Carbon fibre coated with SiC

Synthesis of Silicon Carbide Particulate and Fibre by Reaction-Conversion Method

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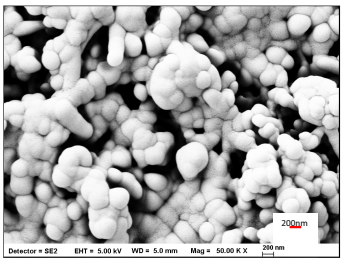

FE-SEM micrographs of SiC powder

ABSTRACT

A programme has been initiated to synthesize fully converted silicon carbide (SiC) powder and fully/ partially converted SiC fibre from the carbon particulate and fibre respectively. By reacting silicon monoxide with carbon (reaction conversion method) at temperature ~150^{0}C, ultrafine SiC powder was prepared. Yield of the process was more than 80%. SiC produced by this method mimicked the original size and shape of the initial carbon powder. Fully converted SiC fibre and SiC coated Carbon fibre (partially converted) was also produced by this method. Indeed this method was optimized and successfully used to prepare reel to reel SiC coated carbon fibre in 500 meter length.

KEYWORDS: *Silicon carbide (SiC), Carbon fibre, Composite*

Introduction

Silicon carbide (SiC) based non-oxide ceramics in different forms found a wide range of applications - from conventional low-tech fields like abrasive and heat management (kiln furniture, heating elements etc.,) to highly sophisticated applications such as in modern jet engines and electronic wafers. Indeed, in the structural ceramic field, SiC is one of the most promising non-oxide materials owing to its high thermal conductivity, superior oxidation resistance, low thermal expansion coefficient, excellent wear and corrosion resistance, high mechanical strength even at elevated temperature, low creep, high stiffness and chemical inertness[1]. Moreover, adequate radiation tolerance of SiC[2] makes it a potential candidate as a refractory nuclear material. This journey began with the earlier developmental effort for tri-layered isotropic micro-encapsulated fuel for a high-temperature gas-cooled reactor[3]. However, the major drawback of monolithic SiC is its brittleness, which makes this material unreliable, especially in accidental conditions. A composite of SiC particulate(p) with SiC fibre(f) provides the solution from such uncertainty due to its damage tolerance and highly predictable failure properties. In the aftermath of the nuclear accident in Fukushima, Japan, in 2011, the renewed interest in SiC(f)-SiC(p) composite as accident tolerant fuel (ATF) rod material gained interest[4]. Two major components needed to develop ATF clad are SiC fibre and ultrafine SiC powder. One of the most cost-effective and straightforward processes for producing continuous SiC fibre is the direct conversion of readily available carbon (C) fibre to SiC fibre[5-7]. In this, 'C' reacts with silicon monoxide (SiO) to form SiC. The gas-solid reaction is given below:

$$2C+SiO = SiC + CO \quad (1)$$

SiC has been synthesized by the above mentioned (Eq.1) gas-solid reaction [8-11]. Same reaction can also provide a coating of SiC on the C-fibre. Such type of fibre is deemed superior to the uncoated C fibre due to the former's better chemical and physical compatibility with metal and ceramic matrices and excellent oxidation resistance property[12-14].

To realize the accident tolerant fuel cladding concept, a programme on the indigenous development of SiC fibre has been initiated recently. In this, the first step was to form fully converted SiC fibre. Besides, an attempt was also made to prepare SiC coated carbon fibre in continuous mode. In addition, the above-mentioned direct reaction, which we termed as reaction-conversion method, has also been used to prepare ultrafine SiC powder.

Experimental Procedure

A mixture of silicon (Si) and silicon dioxide (SiO_2) in a 1:1 molar ratio was used to generate SiO gas. The mixture was compacted at a pressure of 150 MPa and placed on an alumina boat. Both powder synthesis and fibre making were carried out in protective argon (Ar) gas environment. At elevated temperature, SiO reacted with C to form SiC. After several trial-and-error runs, the reaction temperature was fixed at 150^{0}C. A schematic of the experimental set-up for powder and fibre synthesis has been shown in Fig.1(a and b).

The phase evolution was studied by X-ray diffraction (XRD) and Raman-scattering technique. The microstructure of the synthesised fibre was observed under a scanning electron microscope (SEM). Elemental mapping was carried out using the SEM-EDS technique.

Results and Discussion

Conversion of 'C' to SiC was carried out in static and continuous mode in protective Ar gas environment. Well dispersed ultrafine mixed-phase silicon carbide powder, which will be used for developing SiC-based structural components for the nuclear reactor has also been synthesized by this method. Initially, the time and temperature of the reaction were optimised for the synthesis of the powder. It was observed that with an increase in reaction time, the content of un-reacted 'C' decreased, and the amount of SiC increased. In the present study, it was found out that the synthesized SiC was a mixture

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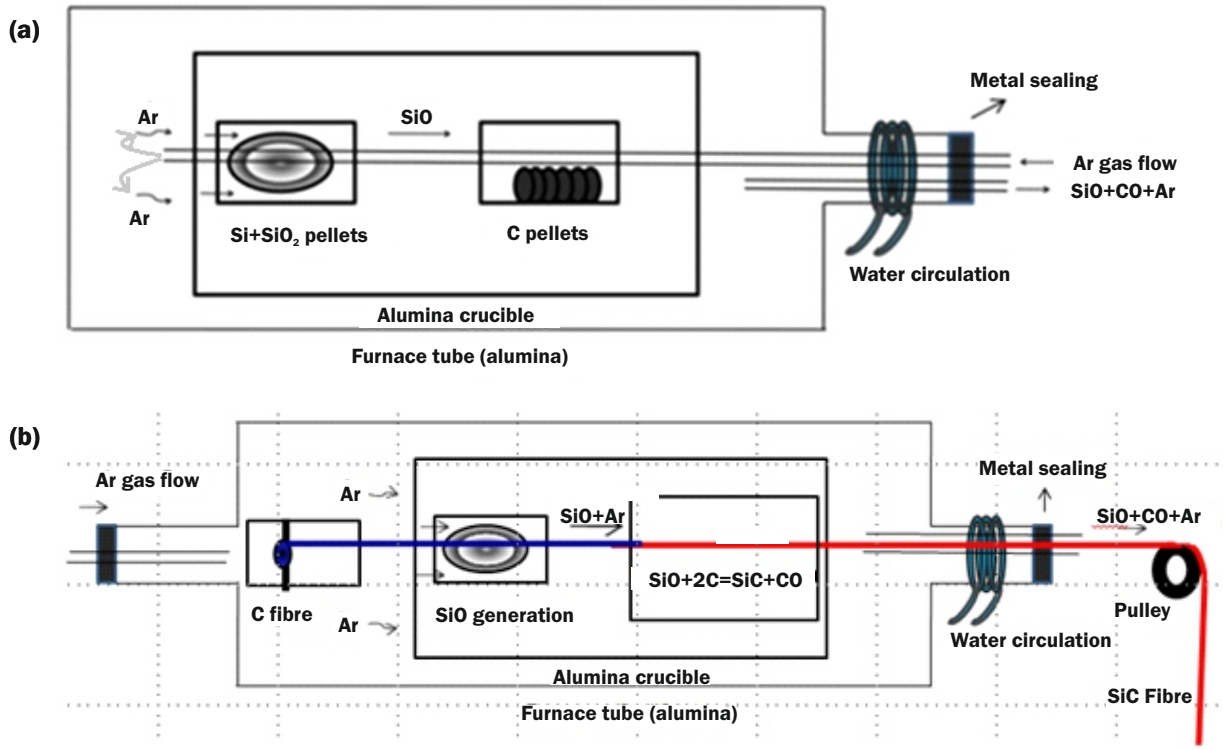

Fig.1: Schematic of reaction set-up for SiC synthesis by gas solid reaction (a) for powder synthesis and (b) 20m long fibre drawing.

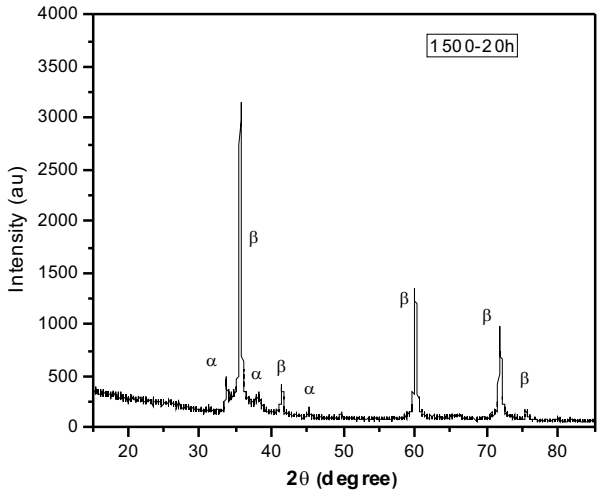

Fig.2: XRD patterns for converted C pellets obtained after 20h holding at 1500°C.

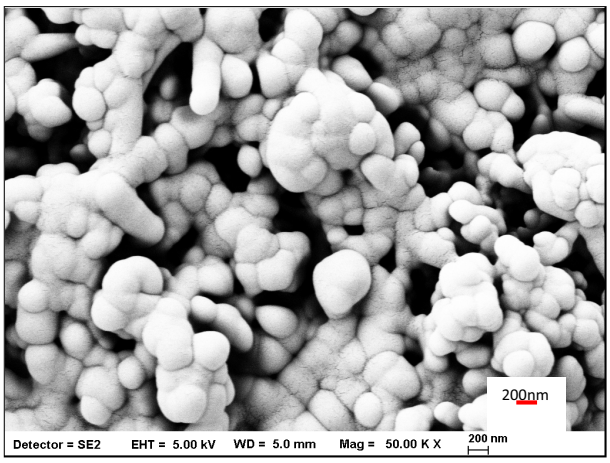

Fig.3: FE-SEM micrographs of SiC powder synthesized by reaction-conversion method.

of alpha-SiC (2H-SiC, H stands for hexagonal) and β-SiC (3C-SiC, C stands for cubic). More than 85% yield was observed for a reaction duration of 10 h. The flow rate of the carrier gas directly influenced the formation of SiC polytype. The amount of 2H-SiC in the end product was more (>10%) when the reaction was carried out at a higher flow rate of Ar gas. In the Fig.2, an X-ray diffractogram of SiC obtained after 20 hours of reaction at higher Ar gas flow rate has been shown. XRD result reveals the presence of 3C-SiC as a major phase along with a small fraction of 2H-SiC. Our observation is contradictory to the result reported by Frolova *et al*[15], who claimed formation of a mixture of 3C and 6H SiC as the gas-solid reaction product. Most importantly, the reported amount of 6H in the reaction product was significant (>30%)[15]. In the present investigation, the characteristic reflection for 6H was absent both in the X-ray diffractogram and Raman spectroscopy data. Surprisingly, the characteristic XRD peak of 6H-SiC was absent in the x-ray diffractogram reported in the work by Frolova *et al*[15]. We have further confirmed the presence of 2H-SiC in the reaction product from the Raman study (result was not included here).

The micrographic feature shown in Fig.3 reveals the formation of very fine powder (individual particle in size range of 50-250 nm). Particles were present both as a single entity as well as in agglomerated form. Broadened nature of 2H-SiC peak corroborates this finding. The size of the agglomerate was found to be ~ 500 nm. Most interestingly, the synthesised powder mimicked the shape and size of the starting carbon powder. Particle size distribution of the ground powder (result was not included here) showed a narrow size distribution and the average size was ~ 300 nm (particle size distribution by laser scattering method measure agglomerate size).

Reel to reel synthesis of composite SiC fibre (core-

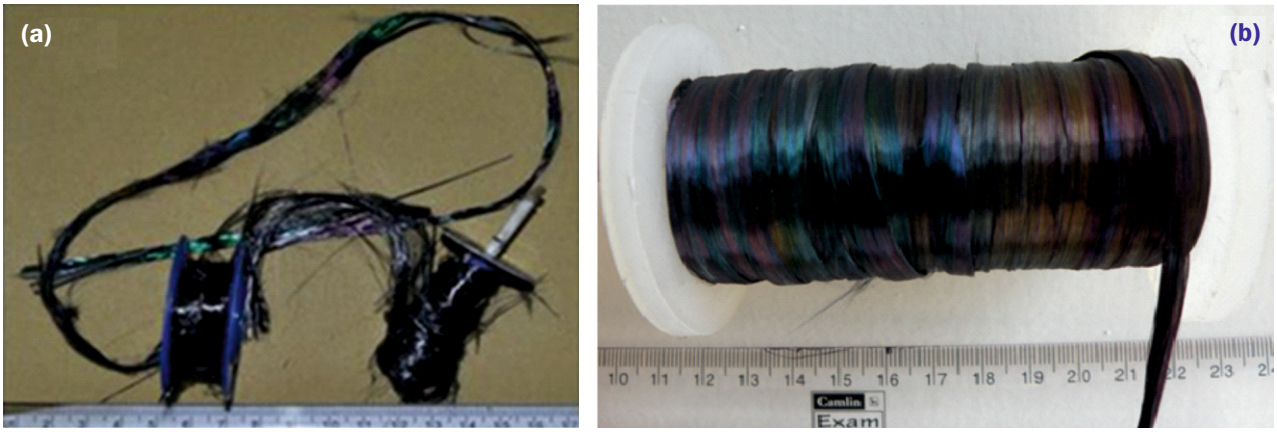

Fig.4: Reel to reel produced SiC fibre. (a) almost fully converted SiC fibre (5 m length), (b) SiC coated carbon fibre (>20 m length).

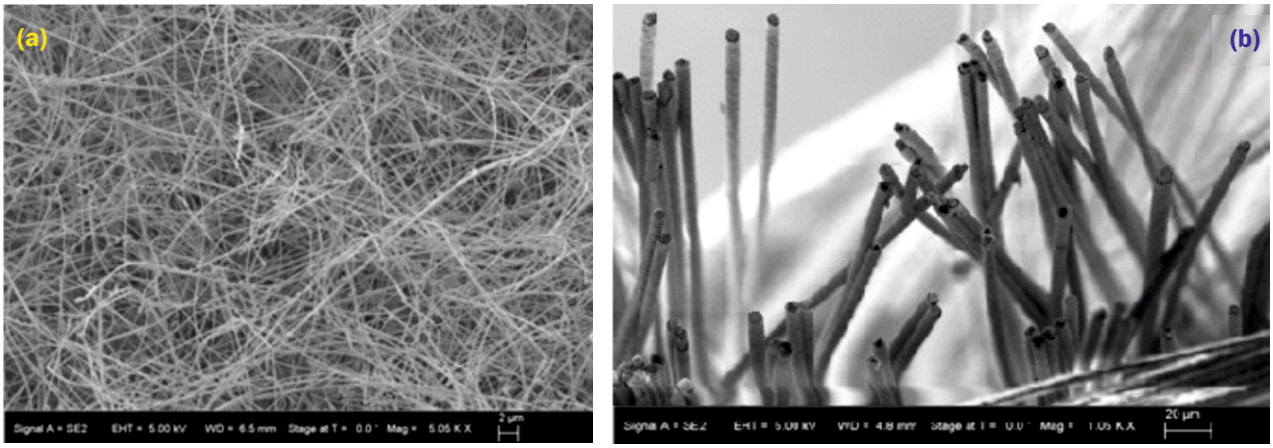

Fig.5: FE-SEM micrographs of fully converted (a) β-SiC fibre and (b) a mixture of fully and partially converted hollow core SiC fibre consisting of β and 2H-SiC phases. Diameter of the original carbon fibre (~6-7 micrometer) remained same even after conversion.

carbon with SiC periphery) in different length, starting from 5m to 500m was successfully carried out in semi-automatic mode (Fig.4). The fibre, unlike powder had different colour shades-rainbow, green, bluish, purple, and black. Upon observation under SEM, it was found out that the thickness of SiC was almost constant irrespective of different colour obtained. Hence thickness of in situ formed SiC didn't decide the colour of the fibre. The phase composition in the fibre was uniform. Hence, polytype of SiC was not the deciding factor. Most probably, the thin SiO_2 layer formed on the outer surface of the fibre was responsible for providing different colour shades [6]. This is to be noted that when the experiment was carried out in static mode, the fibre had shown usual SiC colour (greyish). Like powder, the major phase present in the fibre was β-SiC. The x-ray diffractogram also confirmed the presence of hexagonal polytype of SiC in the fibre. In addition, by optimising reaction temperature and duration of reaction along with gas flow rate, fully converted SiC fibre was made. However, fully converted fibre was more brittle than partially converted fibre (as observed). Fibre synthesis was also carried out in batch. In this, fully converted chopped fibre was produced. Micrographs of different types of SiC fibre produced in-house are shown in Fig.5. Depending on the reaction temperature and gas flow rate, the morphology of the fibre varied. Fig. 5(a) shows the formation of almost fully converted β-SiC fibre when gas flow rate was slow (amount of unreacted carbon at the core was negligible). Whereas a mixture of 2H and 3C-SiC was obtained when the gas flow rate was relatively faster. In the second case (5(b)), the resultant fibre had a hollow core. SiO reacting with carbon formed the SiC at the surface of the C-fibre. At the letter stage, C diffused out through the barrier layer to react with the SiO to form SiC. This caused formation of hollow core. The 2D woven-mat of C has also been successfully converted to SiC coated 2D C-mat by this method. This mat was used to prepare SiC-SiC composite.

Conclusions

Reaction conversion is useful in converting carbon to SiC. This method was successfully applied to synthesize ultrafine SiC powder from C-black. Morphology, i.e. size and shape of the starting powder was retained in the final product. Yield of the process was more than 80%. Reaction conversion can be used either as a batch process or in continuous mode. Batch mode has the potential to fully convert carbon fibre into SiC. In continuous mode, nearly 500m long SiC coated C fibre, where the average thickness of the SiC was ~ 250 nm was prepared successfully.

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