Analytical Electron Microscopy of W-Core β -SiC Fibers for Use in an SiC-Based Composite Material for Fusion Applications

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Abstract: In this work, the interactions between tungsten (W) and silicon carbide (SiC) in Sigma™ SiC fibers at high temperatures were characterized using scanning and transmission electron microscopy. These fibers could have the potential for use in fusion-related applications owing to their high thermal conductivity compared with pure SiC-based fibers. The as-received fibers were composed of a 100- μ m-thick shell of radially textured β -SiC grains and a 15- μ m-thick tungsten core, composed of a few hundreds of nm-sized elongated tungsten grains. The interfaces between the tungsten and the SiC and the SiC and the outer coatings were sharp and smooth. After heat treatment at 1,600°C for 3 h in Ar, the tungsten core reacted with SiC to form a rough interface surface. Inside the core, W_5Si_3 , W_3Si , and W_2C phases were detected using energy-dispersive X-ray spectroscopy and electron-diffraction techniques. The mechanical properties of the fibers deteriorate after the heat treatment.

Key words: SEM, TEM, silicon carbide, fibers, fusion

INTRODUCTION

Silicon carbide (SiC)-based fiber/matrix composite materials are, owing to their low activation in a neutron flux, an operating temperature $>1,000^\circ\text{C}$, and radiation defects resistance, practically the only nonmagnetic materials that could be used in structural applications in the next generation of fusion reactors. Besides the mentioned properties, the composite should have a high wear resistance under the conditions of service, a resistance to structural or lattice damage owing to the impinging high-energy neutrons, a high thermal conductivity, and a gas impermeability (Hasegawa et al., 2000; Naslain, 2004; Andreani et al., 2006; Lässer et al., 2007; Novak et al., 2010). The SiC should be in the cubic (β) form, which is less prone to irradiation damage and with a very small amount of porosity.

According to the present state of the art, a composite material prepared by chemical vapor infiltration (CVI) and polymer infiltration and pyrolysis does not completely meet the required properties. Although the CVI method enables the production of pure SiC with very low neutron activation, both methods are very slow and costly and/or result in an incomplete filling of the gaps between the fibers in the tows. The porosity at the micro and macro levels, the gas permeability, and the thermal conductivity are still not in the required range (Chawla, 1987; Hasegawa et al., 2000). The preparation temperature of the matrix material is expected to be around 1,600°C, with an operating temperature around 1,000°C.

Insufficient thermal conductivity is one of the main drawbacks to SiC/SiC composites proposed for use in the

structural parts of a fusion reactor beyond ITER. One possible solution to increasing the thermal conductivity is the incorporation of tungsten filaments in the composite material, with its intrinsic room temperature thermal conductivity being 170 W/mK. With the proper amount and geometry of W filaments through the thickness in a SiC-based matrix, the requested thermal conductivity of 30 W/mK should be achieved. As an alternative to pure W filaments, SiC-coated W or W-core SiC fibers could be used.

The main objective of the work is the potential interactions between W and SiC in W-core SiC fibers at high temperatures. According to the literature data (Chawla, 1987; Harris, 2002; Wawner, 2000), the reaction products may have a detrimental or, if controlled, beneficial effect on the mechanical properties of the material. The W/SiC interfaces were investigated with scanning and transmission electron microscopy (SEM and TEM) and microanalysis. The preparation of the electron-transparent sections of the ceramic fibers is a challenging task that often limits the use of TEM studies for such fibers. Various TEM sample preparation methods were tested; the most efficient method combines a technique for preparing densely packed fiber/epoxy specimens and mechanical polishing to a thickness of $<5\ \mu\text{m}$, thus minimizing the time of the ion milling. Alternatively, the wedge-polishing method without any ion milling was also used.

MATERIALS AND METHODS

As model materials, different grades of Sigma fibers from TISICS Ltd, UK were used: SM 1040, SM 1240, SM 3156, and Hot Fiber. All the fibers consist of a 15- μ m W-core with deposited SiC with various grades of purity and stoichiometry on the top. In some cases, different outer coat-

ings were added to the SiC. The SM 1040 fiber has a total diameter of $\sim 95\ \mu\text{m}$ with no outer coating, and the SM 1240 fiber has a diameter of $\sim 105\ \mu\text{m}$ with $\sim 3\text{--}4\ \mu\text{m}$ carbon and $0.8\text{--}1.2\ \mu\text{m}$ titanium boride outer coatings. In both cases, the SiC is nonstoichiometric with some free silicon and silicon-rich phases. The SM 3156 fiber is $\sim 140\ \mu\text{m}$ in diameter, with $\sim 3\text{--}4\ \mu\text{m}$ carbon outer coating. The SiC is almost stoichiometric. Hot Fiber is a titanium-carbide-coated W-core with an SiC layer. All the fibers were thermally treated at $1,600^\circ\text{C}$ for 3 h in pure Ar. The selected conditions are comparable to the conditions for the production of SiC-based composite material.

The microstructure of the fibers, the interactions between the W-core and the SiC, and the interactions between the SiC and outer coatings were investigated with scanning (JEOL FEG-SEM 7600F) and transmission (JEOL 2010 F FEGSTEM) electron microscopy and microanalysis. High-resolution TEM, Z-contrast imaging (STEM/HAADF), and different techniques of electron diffraction were used for the phase identification and energy-dispersive X-ray spectroscopy (EDXS) for determining the chemical composition of the individual phases.

TEM Specimen Preparation

One batch of TEM samples was prepared from a glued bundle of fibers by mechanical polishing on a diamond-lapping film in the longitudinal section down to a thickness of $\sim 10\ \mu\text{m}$. The thinned samples were milled in an ion miller (Bal-Tec RES 010, Balzers) at 4 keV with an incidence angle of 10° until a perforation was observed.

To get enough thin area at the W/SiC interface, the specimens were also prepared using a wedge-shaped polishing cross-section method using an automatic Allied Multi-Prep System. The fibers, embedded with epoxy resin and placed in preformed channels between two monocrystalline silicon plates (Fig. 1a), were polished on diamond-lapping films at a very small wedge angle of 1.5° until interference fringes became visible under the optical microscope. The final polishing step involved a $0.5\text{-}\mu\text{m}$ diamond-lapping film and $0.05\text{-}\mu\text{m}$ colloidal silica until the electron transparency was observed (Fig. 1b). The specimens were removed from the glass support and mounted on a Cu grid for the TEM observation (Voyles et al., 2003; Eberg et al., 2008).

RESULTS AND DISCUSSION

Figure 2 shows the optical and FEG-SEM micrographs of the as-received SM 1240 and SM 3156 fibers' microstructure at room temperature. It consists of the W-core, SiC, and various outer coatings, such as carbon and titanium boride (SM 1240) and carbon coating (SM 3156). The W-core is composed of a few hundreds of nm-sized W-grains (Fig. 3a), elongated in the longitudinal direction. The SiC phase consisted of around $1\ \mu\text{m}$, radially textured, β -SiC crystals (Fig. 3b), confirmed with electron diffraction. The interfaces between the SiC and the other coatings are sharp and smooth. In the optical microscopy images, some gradients

Figure 1. Optical micrographs of tripod-polished specimen using a wedge-shape method for the W/SiC interface: (a) before polishing and (b) after the procedure, the interference fringes at the edge of the specimen are clearly visible.

Figure 2. Optical and FEG-SEM micrographs of the SM 1240 (a, b) and SM 3156 (c, d) fibers' microstructure at room temperature. It consists of the tungsten core, SiC, and different outer coatings. The SM 1240 fiber has carbon and titanium boride coatings and the SM 3156 fiber has a carbon coating.

of color (brightness) inside the SiC phase were observed in all the samples except in SM 3156 (Fig. 2a). These gradients most probably originated from the nonstoichiometry of the SiC and the different grain size across the diameter. Minor changes in the conditions during the preparation of the fibers can lead to a significantly different microstructure within SiC (Cheng et al., 1999). The carbon layer is amorphous in all samples; in SM 3156, an up to $0.5\text{-}\mu\text{m}$ -thick amorphous SiC layer was found to be present. Outer layers (carbon, titanium boride, or amorphous SiC) were added

Figure 3. Transmission electron microscope (TEM) micrograph (bright-field image) of the W/SiC interface (a) and TEM micrograph of the C/SiC interface (b) in sample SM 3156 at room temperature. The SiC crystal grains are radially textured.

Figure 4. FEG-SEM micrographs of SM 3156 fiber (a,b) and Hot Fiber (c). Transmission electron microscope micrograph of W/SiC interface in Hot Fiber (d) after heating at 1,600°C for 3 h in pure Ar. W-core reacted with SiC forming a rough W/SiC interface. The ring defects in the fiber are rich in oxygen and calcium.

during the fabrication of the fibers to prevent the reaction between the fibers and the matrix material and to enhance the mechanical properties by enabling crack deflection at the matrix/fiber interface.

After heating the samples at 1,600°C for 3 h in pure Ar, the W-core reacted with SiC forming a rough W/SiC interface, which is seen in Figures 4a and 4b. In all the samples except SM 3156 (the only one with stoichiometric SiC), circular defects with a large quantity of pores were found. Traces of oxygen and calcium were detected at the circular defects using SEM/EDXS (Figs. 4c, 4d). These defects were most probably formed during heat treatment owing to the partial densification (sintering) of the originally nonuniformly dense SiC material.

The changes inside the W-core and the possible reactions between the SiC and W after heating were explained with a ternary phase diagram in the W–Si–C system at 1,800°C, which is presented in Figure 5 (Brukl, 1965). The possible compounds at that temperature are W, W₂C, WC, W₅Si₃, WSi₂, SiC, and C. Three main phases, presented in Figure 6, were found inside the W-core using EDXS and electron diffraction: W₅Si₃, W₃Si, and W₂C. The presence of these phases was determined with EDXS analyses and elec-

Figure 5. Possible phases in the ternary phase diagram in the W–Si–C system at 1,800°C.

Figure 6. STEM/HAADF (Z-contrast) micrograph of W/SiC interface in Hot Fiber after thermal treatment at 1,600°C for 3 h in pure Ar. Inside the W-core, W₅Si₃, W₃Si, and W₂C phases were detected.

tron diffraction. The differences in the contrasts of the various phases in Figure 6 are a consequence of the imaging method, sample thickness, and diffraction contrast. The intensity of the signal in the Z-contrast imaging should be approximately proportional to Z^2 , but still some classical diffraction contrast could also be present. Owing to the differences in the mechanical properties, various phases were thinned down to different thicknesses, which would also have a strong influence on the intensity. This could explain the unusual contrasts in Figure 6, where the phases with a higher Z (W₃Si) are darker than the phases with a lower Z (W₅Si₃).

After the heat treatment, the fibers become extremely brittle and very difficult to handle.

CONCLUSIONS

The use of SigmaTM fibers composed of a W-core and an SiC shell, as a reinforcement in a ceramic composite material based on SiC, is an attractive option to increase the thermal conductivity of the structural material with a poten-

tial to be used in a future fusion reactor. The SEM and TEM microstructural investigations of the as-received and thermally treated (1,600°C, 3 h) fibers were performed. On summarizing the results, we found the following.

Fibers are composed of a 100- μ m-thick shell of radially textured β -SiC crystals. The 15- μ m-thick W-core is composed of a few hundreds of nm-sized elongated W-grains. The interfaces between the W and the SiC and the SiC and the outer coatings were sharp and smooth.

After heat treatment at 1,600°C for 3 h in Ar, the W-core reacted with the SiC forming a rough interface surface. Inside the core, the W_5Si_3 , W_3Si , and W_2C phases were found. Circular defects with a large amount of pores were present inside the SiC layer in samples with nonstoichiometric SiC where small concentrations of the elements Ca, Ti, and O were found. The reaction of the W-core with the SiC layer worsens the mechanical properties, and Sigma fibers of the investigated grades could not be directly used for SiC-based composite material preparation. Introducing some buffer layer between the W and the SiC, which would prevent the diffusion across the interface, would probably solve the described problems.

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