

Microstructure and properties of Web-type polycrystalline SiC fiber prepared by electrospinning and sintering of aluminum doped polycarbosilane

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Fine diameter polycrystalline silicon carbide fibers were prepared by electrospinning and sintering of aluminum doped polycarbosilane. Fully dense and completely polycrystalline SiC fibers were obtained after sintering at 2000 °C. The diameter of the fibers was in the range of 0.5 to 2 μm. The SiC crystallite size in the fiber sintered at 2000 °C was about 200 nm and many stacking faults and twins were observed inside the SiC crystallites. A residual carbon phase was segregated on the fiber surface and at the grain boundaries in the form of microcrystalline graphite. When oxidized at 1200 °C, the fiber showed good adhesion with the oxidation layer formed on the fiber surface.

Key words: Polycrystalline SiC web, Electrospinning, Polyaluminocarbosilane, Sintering, Residual carbon, Energy efficiency.

Introduction

Silicon carbide fibers have been used as reinforcements for SiC_f/SiC composites for various high-temperature applications [1-4]. For the reinforcement of the composites, the SiC fibers are required to exhibit excellent mechanical strength, elastic modulus, creep resistance, and oxidation resistance at high temperature. Since Yajima's first work, there have been significant technological advances in SiC fibers derived from polycarbosilane [1, 5]. Ichikawa *et al.* developed polycrystalline SiC fibers with stoichiometric C/Si ratios using electron beam cured polycarbosilane fiber by pyrolysis in a hydrogen atmosphere [6]. However, Ishikawa *et al.* showed that the addition of small amounts of aluminum in the polycarbosilane could lead to fully dense and completely polycrystalline SiC fibers with nearly stoichiometric in C/Si ratios after sintering at around 2000 °C [1, 6]. Further, the aluminum was thought to play a role as a solute for the SiC solid solution, resulting in increased densification of the SiC fibers after finely controlled pyrolysis. These sintered fibers may find potentially promising applications in high-temperature SiC_f/SiC composites because the material has already experienced high-temperature sintering and the microstructure of the fiber can be expected to be stable after the composite fabrication.

Recently, SiC fibers have been considered as candidates for good catalytic supports, gas-fueled porous radiation heaters [7, 8], ceramic fiber separators for thermal batteries [9, 10], and filtration media for diesel particulate filters (DPF) [11, 12]. For these applications, it is necessary to fabricate fibers with smaller diameters and an increased specific surface area. The high-temperature stability of the fiber is important because with small fiber diameters, the scale of oxidation can easily span all across the fiber diameter in the operation atmosphere and oxidation can lead to the loss of the inherent properties of the material. It is noteworthy that the reports on the oxidation behavior of SiC fibers with diameters ranging between 0.5 and 2 μm, which are significantly small diameters, are virtually absent.

We have designed the strategies to obtain fine SiC fibers that exhibit oxidation resistance at high temperatures, and have developed electrospinning of small fiber diameters and the doping of aluminum in polycarbosilane (PCS) for obtaining fully crystalline microstructures. Electrospinning is a remarkable technique for obtaining nano/microscale ceramic fibers [13-17]. Oxide-based ceramic nanofibers were prepared by electrospinning of a sol-gel solution followed by sintering at specified temperatures [13, 15]. Non-oxide ceramic fibers were also prepared by electrospinning using a polymer precursor route, which is a novel method for fabricating ceramic fibers through an organic-to-inorganic conversion using polymer precursors [13, 16, 17]. In this work, we have prepared web-type polycrystalline SiC fibers by electrospinning using aluminum doped PCS (Al-PCS). During the fabrication of these fibers,

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Table 1. List and summaries of the sample.

Mark	Description	Preparation method
PCS	polycarbosilane	Kumada rearrangement of PDMS using zeolite catalyst
Al-PCS	polyaluminocarbosilane	One pot reaction of PDMS with aluminum acetylacetonate using zeolite catalyst
Al-SiC-1200	Al doped SiC web	Electrospinning Al-PCS solution and pyrolyzed (or sintered) at the temperature between 1200 and 2000 °C
Al-SiC-1400		
Al-SiC-1600		
Al-SiC-1800		
Al-SiC-2000		

sintering conditions were carefully controlled and the microstructure and oxidation behavior of the fully dense polycrystalline SiC fibers were investigated.

Experimental Procedures

Al-PCS was synthesized by the direct reaction of polydimethylsilane (PDMS) with aluminum (III)-acetylacetonate (Al-acac) in the presence of a zeolite catalyst. The catalytic reaction was carried out through a 2-step process at 350 °C and 400 °C [18]. PDMS was mixed with 1-5% of Al-acac and 1-5% of ZSM-5 catalyst, and the mixture was placed into an autoclave reaction vessel under inert atmosphere. The autoclave was heated to 350 °C for 10 hrs to convert PDMS into the PCS skeleton including a combination of Al-acac in the first reaction step. The reaction temperature was subsequently increased to 400 °C and the temperature was maintained for 15-20 hrs to lead to polymerization in the second step. During this step, vacuum distillation was additionally performed in the vacuum furnace (held at 250 °C for 1 hr) to remove the low molecular weight (M_w) portion and to control the polydispersity of the reaction products. Subsequently, the yellow colored Al-PCS was obtained at room temperature.

The Al-PCS obtained was dissolved into a solvent mixture of toluene and 20-30% of N, N-dimethyl formamide (DMF) at various concentrations (1.0-1.3 g/ml). The solvent mixture was used to enhance the spinning performance [19-21]. The Al-PCS solvent mixture was stirred for 24 hrs at room temperature to obtain a uniform solution.

The electrospinning system and the overall process are described in Fig. 1 [13, 17]. The Al-PCS solution was loaded into a syringe with a capacity of 5 ml and subjected to electrospinning using a metallic needle with a diameter of 0.5 mm at the rate of 0.5 mm/hr under an applied voltage in the range 15-25 kV. The solution could be stretched without any drop formation at 20-23 kV. The distance between the needle tip and the collector was 100 mm. Subsequently, samples with dimensions of $50 \times 50 \text{ mm}^2$ obtained from the electrospun webs were subjected to thermal curing at 200 °C for 1 hr in a muffle furnace and then sintered at a temperature in the range 1200-2000 °C for 1 hr in argon atmosphere in a graphite furnace. The various samples are listed in table 1.

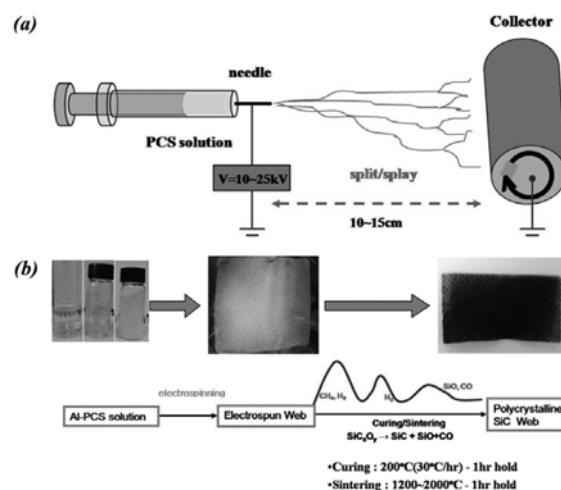


Fig. 1. Schematic illustration of the experimental procedure: (a) overall process for preparing the polycrystalline SiC web and (b) setup for the electrospinning of Al-PCS solution.

Fourier transform infrared (FT-IR) spectra were obtained using a FTS-175C spectrometer in the range $4000\text{-}400 \text{ cm}^{-1}$. Attenuated total reflectance (ATR) and transperance method were used alternatively. Gel permeation chromatography (GPC, Waters 2414 refractive index detector, 515 HPLC pump) with three consecutive Styragel columns (HR1, HR2, and HR3) was carried out using tetrahydrofuran as the solvent. The thermal decomposition behavior of Al-PCS at temperatures up to 1200 °C was characterized using thermogravimetric analysis (TGA, Mettler-Toledo 851e TGA/SDTA instrument) under argon atmosphere. The microstructure and morphology of the sintered Al-SiC web or the single fibers were observed using a field-emission scanning electron microscope (FE-SEM, JSM-6700F, Jeol, Japan). The phase changes occurring at various sintering conditions were characterized by X-ray diffraction (XRD, FR-150, Enraf-Nonius Co., Netherlands).

The nanostructure of the material was analyzed using high-resolution transmission electron microscopy (HR-TEM, JEM-4010, Jeol, Japan). The study of the changes in the phase of the residual carbon as a function of the sintering temperature was carried out using Raman spectroscopy (NRS-3100, JASCO, Japan) at an excitation wavelength of 532 nm excitation at a resolution of 1 cm^{-1} .

Results and Discussions

Synthesis of Al-PCS

Fig. 2 shows the comparison of the FT-IR spectra of (a) PCS and (b) Al-PCS. The characteristic absorption bands evolved at 2950 cm^{-1} (C-H stretching), 2100 cm^{-1} (Si-H stretching), 1400 cm^{-1} (Si-CH₃ deformation), 1360 cm^{-1} (C-H₂ stretching in Si-CH₂-Si), 1242 cm^{-1} (Si-CH₃ deformation), 1020 cm^{-1} (CH₂ wagging of Si-CH₂-Si), and 825 cm^{-1} (Si-C stretching) [22]. The complex bands at $1200\text{--}1600\text{ cm}^{-1}$ in Fig. 2(b) correspond to the diketones of Al-acac. New bands were detected between 1600 cm^{-1} and 1450 cm^{-1} , which may have been caused by the delocalization of the C=O or C=C bonds in the decomposed diketone and by the formation of Si-O, Al-O, and Si-Al-O bonds during the reaction of Al-acac with carbosilane structures, as shown in the inset of Fig. 2 [18, 22, 23]. The peak intensity of the Si-H bonds in Fig. 2(b) was low when compared to that shown by PCS because Si-H, with its weak bond strength, acts as a good crosslinking site. Further, this could also be an indication of the substitution of Al-acac [18, 23-25].

Fig. 3 shows the GPC curves of (a) PCS and (b) Al-PCS. The M_w distribution of PCS was mainly detected at the elution time of 18-27 min and a weak shoulder was also detected at high M_w (at around 20 min). Al-PCS was similar to PCS, with the exception of the appearance of an additional strong peak in the M_w distribution at around 20. This strong peak reached the higher M_w region due to the bonds formed between the Al-acac radical and the carbosilane skeleton. Ishikawa *et al.*, who synthesized the polyaluminocarbosi-lane by the two step process, have also discussed the formation of high M_w fraction in GPC [23]. In our case, the Al-acac directly reacted with the (CH₃)₂Si radicals in PDMS and the complex reaction was possible.

In general, the thermal decomposition of Al-PCS showed a behavior similar to that of PCS, as shown in Fig. 4. The weight changed between 300 and 600 °C and included the evaporation of the lower M_w portion and the evolution of hydrocarbons such as CH₄ and C₂H₆ [17, 18, 26]. A small change above 600 °C was recorded because of the evolution of hydrogen gas. The weight change at around 200 °C could be attributed to the small amount of residual diketone that dissociated from Al-acac and remained in the Al-PCS after the synthesis.

Electrospinning and sintering of the Al-PCS fiber web

The concentration of Al-PCS dissolved in 30% DMF/toluene solvent mixture affected the fiber morphology and diameter of the as-spun web, as shown in Fig. 5. The as-spun polymer web had broad range of fiber diameters and consisted of many beads when the 1.1 g/ml solution was used. Beads were formed frequently during the spinning of the less viscous solutions and

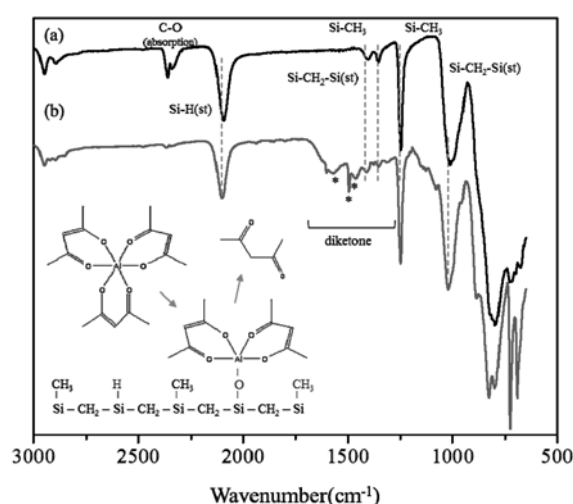


Fig. 2. FT-IR spectra of (a) PCS, (b) aluminum(III)-acetylacetonate, and (c) Al-PCS. Inset shows the reaction model of aluminum(III)-acetylacetonate with PCS back-bone.

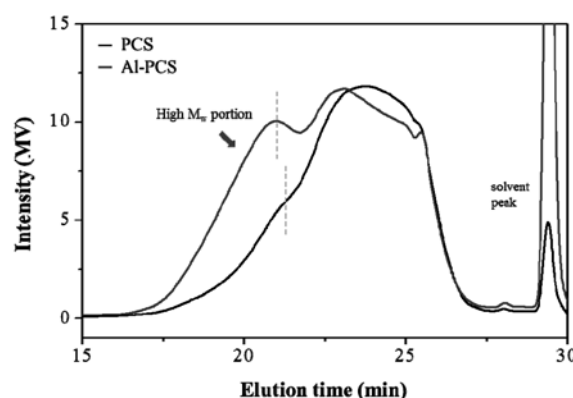


Fig. 3. GPC curves of (a) PCS and (b) Al-PCS, relatively.

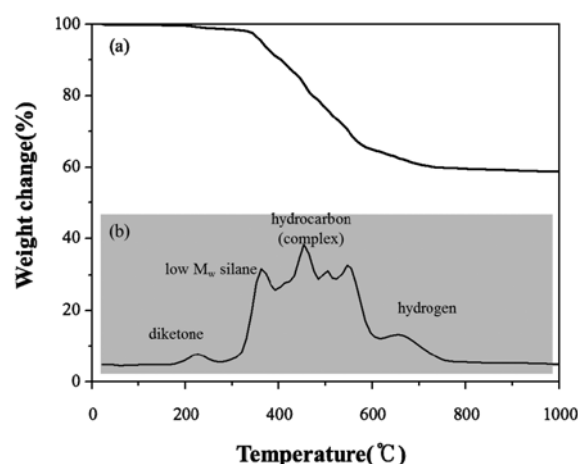


Fig. 4. (a) TGA and (b) DTG curves of Al-PCS.

they were distorted because of the evaporation of the residual solvent [17, 27, 28]. Thick fibers with a belt-like shape and diameters ranging to nearly $8\text{ }\mu\text{m}$ were formed from solutions with concentration of 1.4 g/ml. These fibers were adhered to each other. Due to the excessively high concentration of Al-PCS, the viscosity

of the spinning solution increased excessively to sufficiently stretch the fiber with an applied electric field of 2 kV/cm. Since the large diameter fibers reached the receiving drum without splitting, the fiber consisted of a sufficient amount of solvent within them and were adhered well together. With solutions of concentration of 1.3 g/ml, the fiber diameters became smaller and uniform and the beads also disappeared. The Al-PCS web spun using the 1.3 g/ml solution was thermally oxidized at 200 °C and sintered at above 2000 °C (Figure 5(d)). The fiber diameters were between 1 and 3 μ m and submicron fibers were also occasionally observed.

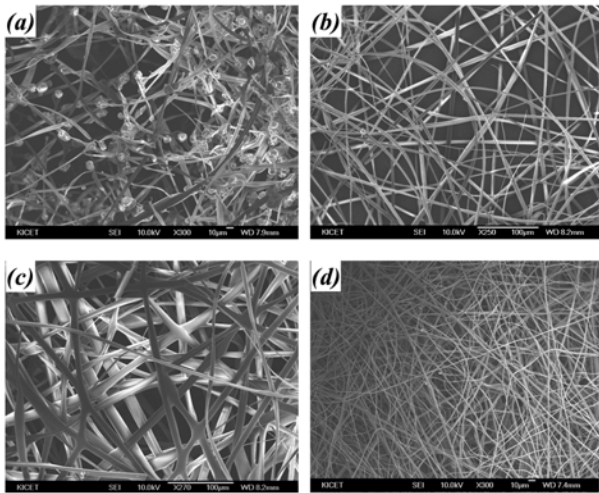


Fig. 5. SEM images of the Al-PCS samples electrospun at a solution compositions of (a) 1.1, (b) 1.3, and (c) 1.4 g/ml, and (d) Al-SiC-2000 sample after sintering sample (b) at 2000 °C.

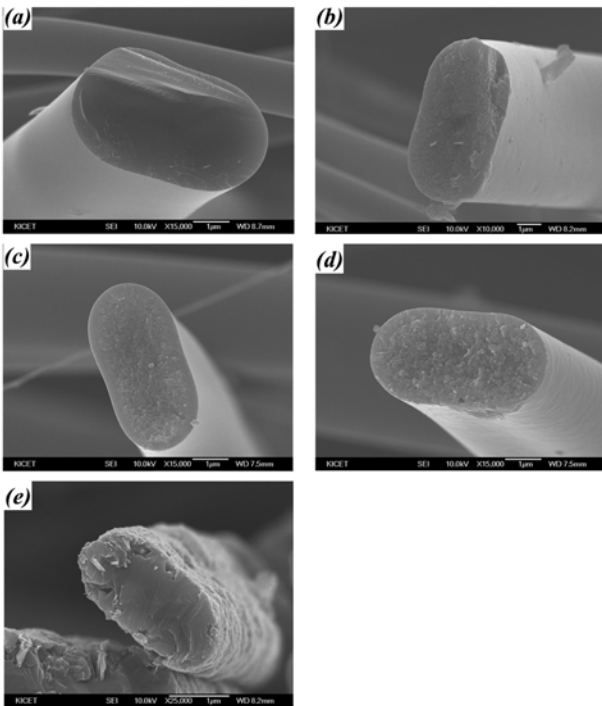


Fig. 6. FE-SEM images of the single fiber in Al-SiC samples sintered at (a) 1200 °C, (b) 1400 °C, (c) 1600 °C, (d) 1800 °C and (e) 2000 °C.

During thermal oxidation, oxygen was introduced, which combined with the pendants of the Al-PCS molecular structure and an appreciable amount of oxygen entered into the fiber after pyrolysis at 1200 °C.

Fig. 6 shows the cross sectional images of the Al-SiC fibers sintered at temperatures ranging from 1200 to 2000 °C. The overall cross section of the fiber resembled the shape of a peanut, which can be explained by the fiber thinning mechanism previously proposed [13, 17]. The cross section of the Al-SiC-1200 sample was very dense and the fracture origin could be observed in a hackled region, which resembles the typical fracture behavior of amorphous fibers. The Al-SiC-1600 sample was porous within, but relatively dense near the surface. This core-shell like structure could be caused by the compositional difference that developed during the oxidative curing. Oxygen was substituted with hydrogen and/or methyl groups from surface of the Al-PCS fiber and the relatively high oxygen content can be expected to be distributed near the surface. In the Al-SiC-1800 sample, the core-shell like microstructure became porous on the whole. At 1800 °C, SiC crystals grew to several tens of nanometers and partially necked together. In the case of the Al-SiC-2000 sample, the fibers were very dense and their grain sizes increased to up to 200 nm and consisted of step-like morphologies, which were frequently observed during the growth of (111) plane of β -SiC [29, 30].

The XRD patterns of the Al-SiC webs obtained at various sintering temperatures are shown in Fig. 7. There were no distinct peaks with the exception of broad peaks at 1200 °C. However, a main peak related to (111) of β -SiC was assigned at $2\theta = 35.6^\circ$ and minor peaks of (220) and (311) were also involved in the sample sintered at 1400 °C [31–33]. The size of the SiC crystallite in the Al-SiC-1600 sample was calculated as 20 nm by the Scherrer's equation. The weak peak at $2\theta = 33.9^\circ$ could be assigned to the (101) plane of α -SiC phase. The stacking faults and twins present in the β -crystals are thought to have caused the evolution of the peak at the same position as that shown in the high-resolution TEM images (Fig. 8) [30, 34, 35]. These stacking faults are easily formed in the {111} planes of the 3C-SiC poly-type because of the decrease in their formation energy [35]. In Al-SiC-2000 samples, we could find another weak peak at $2\theta = 26.2^\circ$, although the peak was too small to be identified. This peak could be assigned to two different phases of graphite [18, 32, 33] and α -cristobalite [34]. However, the silica phase was unstable and decomposed or vaporized at 1500 °C by the reaction $\text{SiO}(\text{g}) + 3\text{C}(\text{s}) \rightarrow \text{SiC}(\text{s}) + 2\text{CO}(\text{g})$. However, the residual carbon in the fiber segregated at the grain boundaries or junctions and transformed into graphitic phase [33, 37].

Fig. 9 shows the Raman spectra of the Al-SiC web sintered at temperatures ranging from 1200 to 2000 °C. There were two different regions in the Raman spectra;

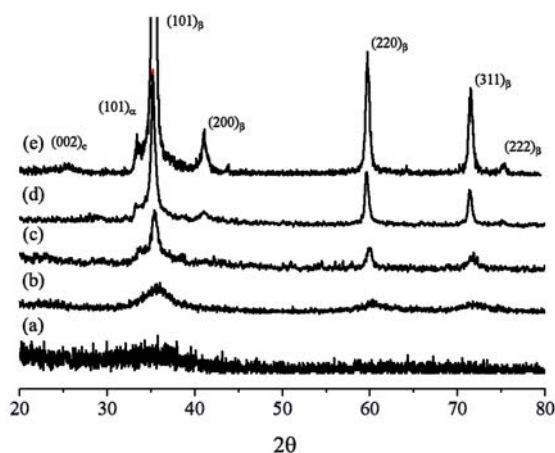


Fig. 7. XRD patterns of Al-SiC samples sintered at (a) 1200 °C, (b) 1400 °C, (c) 1600 °C, and (d) 1800 °C and (e) 2000 °C.

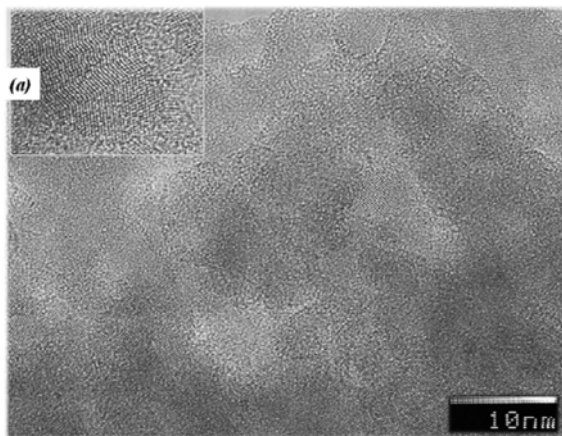


Fig. 8. HR-TEM image of the Al-SiC-1400. Inset shows the stacking fault in the crystallite.

(i) 700-1000 cm^{-1} and (ii) 1300-1700 cm^{-1} . Two sharp bands in region (i) were assigned to SiC polycrystals i.e., a transverse optic (TO) phonon at around 795 cm^{-1} and a longitudinal optic phonon (LO) at 973 cm^{-1} [36-39]. In samples sintered below 1800 °C, the bands for SiC crystals in the web were not identified. This was the case despite the presence of crystals that had grown up to tens of nanometers in size because the crystals were wrapped in the amorphous matrix phase. In the case of the fiber sintered at 2000 °C, a strong and sharp TO band with a broad shoulder was observed and the LO band was relatively weaker than the TO band and was slightly down-shifted (973 $\rightarrow$ 963 cm^{-1}). This observation can be understood from the fact that the SiC crystals were small and included many defects such as grain boundaries (GBs), stacking faults, and twins [29, 30]. The other two broad bands in region (ii) were related to the carbon phase and corresponded to the D band at 1330-1360 cm^{-1} and the G band at 1500-1600 cm^{-1} [36-40]. A hidden band marked H presented between the D and G bands in Fig. 9 could have been caused by the presence of oxygen, which was intro-

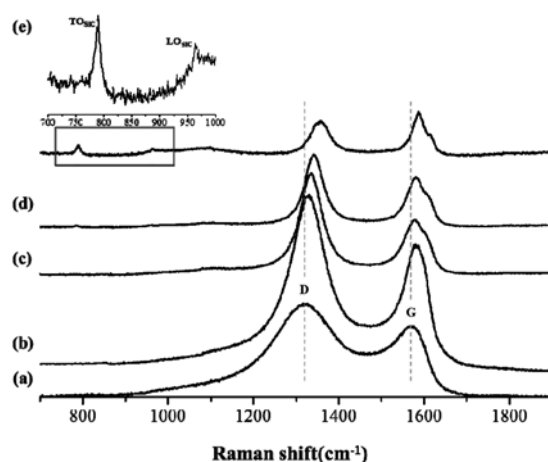


Fig. 9. Raman spectra of Al-SiC samples sintered at (a) 1200 °C, (b) 1400 °C, (c) 1600 °C, (d) 1800 °C and (e) 2000 °C.

duced as impurity atoms during the curing process [41]. This band gradually disappeared with increase in the sintering temperature because the oxygen was removed through the reaction with the residual carbon or silicon. The G band in Fig. 9(e) became stronger with increase in the sintering temperature and up-shifted in the graph. When an intense D band is observed, the presence of glassy or nanocrystalline structures of carbon can be deduced, while microcrystalline graphite leads to a strong G band [36, 39]. Sintering of the Al-SiC fiber web can be considered to include several steps. (a) First, nanocrystalline SiC forms with increasing C and O concentrations in the amorphous matrix. (b) Then, the matrix decomposes into CO (g) and SiO (g) leaving behind residual carbon. (c) Then, SiC grain growth with densification and ordering of residual carbon occurs. (d) Finally, complete densification with the segregation of residual carbon in the form of a second phase (nanocrystalline graphite) at the grain boundaries occurs [6, 42]. Thermal analysis was carried out to determine the amount of the second phase that remained after sintering. Fig. 10 shows the weight change in the Al-SiC-2000 sample under oxidative conditions at 700 °C along with the cross sectional morphology of the fiber in the inset [43, 44]. Despite the weight losses amounting to approximately 2%, the cross sectional images were identical, although the surface became clearer. This indicated that almost all of the secondary graphitic phase was distributed on the surface and the fiber was very dense inside.

The FE-SEM image along with the results of the energy dispersive X-ray analysis of the Al-SiC-2000 sample oxidized at 1200 °C for 1 hr is shown in Fig. 11. An oxidation layer of approximately 300-500 nm was formed on the fiber surface with good adhesion at the interface and this layer was limited only to the outermost surface of the fiber.

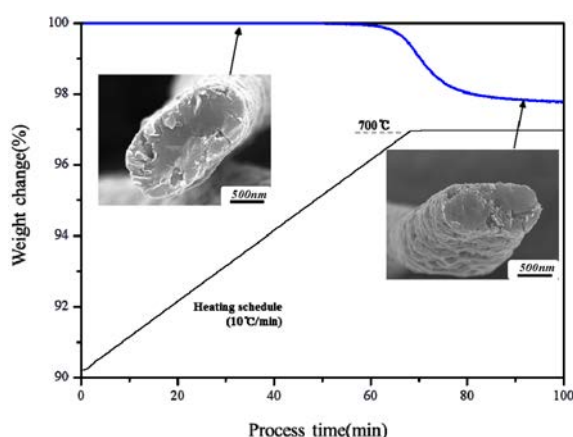


Fig. 10. Weight change along with the cross sectional morphology in the Al-SiC-2000 sample under oxidation condition at 700 °C.

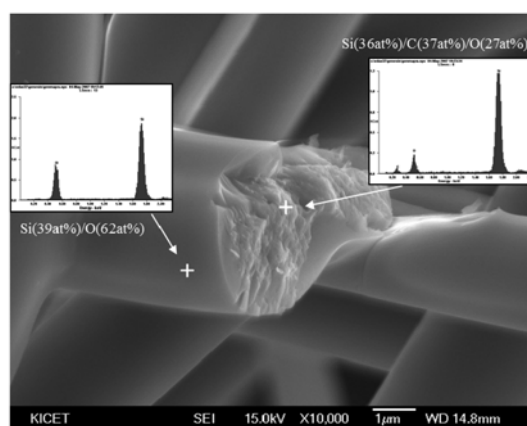


Fig. 11. FE-SEM images along with the energy dispersive X-ray analysis of the Al-SiC-2000 sample oxidized at 1200 °C for 1 hr.

Conclusions

Polycrystalline SiC fibers were successfully fabricated in the form of a non-woven web by electrospinning and sintering of Al-PCS. The fibers became dense and fully crystallized after sintering at 2000 °C; whereas, approximately 2% of the excess carbon segregated as a nanocrystalline phase on the surface and among the GBs. An oxidation layer of 300-500 nm was formed when the fibers were oxidized at 1200 °C and the layer showed good adhesion with the fiber itself. The polycrystalline SiC fibers we have fabricated are expected to be promising candidates for functional applications at high temperatures as catalytic filters, separators for thermal batteries, and for high-temperature particulate filters.

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