm. Other microstructural features were observed by scanning electron microscopy (Philips XL30 FEG–SEM). The Young's modulus of each layer was obtained by nanoindentation (Nanoindenter XP, MTS systems) using continuous stiffness measurement (CSM) and a Berkovich indenter. A maximum penetration depth of 500 nm was established and indentations within each array were typically 10 µm apart on polished cross-sections. Samples used for X-ray diffraction (XRD) analysis were produced by burning the PyC layers at 800 °C in a TG/DSC equipment (NETZSCH STA 449C). Powder XRD measurements were performed using a Philips PW1830 XRD instrument.

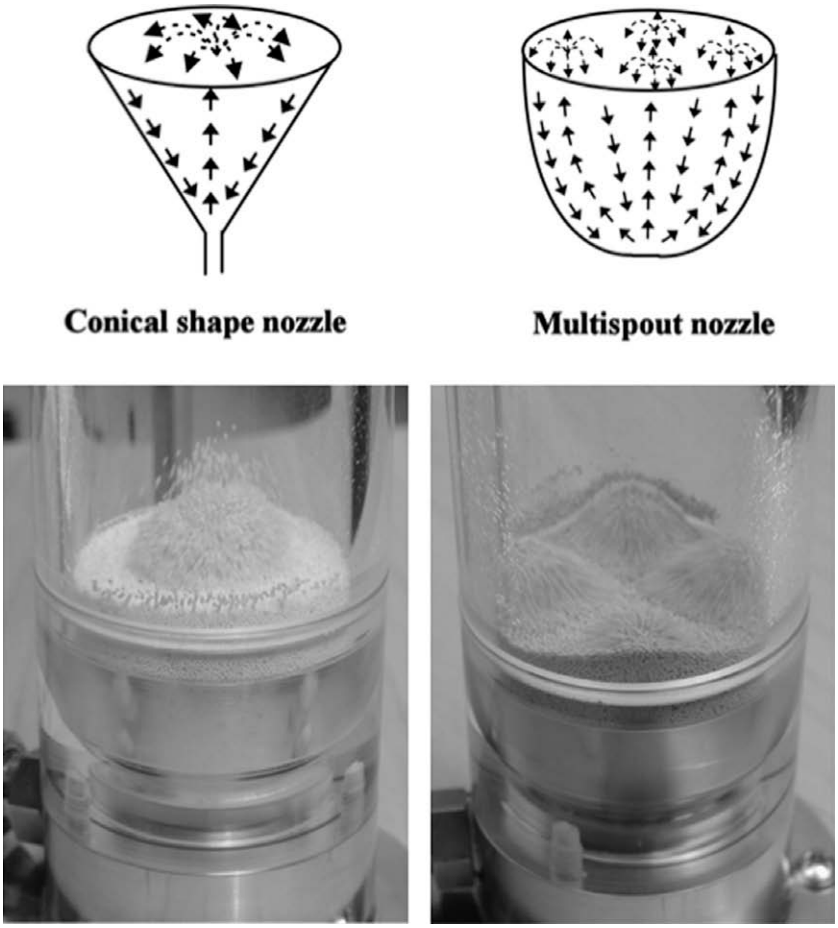

Fig. 2. Schematic diagram and cold fluidisation tests images showing the difference between a single spout and the multispout system with four deposition areas. Arrows show the movement of the particles.

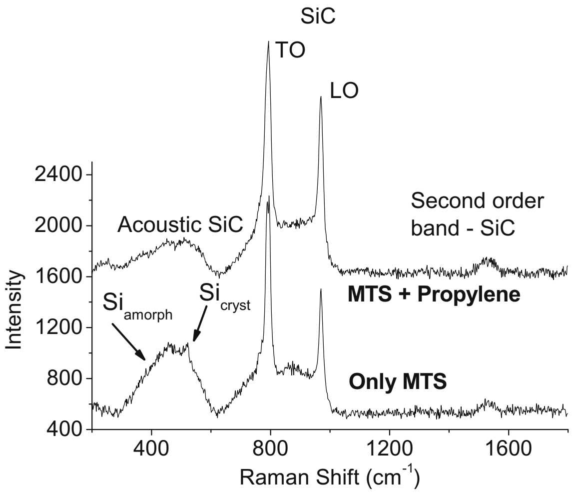

Fig. 3. Effect of propylene on the stoichiometry of SiC. Si_{amorph} and Si_{cryst} refer to amorphous and crystalline phases, respectively.

3. Results and discussion

3.1. Multispout deposition

One of the factors that could reduce the performance of the coated fuel is the formation of asymmetric coatings. It has been observed that odd-shape particles, in comparison with spherical shapes, present a higher probability of failure [28,29]. In our coater, which generates a multispout system during FBCVD (Fig. 2), odd-shape particles have not been observed among all the samples analyzed by polishing the samples to the cross-section (Fig 1). By comparing fluidizations between a single and four spouts (Fig. 2), it was observed that the particles in the multispout bed showed much better mixing and circulation from top to bottom than those in the single spout system. This enhanced mixing ensures that the particles spend considerably less time out of the spout where little or no deposition of SiC or PyC occurs [7]. Furthermore, considering that the temperature gradient inside the furnace could have an important effect on the type and properties of the PyC or SiC produced [30,31], an increased circulation would also ensure that the particles do not remain stationary for long periods of time, therefore producing coatings with more uniform characteristics. It is also possible that the continuous movement of the particles against the walls of the crucible might create sites for nucleation and incorporate more soot particles which ensure the formation of more random structure or lower anisotropies in PyC [31,32]. These observations are similar to the results found by Lackey et al. [9] who showed that by using a porous plate and better gas distribution, particles with better sphericity and PyC coatings with lower anisotropy were obtained.

3.2. SiC deposition with the addition of propylene

In addition to improving the overall shape of the coating, we attempted to produce stoichiometric SiC coatings with grain sizes smaller than 1 μm. Considering that grain size in SiC is largely controlled by deposition temperature [14,19], (reducing with lower deposition temperatures) our goal was to produce SiC coatings at temperatures below 1500 °C. In order to achieve this purpose it was necessary to avoid the codeposition of excess silicon which is generally formed at lower temperatures. Silicon is codeposited at low deposition temperatures due to the fact that the silicon bearing molecules, resulting from the decomposition of MTS, have a higher sticking coefficient than carbon species [17,33]. This would mean that Si–Si bonds are formed due to the lack of reactive carbon molecules that could form Si–C bonds. In order to avoid this problem, small amounts of hydrocarbons have been used to add reactive carbon intermediate species [13,34,35]. For our experiments, 0.5 vol.% propylene was used in combination with MTS for the deposition of SiC. The decomposition of propylene not only results in the formation of small reactive radicals but also its decomposition in a hydrogen environment reduces the possibility of gas maturation and the formation of larger and more complex molecules with lower sticking coefficients that otherwise would reduce the efficiency of this molecule in reacting with the substrate [36,37]. Fig. 3 shows that the addition of 0.5 vol.% propylene was sufficient to ensure the complete removal of excess Si (amorphous and crystalline phases, as detected by Raman spectroscopy) in SiC produced with MTS and H_2. The addition of propylene not only improved the stoichiometry of the coating but also changed its microstructure (Fig. 4). The SiC produced without any hydrocarbon showed large grain columns of around 3 μm in length, whereas propylene addition resulted in the formation of columns around 0.8 μm in length. Fig. 5 shows that there is no change in grain size across the SiC coating produced from MTS/H2 plus propylene, in comparison with those reported recently [20,21]. The formation of uniform grain size could result from improved fluidization obtained by the use of a multispout bed while the small grain size could be due to low deposition temperature. Grain growth or the nucleation of new grains is controlled by the deposition temperature, supersaturation, the existence of surface defects or contamination [6,38]. At low

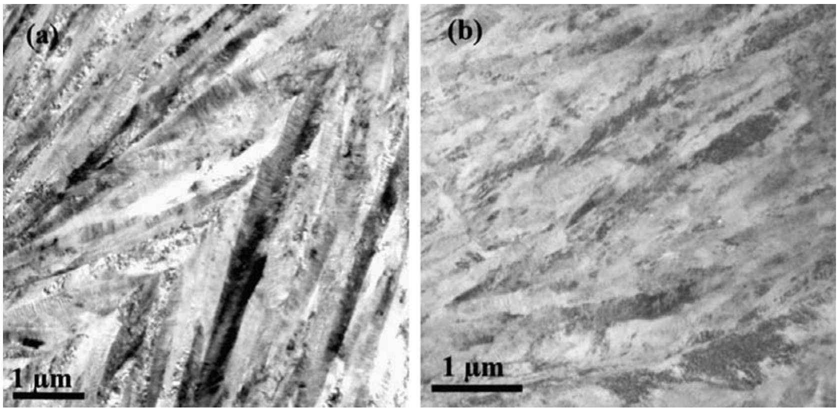

Fig. 4. TEM images of SiC close to the SiC/OPyC interface, produced at 1300 °C with: (a) 9.1 vol.% MTS and (b) 9.1 vol.% MTS + 0.5 vol.% propylene.

deposition temperatures the probability of diffusion of new arriving adatoms to the pre-existing grains reduces (Fig. 6), thus leading to the nucleation of new grains. Additionally, small amounts of carbon resulting from the use of propylene, together with the continuous friction between the particles and the graphite walls of the crucible, might produce nucleation sites that would encourage the formation of new grains.

Table 1
Young's modulus of each component of a TRISO particle with a SiC coating produced at 1300 °C.

Layer	1300-TRISO Young's modulus (GPa)
Buffer	13.97 ± 0.82
IPyC	27.23 ± 0.45
SiC	434.94 ± 1.97
OPyC	30.28 ± 1.44

The heat treatment introduced during the deposition of SiC at 1500 °C has a negative effect on the properties of the IPyC by increasing its anisotropy and reducing its Young's modulus [23,39]. In order to detect a possible change in microstructure or mechanical properties, Raman spectroscopy and nanoindentation tests were performed across the layers. Fig. 7 shows the Raman spectra of each layer of the coated particle. The signals of the buffer layer are characteristic of a highly disordered graphene structure with a high level of tortuosity and low anisotropy [31]. The IPyC and OPyC on the other hand have a signal similar to that found for turbostratic carbons with medium textured graphene layers [31,40]. The IPyC signal did not show signs of a change in microstructure due the SiC depositon, i.e., the presence of a stronger G signal and the reduction or disappearance of the D band, such as those found in highly textured carbons [41–43]. Previously it has been observed that Young's modulus of the IPyC can reduce from around 29 GPa to approximately 19 GPa due to the effect of SiC deposition [39]. Nanoindentation (Table 1) did not show a drastic change in the Young's modulus of the IPyC (27 GPa) compared to the OPyC (30 GPa), thus supporting the idea that the IPyC has retained its original properties.

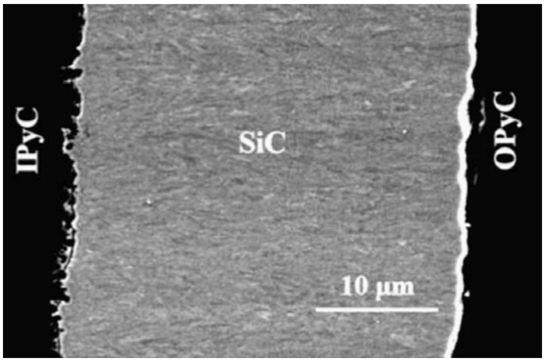

Fig. 5. SiC coating with uniform grain size produced at 1300 °C, 9.1 vol.% MTS and 0.5 vol.% propylene. High magnification image can be seen in Fig. 4(b).

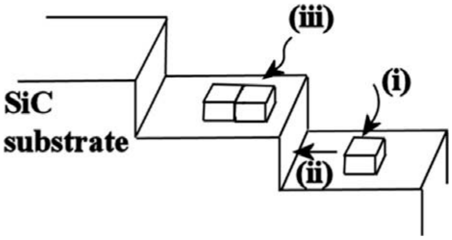

Fig. 6. Schematic representation showing the nucleation of new grains or grain growth. (i) Incorporation of new growth adatoms, (ii) migration of adatoms to pre-existing grains, (iii) nucleation of new grains when the probability of diffusion of new adatoms is reduced, i.e., at low deposition temperatures.

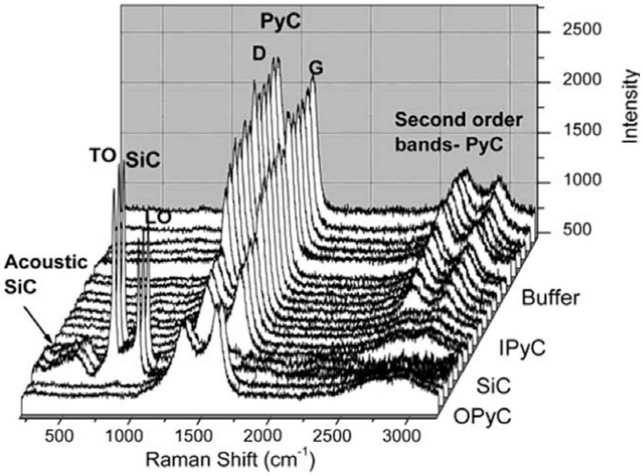

Fig. 7. Raman spectra of the cross-section of a TRISO coated particle with SiC produced at 1300 °C. The IPyC appeared not to be affected by the deposition of SiC.

3.3. SiC deposition with the addition of argon

In addition to the use of a hydrocarbon to modify the stoichiometry of SiC, the use of argon has been previously suggested and explored for the formation of coated fuel particles [19,44–46]. According to the work of Minato and Fukuda [44], the addition of argon to the reaction mixture can effectively change the stoichiometry of SiC by promoting the formation of carbon. Fig. 8 shows the effect of argon on the stoichiometry of SiC. Without any argon addition, the signal found between 300 and 600 cm^{-1} might correspond to an amorphous Si. As argon concentration was increased to 50 and 80 vol.%, it appears that stoichiometric SiC coatings were produced. XRD of the same samples detected only SiC for all these cases (Fig. 9). Additionally, the β* signal suggests the existence of stacking faults in the SiC structure [47].

In addition to changes in stoichiometry, argon also produced a change in microstructure. Fig. 10 shows the effect of argon on the SiC top surface, produced at 1400 °C. Without argon addition,

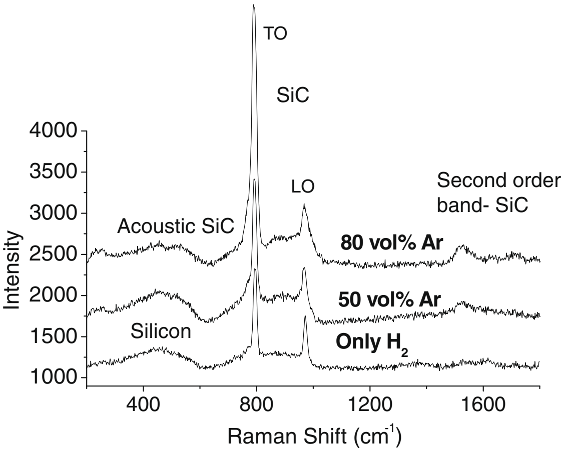

Fig. 8. Effect of Ar on the stoichiometry of SiC produced at 1400 °C and 1.27 vol.% MTS.

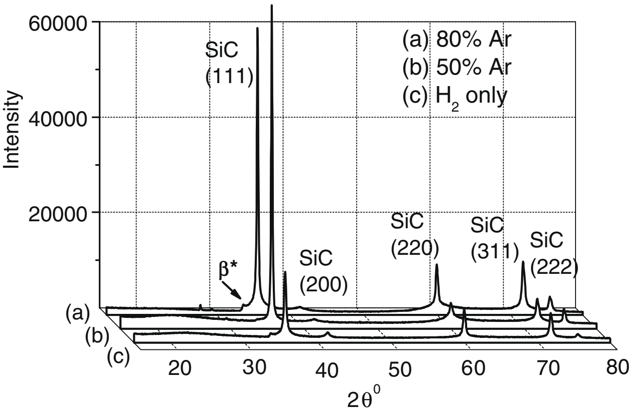

Fig. 9. XRD pattern of SiC produced at 1400 °C, 1.27 vol.% MTS and different concentrations of argon.

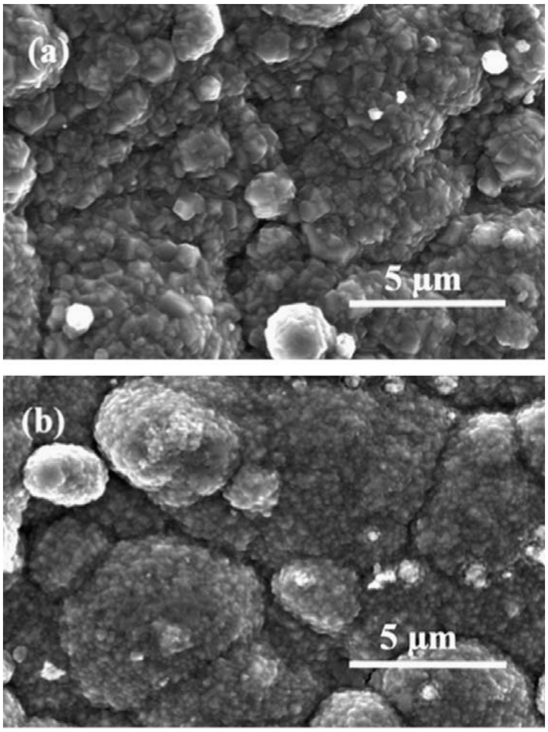

Fig. 10. SiC top surface deposited at 1400 °C and 1.27 vol.% MTS in a hydrogen environment (a) and with the addition of 50 vol.% argon (b).

the SiC produced show small faceted structures (smaller than 1 µm) in the globular-like structure (Fig. 10(a)). When 50 vol.% argon was added, such small faceted structure disappeared, producing only a globular morphology (Fig. 10(b)), which is similar to those generally produced at 1300 °C without addition of argon [13]. Furthermore, without the addition of argon the microstructure was composed of small columnar grains between 1–2 µm in length and a considerable amount of porosity in a laminar arrangement (Fig. 11(a)). The addition of 50 vol.% argon appeared to have reduced significantly both porosity and grain size with grains between 0.5 and 1 µm (Fig. 11(b)). Further increase in argon concentration up to 80 vol.% resulted in the removal of the porosity and the formation of long columnar grains between 2–4 µm in length (Fig. 11(c)). It should be noted that grain sizes did not change with coating thickness in these cases.

The effect that argon has on SiC deposition is not by participating in any reaction for the formation of SiC, but by reducing the concentration of hydrogen which is an important reactant in both the decomposition of MTS and the reactions leading to the formation of SiC [48,49]. As hydrogen concentration decreases, the heterogeneous reactions leading to the formation of carbon sites are favoured, therefore eliminating the excess Si and promoting the formation of stoichiometric SiC [44,46]. If the concentration of argon is much higher, carbon–carbon bonding will form, thus resulting in excess carbon. Since the presence of argon reduces the concentration of hydrogen, the overall effect of argon addition will be similar to that found for an increase in MTS concentration. This similar effect to MTS concentration is observed by the reduction of porosity at high concentrations of MTS and by changes in grain size [13]. In terms of the usefulness of Ar for the deposition of SiC, it has been shown that relatively dense stoichiometric SiC coatings with small grains (below 1 µm) can be produced with 50 vol.% Ar. Although higher MTS concentrations could reduce the amount of porosity, it is not clear whether this increase in MTS concentration could also produce smaller grains, as was obtained with 50 vol.% Ar, since previous results would suggest that larger grain sizes

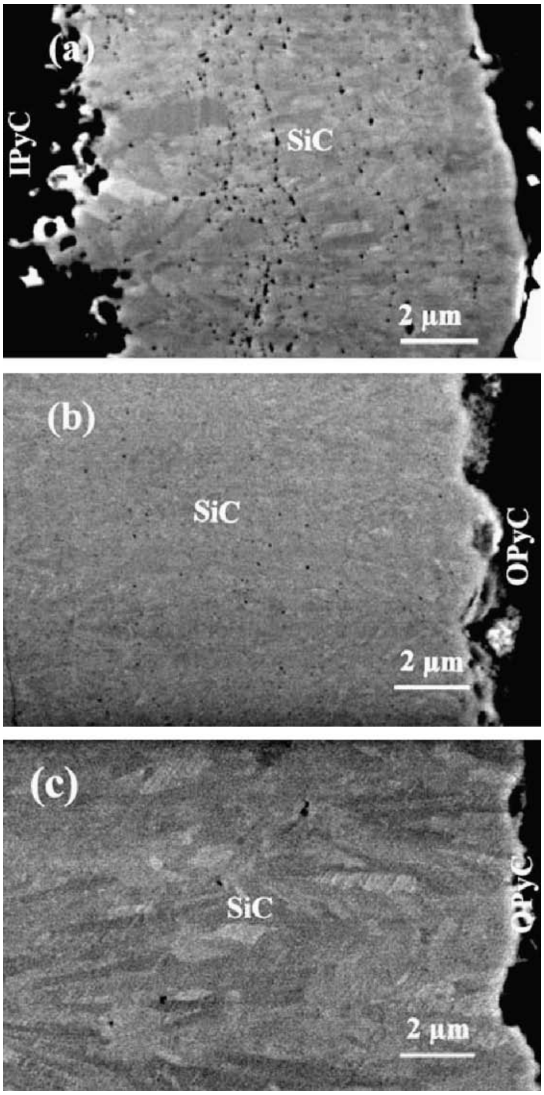

Fig. 11. Effect of Ar on the microstructure of SiC coatings produced at 1400 °C with 1.27 vol.% MTS. (a) only hydrogen; (b) with addition of 50 vol.% Ar; (c) with the addition of 80 vol.% Ar.

are produced with higher MTS concentration [11]. The use of higher concentrations of argon would not have any advantage in terms of stoichiometry and grain size but it could be detrimental since excess carbon and larger grains could be produced.

The use of uranium kernel instead of alumina would modify the deposition conditions at which similar properties can be obtained. For instance, if the surface area/volume ratio remains the same, higher flow rates will be needed in order to ensure similar fluidisation. This change in flow rate would reduce the residence time of the reactive species, thus reducing gas maturation. In order to achieve similar results, higher deposition temperatures and/or gas concentrations would be needed in order to promote similar heterogeneous reactions. Although the same deposition conditions can not be used between the two systems, the use of alumina or zirconia particles can be used to explore a new range of deposition conditions that could even lead to the deposition of nanosize grains, which could open an interesting area of research due to their superior mechanical properties and radiation resistance [50,51].

4. Conclusions

A new configuration of fluidised bed was explored. The formation of four spouts provided more uniform particle movement in the CVD reactor, thus allowing the formation of particles with good sphericity and uniform properties. SiC coatings deposited at 1300 °C with the addition of propylene, showed the formation of SiC with grain sizes of around 0.8 μm and without any visible change in grain size across the coating. The addition of argon had similar effects by avoiding the formation of porosity and reducing the grain size below 1 μm (50 vol.% Ar). High concentrations of argon produced larger grains (80 vol.% Ar). The microstructure and Young's modulus of the four layers of the particle were investigated by Raman spectroscopy and nanoindentation. There was no significant effect of SiC deposition at 1300 °C on these properties of the IPyC, thus the formation of pyrocarbons with high anisotropy was avoided. Due to the advances on the reduction of grain size in SiC, current work is focused on reducing the grain size as much as possible with the aim of producing nanosize grains.

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