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SYNTHESIS AND ANALYSIS OF ALPHA SILICON CARBIDE COMPONENTS FOR ENCAPSULATION OF FUEL RODS AND PELLETS

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ABSTRACT

The chemical, mechanical and thermal properties of silicon carbide (SiC) along with its low neutron activation make it an attractive material for encapsulating fuel rods and fuel pellets. The alpha phase of SiC has particularly attractive thermal properties. Unfortunately, it requires very high temperature processing and continuous alpha SiC fiber is not available commercially. This paper describes a method for fabricating continuous, composite (SiC/C) fibers as well as monolithic SiC fibers by direct conversion of carbon fibers using SiO vapor at ~ 1600^{O}C. EDS analysis indicates the converted SiC product contains 1:1 stoichiometric amounts of C and Si. Hexagonal (α) SiC was found to be the dominant crystal structure by x-ray diffraction.

INTRODUCTION

Property Overview

Silicon carbide is a refractory ceramic with numerous commercial applications. The material's unique combination of high strength and hardness, chemical inertness, and attractive thermal properties (high conductivity, low expansion, and thermal shock resistance) make it useful for such varied applications as abrasives and wear components, high temperature semiconductors, armor, jewelry (as a diamond simulant), and reinforcement in composites. SiC exhibits excellent radiation stability, is composed of low activation elements, and retains its strength and shape under high radiation dose conditions.

Today, beta (cubic) silicon carbide (β-SiC) is used in advanced nuclear fuel element designs to provide high thermal conductivity containment and structural support to oxide-based fuel. Tristructural Isotropic (TRISO) coated fuel particles used in gas-cooled reactors contain one layer of SiC and three layers of pyrolytic carbon surrounding the fuel kernel. Here the β-SiC acts as a pressure vessel for fission products, providing structural integrity while retaining solid fission products inside the fuel pellet [1]. In pressurized and light water reactors (PWR and LWR), an all β-SiC fuel rod cladding is in the development and testing stage [2]. In an alternate design [3], SiC over-braided metal fuel rod jackets could provide additional structural support, increasing the margin of safety of the metal fuel rods. Prolonged fuel rod service life, and use of alternate fuel rod alloys are other potential benefits.

SiC exhibits polymorphism. All polytypes have a hexagonal frame consisting of adjacent Si and C layers, and more than 250 polytypes have been identified. One stacking arrangement results in the cubic 3C-SiC (β) structure. All hexagonal stacking arrangements (2H, 4H, 6H, etc.) are grouped together as α-SiC with the 6H polytype being the most prevalent. The number in the notation determines the number of layers before the stacking arrangement repeats itself and the letter designates the crystal structure [4].

The properties and applications of SiC depend on its crystal structure, density and purity. These are dictated by the processing method. For example, thermal conductivity largely depends on crystal orientation and impurity concentration. Values close to the theoretical limit have been measured by Slack et. al. for highly perfect α-SiC platelets (4H polytype) formed by the Lely process. The thermal conductivity was determined to be 490 W/m-K, comparing favorably to Cu (400 W/m-K) and Ag (418 W/m-K) [5]. The thermal conductivity of α-SiC is significantly higher than measured values for the 3C-SiC polytype (β-SiC) formed by CVD (13.7 W/m-K) [6]. The combination of high thermal conductivity and low thermal expansion coefficient (~4.0-4.8 x10^{6}/^{O}C) gives rise to excellent thermal shock resistance [7]. Similarly, electronic bandgap depends on the polytype (e.g., 2.39 eV for 3C-SiC and 3.33eV

for 2H-SiC). The wide bandgap makes it possible to use SiC for very high temperature semiconductor operation. Thermal ionization of electrons from the valence band to the conduction band, which is the primary limitation of Si-based devices, is not a problem with SiC.

Fabrication Methods

While common as interstellar dust near carbon-rich suns, naturally occurring SiC on earth is extremely rare and exists as the mineral moissanite. Synthetic SiC is fabricated using high temperature processing. It was first manufactured by Acheson in 1891 by carbon reduction of silica in an electric furnace:

$$3C\ (s) + SiO2\ (s) \rightarrow SiC\ (s) + 2CO\ (g)$$

Lower temperatures (< 1600^{O}C) away from the electrodes favor the formation of β-SiC while at higher temperatures (~2100^{O}C) colorless, green and pale yellow crystals of α-SiC predominate. The color changes to blue and black as the crystals become less pure. High purity α-SiC is formed by the Lely process in which SiC is sublimated at 2500^{O}C in an argon atmosphere. Flake-like α-SiC crystals grow by deposition of the vapor onto a substrate [23]. The vapor constituents during sublimation are mainly Si, Si_2C, and SiC_2 in specific ratios depending on the temperature [8,9].

Commercial beta or alpha SiC powders formed by the Acheson process can be mixed with boron and carbon, heated, and bonded by sintering at 2000^{O}C to form simple shapes such as rods, plates and tubes. Shapes can also be made by reaction bonding in which Si powders (mixed with SiC and C powders) are melted to bridge the interstices between SiC particles. However, impurities, particularly at grain boundaries, limit their thermo-mechanical properties for some applications. Residual Si in reaction bonded SiC reduces strength of the material while boron-containing sintering aids have been shown to adversely affect properties of sintered SiC following irradiation. For example, Wu et. al evaluated the thermal and mechanical properties of neutron-irradiated sintered SiC as a function of dosage (14-30 dpa) and irradiation temperature (420-540^{O}C) [10]. They found that sintered SiC shows a decrease in linear thermal expansion coefficient and a pronounced decrease in thermal conductivity. As pointed out by Snead et. al., the boron-containing sintering aid segregates to grain boundaries and does not behave well under neutron irradiation due to the large (n,α) cross section of the ^{10}B isotope [1]. Thermal conductivity of β-SiC has been found to decrease following irradiation [11-13].

High purity, high-density β-SiC can be formed by chemical vapor deposition (CVD). Gas-phase components, which include a Si-containing compound such as methyltrichlorosilane, react to form a condensed phase with gaseous byproducts [14-16]. β-SiC can also be formed by pyrolysis of Si-containing polymers such as polycarbosilane, polyvinylsilane, polysilazane and polyureasilazane. During pyrolysis there is significant shrinkage and void formation due to gas evolution. As a result, polymer pyrolysis has been applied industrially only to the preparation of low-dimensional components such as ceramic coatings, films and fibers.

It is desirable to develop simpler and more direct processing methods for α-SiC. This paper summarizes a novel approach to fabricate SiC fibers by direct conversion of carbon using SiO vapor in a tube furnace at about 1600^{O}C. Fiber morphology was examined using scanning electron microscopy (SEM). Element analysis was determined by energy dispersive spectroscopy (EDS, and crystal structure was evaluated using x-ray diffraction. Preliminary analysis indicates that stoichiometric SiC is produced that is predominantly α-SiC.

EXPERIMENTAL

An in-depth summary of the method and apparatus used in this study has been reported [17]. Briefly, a mixture of Si and SiO_2 was heated in an alumina crucible in a high temperature tube furnace [18] to generate SiO vapor according to the following reaction:

$$Si\ (l) + SiO_2\ (s) \rightarrow 2SiO\ (g).$$

Commercial polyacrylonitrile (PAN)-based carbon fibers [19] containing 3000 filament count tows were heated to 1550-1600^{O}C and continuously drawn along the furnace axis. SiO vapor diffused into the Ar carrier gas as the fiber was drawn through the hot furnace zone. The fiber draw rate was adjusted to vary local fiber reaction time with SiO. A thermocouple monitored the temperature of the reactant gas generator and fibers. Feedback power control for the furnace was provided using a Eurotherm controller (Model 2404) in conjunction with SCR circuitry (Eurtherm model 832). SiC was formed by the direct conversion of the fibers:

$$SiO\ (g) + 2C\ (s) \rightarrow SiC\ (s) + CO\ (g).$$

After reaction, the fibers were cooled by exposure to room temperature argon. In a typical run, fiber was drawn onto multiple take-up spools, each with about 12 m of processed SiC fiber. Samples were removed from a take-up spool and sectioned for analysis. SEM and EDS analysis were performed using a Quanta FEG 650 instrument equipped with EDAX Genesis analysis software. X-ray diffraction was conducted using a Bruker-AXS D8 Advance System instrument and EVA Search Match graphics-generating software.

RESULTS AND DISCUSSION

The as-supplied carbon fibers used in the experiments were PAN-based fibers containing 3000 individual C filaments, each about 7 μm diameter (Fig. 1a). The fibers were exposed to SiO vapor in Ar carrier gas at elevated temperature for a limited time. This resulted in the conversion of C to SiC at the exposed

surface of the filaments to form a shell. A shell measuring ~200 nm, is illustrated in Figure 1b. As reaction progressed, the carbon filament diameter decreased as the SiC shell thickened. A sample with a 1 μm thick SiC shell is illustrated in Figure 1c. It was formed at the same temperature (1600^{O}C) as the previous sample but twice the dwell time in the reaction zone. As dwell time at temperature was further increased, the fiber was completely converted to SiC and adopted a tubular geometry with an ID of about 2.5 μm and an OD of about 8 μm, as shown in Figure 1d.

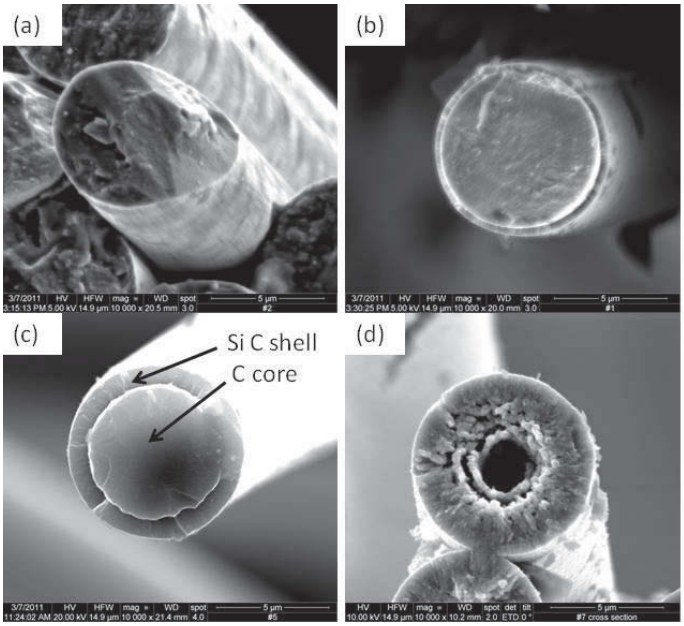

Figure 1. SEM photomicrographs of cross sections of C fibers during conversion to SiC. (a) As-received (unconverted) PAN-based carbon fibers. (b) Partially converted carbon fiber with ~200 nm thick SiC shell. (c) Partially converted C fiber with 1 μm thick SiC shell. (d) Fully converted SiC tube.

Longitudinal views of fibers are given in Figure 2 for partially converted fibers (Fig. 2a) and fully-converted fibers (Fig. 2b). The shell thickness appeared to be quite uniform for the individual filaments making up a fiber bundle indicating the reactant vapor was able to penetrate the inter-filament gaps.

During manufacture of the commercial PAN-based C fibers, the filaments are typically coated with an organic compound (sizing) to protect the surface and simplify handling as the filaments are bundled into fibers (tows) and woven into fabrics. EDS analysis of the fibers indicated that the core contains small amounts of residual O and N impurities while the outside of the fibers also contains Na and Al impurities. EDS analysis of a fiber during the early stages of conversion to SiC is given in Figure 3. Element analysis of the core (Fig. 3b) and shell (Fig. 3c) are included with the spectra. The SiC shell is characterized by 1:1 stoichiometric amounts of Si and C with residual Na, Al, N and O impurities retained from the starting C fibers. Similar results are found for thicker SiC shells (Fig. 4a), as shown in the spectra of Figure 4b (core) and Figure 4 c (shell). The core of this sample also had a higher level of Si than the previous sample. It should be noted that accurate chemistry analysis using EDS is hampered by sampling volume limitations which result from e-beam penetration into the sample. Composition analysis of thin SiC shells may include signal from the C core.

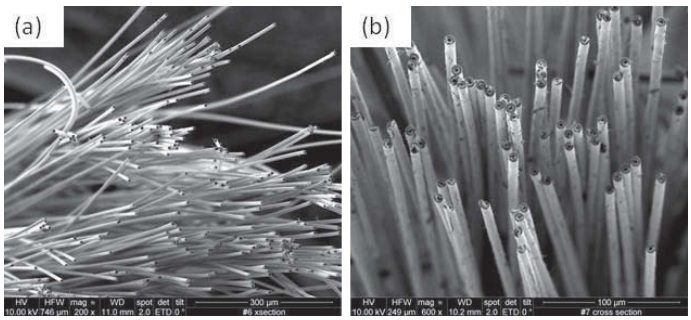

Figure 2. SEM photomicrographs showing a longitudinal view of fibers. (a) Partially converted fibers of Fig. 1b. (b) Fully converted SiC microtubes of Fig. 1d.

Color variations of the SiC fibers have been observed as processing conditions changed. Colors include green, blue and purple. The source of the color variations are likely impurities in the starting reactants, C fibers, and processing conditions. It is known that pure α-SiC is clear but can be prepared with a wide range of colors by doping crystals to form green (N and P doped), blue (Al-doped), brown (B-doped) and black (Al, Si, Fe and C impurities) [6]. A rainbow-like luster on crystals can be caused by a passivation layer of SiO2 on the surface. Shaffer has shown that the refractive index, dispersion, and birefringence of SiC also depend on the polytype [20].

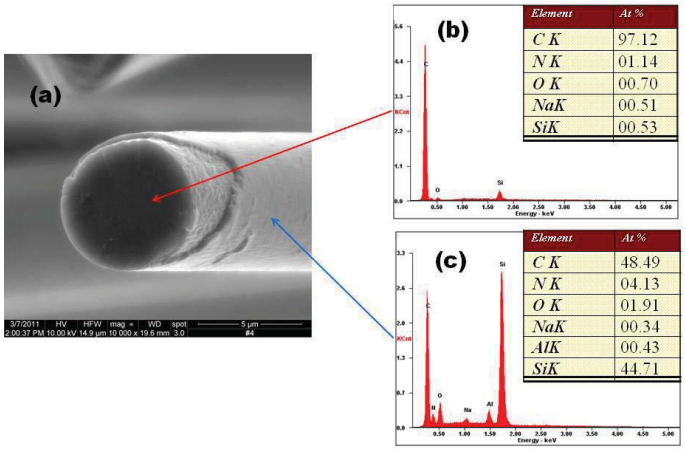

Figure 3. SEM/EDS analysis of a carbon filament partially converted to SiC. (b) EDS analysis of the core. (c) EDS analysis of SiC shell.

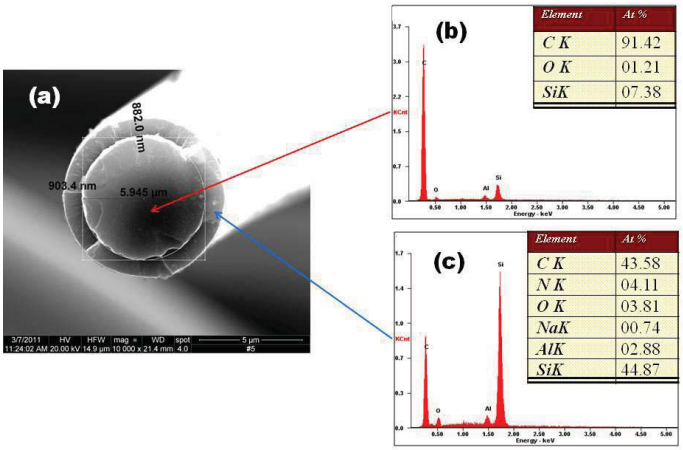

Figure 4. SEM/EDS analysis of a partially converted filament. (a) SEM photomicrograph showing carbon core surrounded by ~ 1 µm thick SiC shell. (b) EDS analysis of core. (c) EDS analysis of outer shell.

Complete conversion resulted in the formation of a SiC tube rather than a solid filament. EDS analysis of the material is given in Figure 5. The shape appears to result from diffusion of carbon outward through the SiC shell as it is forming, along with Si diffusion inward. Formation of a tube suggests a higher diffusion rate for carbon. After C is depleted from the core, continued exposure will result in a rising Si concentration gradient from center to edge. The source of this additional Si is from the reactant vapor as it does not appear in partially reacted SiC/C fibers.

X-ray diffraction analysis was conducted on partially converted fibers. PAN-based C fibers are turbostratic which complicated peak resolution due to carbon peak broadening and overlap with SiC peaks. Hexagonal (α) SiC was dominant but additional analysis is required to deconvolute the amounts of the various polytypes. The presence of some β-SiC can't be ruled out at this time.

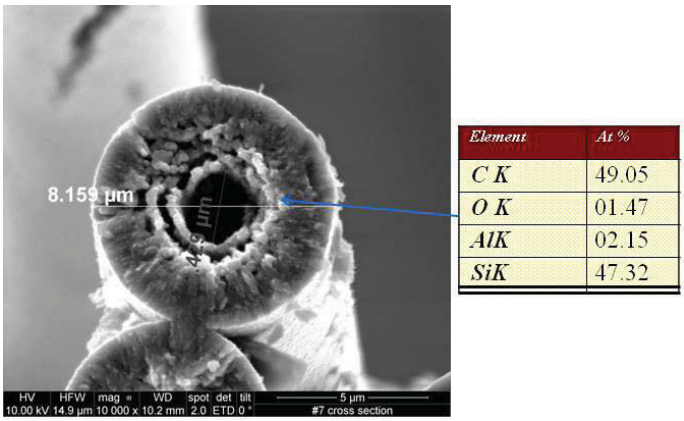

Figure 5. SEM/EDS analysis of fully converted filament. (a) SEM photomicrograph of SiC microtube. (b) EDS analysis of material.

The authors are not aware of a commercial manufacturing process for continuous α-SiC fibers. β-SiC fibers are commercially available including Sylramic fibers from COI industries (San Diego, CA), Hi-Nicalon and Hi-Nicalon S fibers from Nippon Carbon (Tokyo, Japan) and distributed through COI Ceramics, Inc. (San Diego, CA) and Tyranno Fiber from Ube Industries, Ltd. (Tokyo, Japan). These materials are synthesized by pyrolysis of Si-containing polymers and find commercial use in forming ceramic matrix composites and other materials. Sugimoto et. al. has synthesized β-SiC microtubes from polycarbosilane fibers by irradiating uncured fibers in air using an electron beam. This was followed by cross linking, solvent extraction of the core, and firing steps [21]. Airborne SiC fibers have been observed by Bye et. al. during industrial production of SiC in the Acheson process [22]. These fibers were small, with an average diameter of 0.23 µm and length of 4.5 µm, and a maximum length of 100 µm. Selected area electron diffraction indicated they were α-SiC but could not distinguish polytype (2H, 4H, 6H), although multiple polytypes were believed to be present.

SUMMARY

A new method has been demonstrated for fabricating continuous, composite (SiC/C) fibers and monolithic SiC fibers by direct conversion of carbon fibers. Composite fibers consisted of a carbon core surrounded by a shell of SiC. Fully converted fibers adopted a tubular geometry, suggesting a higher diffusion rate for C through the SiC matrix than Si. EDS analysis indicated the converted SiC product contains 1:1 stoichiometric amounts of C and Si, and x-ray diffraction indicated that the hexagonal (α) SiC was the dominant crystal structure. Residual impurities from the starting carbon fibers are retained. Future studies will focus on batch processing of material, process optimization and characterization of microstructure and mechanical properties.

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