

***In situ* monitoring of the mechanical and electrical property changes of amorphous Si–Al–C–O fibers during heating to 1900 °C and correlation of these changes with the accompanying structural and crystallinity changes**

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Abstract¹

Although SiC fibers are promising reinforcement materials for applications in high-temperature environments, the effects of heating on the thermomechanical and thermoelectrical properties of these fibers have not been discussed and correlated with the associated microstructural changes. To bridge this gap, we herein *in situ* monitored the elastic modulus and electrical conductivity changes accompanying the conversion of single amorphous Si–Al–C–O fibers to Si–Al–C polycrystalline fibers during heating to up to 1900 °C in vacuum using an in-house-built device. The weight and tensile strength changes due to heating at 1200–1900 °C in vacuum were correlated with the concomitant fiber crystallinity and microstructural changes. The mechanical and electrical properties of the fibers were related to the porous structure formed by the decomposition of the amorphous

¹ Abbreviations. Si–Al–C–O (AM), energy-dispersive X-ray spectroscopy (EDS), field-emission scanning electron microscopy (FE-SEM), Hi-NicalonTM Type-S (HNS), NicalonTM (N), TyrannoTM-SA grade-3 (SA3), X-ray diffraction (XRD).

SiC_xO_y phase, rigid structure bonded by nanograin sintering–induced grain growth, and carbon layer formed by Si sublimation from the fiber surface.

Keywords: SiC fiber, thermal conversion, mechanical property, electrical property, microstructural analysis

1. Introduction

Since their first synthesis from an organosilicon polymer precursor by Yajima et al. [1], continuous SiC fibers have been researched as the reinforcing components of polymer-, metal-, and ceramic-matrix composites because of their low density, high tensile strength and modulus, and high thermal and oxidation resistance [2–6]. For instance, continuous SiC fiber–reinforced ceramic-matrix (SiC/SiC) composites are used in advanced aerojet engines, gas turbines, and next-generation fission/fusion reactors [7–12]. SiC fibers, classified as those of the first, second, or third generation [2–5], are industrially manufactured by the melt-spinning, curing, and pyrolysis of polycarbosilanes, which are polymers containing Si bonded to C in the backbone [13]. Compared with first- and second-generation SiC fibers, which experience notable strength degradation above 1200 °C because of the decomposition of their amorphous siliconoxycarbide (SiC_xO_y) phase into SiO and CO gases [14–16], third-generation SiC fibers exhibit lower oxygen contents, near-stoichiometric compositions (C/Si $\approx$ 1, mol/mol), higher crystallinities, and better heat resistance (>1500 °C) [6,17]. The development of third-generation SiC fibers has enabled the short-term production of dense and strong high-performance SiC/SiC composites [18–21], some of which exhibit high swelling resistance and strength retention after neutron irradiation [22]. A representative example of third-generation SiC fibers is TyrranoTM-SA, originally prepared by Ishikawa et al. in four steps (polycarbosilane synthesis from Al(acac)₃, thermal oxidation curing, pyrolysis, and sintering) and currently manufactured by Ube Industry, Japan [6]. In other words, third-generation polycrystalline

SiC fibers can be obtained by the heat treatment of the more oxygen- and carbon-rich first-generation amorphous SiC fibers. Al plays an important role in this process, promoting densification above 1800 °C. Unlike those on the tensile strength, modulus, and microstructure changes of Si–Al–C–O fibers after heat treatment, studies probing these changes during heat treatment are few [6,23–26]. Ishikawa et al. examined the thermodynamics of the amorphous → polycrystalline microstructural conversion of SiC fibers [23]. Li et al. used X-ray diffraction (XRD) and nuclear magnetic resonance spectroscopy to probe the structural changes accompanying the thermal degradation of a Si–Al–C–O precursor [25]. Suzuki et al. investigated the effects of heating to >1700 °C in Ar on the tensile strength of Si–Al–C–O fibers based on their detailed microstructural changes observed by small-angle X-ray scattering spectroscopy [26]. However, the changes in the thermomechanical and thermoelectrical properties of SiC fibers at elevated temperatures have not been discussed and correlated with the associated microstructural changes. Previously, we examined the thermomechanical and thermoelectrical properties of third-generation SiC fibers, such as Hi-NicalonTM Type-S (HNS) and TyrannoTM-SA grade-3 (SA3), at elevated temperatures (up to 1800 °C) by the *in situ* measurements of elastic modulus and electrical conductivity in vacuum [27], showing that these fibers exhibited high thermal stability up to ~1800 °C. The strength degradation of these fibers at higher temperatures was ascribed to the increase in the apparent size of β -SiC crystallites and carbonization caused by the release of Si in the annular region of the fibers. Herein, to bridge the abovementioned gap, we built on the results of our previous work and used high-temperature *in situ* measurements to monitor elastic modulus and electrical conductivity during the heating-induced conversion of first-generation amorphous Si–Al–C–O fibers to third-generation polycrystalline Si–Al–C fibers. Furthermore, the microstructure and tensile strength of the latter fibers were assessed and compared with those of three commercially available SiC fibers heat-treated at similar temperatures.

2. Material and methods

2.1 Materials

The examined Si–Al–C–O (AM) fibers, namely first-generation amorphous Si–C–O fibers supplemented with Al as a sintering additive, were produced by heating Al-containing polymetalocarbosilane fibers at 250 °C in air followed by pyrolysis at >1300 °C in nitrogen [26]. Three commercially available SiC fibers were used as references: Nicalon™ 200 series with low volume resistivity (N; first-generation Si–C–O fibers, NGS Advanced Fibers Co., Ltd., Toyama, Japa), Hi-Nicalon™ Type-S (HNS; third-generation Si–C fibers, NGS Advanced Fibers Co., Ltd., Toyama, Japan), and Tyrrano™-SA grade-3 (SA3; third-generation Si–Al–C fibers, Ube Industry, Ltd., Ube, Japan). The physical properties, chemical compositions, and structures of these fibers are listed in Table 1.

	AM	N	HNS	SA3
Diameter (μm)	11 ^[26]	14 ^[2,26]	12 ^[2]	7.5 ^[2,26]
Density (g cm⁻³)	2.48 ^[26]	2.55 ^[2,26]	2.85 ^[26]	3.02-3.10 ^[2,26,29]
Si (at%)	53.4 ^[26]	57.2 ^[26]	68.4 ^[29]	67.8 ^[26]
C (at%)	33.8 ^[26]	32.7 ^[26]	31.3 ^[29]	31.3 ^[26]
O (at%)	12.0 ^[26]	10.1 ^[26]	0.3 ^[29]	0.3 ^[26]
Al (at%)	<2 ^[26]			<2 ^[26]
C/Si (mol/mol)	1.48 ^[26]	1.34 ^[26]	1.07 ^[29]	1.08 ^[26]
Tensile strength (GPa)	2.84 ± 0.48	2.75 ± 0.44	2.62 ± 0.37	2.21 ± 0.38
Tensile modulus (GPa)	180 ± 9.7	183 ± 8.7	345 ± 5.3	399 ± 3.5
Elongation (%)	1.6	1.4	0.8	0.7
Structure	Amorphous	Amorphous	Crystalline	Crystalline

Table 1. Physical properties, chemical compositions, and structures of Si–Al–C–O (AM), Si–C–O

NicalonTM (N), Si–C Hi-NicalonTM Type-S (HNS), and Si–Al–C TyrannoTM-SA grade-3 (SA3) fibers.

2.2 High-temperature *in situ* measurements and characterization of heat-treated fibers

In situ tensile tests were performed for single fibers at 25–1900 °C using an in-house-made mechanical instrument (MecaSiC). Figure 1 shows photographs of the MecaSiC apparatus and single fibers, which were bonded to graphite grips using C34 UCAR cement (gauge length = 25 mm) and featured circular cross-sections. Prior to heating, the mean fiber diameter ($<7.5 \mu\text{m}$ for SA3, $11 \mu\text{m}$ for AM, $12 \mu\text{m}$ for HNS, and $14 \mu\text{m}$ for N) was measured at five different locations using a laser diffraction technique [28]. The fibers were heated to 25–1900 °C in vacuum ($<10^{-4}$ Pa) by passing a direct electric current, which enabled the direct *in situ* estimation of fiber conductivity. Given the small fiber diameter, pyrometer measurements were effective above 1200 °C. Below 1200 °C, the fiber temperature (T) was estimated using the following equation:

$$P_{ele} = \sigma \varepsilon F S \times (T^4 - T_R^4), \quad (1)$$

where P_{ele} is the supplied electrical power, σ is the Stefan–Boltzmann constant ($5.67 \times 10^{-8} \text{ W m}^{-2}\text{K}^{-4}$), ε is the fiber emissivity (equal to unity in our case), F is the shape factor (equal to unity in our case), S is the specimen surface area, and T_R is the ambient temperature (298 K). Further details regarding the accuracy of temperature measurements by the MecaSiC device can be found elsewhere [27,29]. The load cell was located within the vacuum chamber (Fig. 1). Tensile tests were carried out at 25–1900 °C on the same fiber using a temperature step of 50 or 100 °C, with axial strain applied via grip displacement using a compliance calibration technique. At each temperature, three successive tensile tests were performed up to 200 MPa at a strain rate of 10^{-4} s^{-1} (the influence of strain rate variation was not considered). The mean elastic modulus was determined from the slopes of the three stress–strain curves in the elastic domain (50–200 MPa). Fiber electrical resistance (R), which determined from voltage (V) and current (I), was converted into resistivity (ρ) as

$$R(\Omega) = V/I$$

$$\rho (\Omega \text{ m}) = R \times S_0/L_0, \quad (2)$$

where S_0 is the cross-sectional area of the fibers, and L_0 is the fiber length (25 mm). The uncertainty in resistivity was less than 15% and originated from that in fiber diameter, which was measured at 25 °C and assumed to remain constant at higher temperatures (i.e., radial thermal expansion was not considered). Electrical conductivity (κ) was calculated from the resistivity (ρ) as

$$\kappa (\text{S m}^{-1}) = 1/\rho, \quad (3)$$

The *in situ* elastic modulus and conductivity measurements during heating to/cooling from maximum temperatures of 1200–1900 °C were performed at a holding time of 10 min in vacuum ($<10^{-4}$ Pa). In another set of experiments, the fibers (several milligrams) were heated in an electric furnace on a high-purity alumina boat to maximum temperatures of 1200–1900 °C and kept at the desired temperature for 10 min in vacuum ($<10^{-4}$ Pa). The furnace was spontaneously cooled to ambient temperature, and the fibers were collected for characterization. The heating-induced changes in fiber weight were measured using an electronic balance (AP224X, Shimadzu, Kyoto, Japan) with an accuracy of 0.0001 g. The tensile strengths of the pristine fibers and fibers heated to maximum temperatures of 1200–1900 °C were evaluated by tensile testing of 20 single fibers with a gauge length of 25 mm, which was conducted via a mechanical instrument (EZ-LZ, 5 kN, Shimadzu, Japan) equipped with a 10 N load cell under a constant displacement rate of 0.2 mm min⁻¹ at room temperature (25 °C) in accordance with the ISO 19630:2017 standard [30]. The single fibers of the pristine and heated fibers were prepared on a stage using a stereoscope. An appropriate number of fibers was selected from fiber bundles and cut perpendicular to the fiber axis by a razor blade. The core and surface morphologies of the pristine and heated fibers were investigated by field-emission scanning electron microscopy (FE-SEM, 15 kV, 20 mA; S-4700, Hitachi, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS) and Raman spectroscopy (NRS-5100, JASCO, Tokyo, Japan) using an excitation wavelength of 532 nm, a 20× objective lens and a laser power of 1.1 mW. Raman spectra were recorded within the 700–1700 cm⁻¹ range in a back-scattering geometry using a

cooled charge-coupled-device detector with a monochromator. XRD patterns (40kV, 15 mA; MiniFlex, Rigaku, Japan) were recorded in the 2θ range of 10–90° with a scanning speed of 10 °/min and a step size of 0.02° using Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$). The intensities of the peak at 33.6° and 41.4° (2θ) were measured, and their ratio (X) was calculated using the following equation [31]:

$$X = \frac{33.6^\circ \text{ peak intensity } (2\theta)}{41.4^\circ \text{ peak intensity } (2\theta)} \quad (4)$$

A larger X value indicates a higher density of stacking faults in β -SiC [31–33]. The half-width of the (111) reflection peak (35.6 °) was also measured, and the Scherrer equation was used to calculate the apparent size of β -SiC crystallites. This apparent size of the β -SiC crystallites is likely considerably smaller than the actual grain size of the fibers because of the heavy twinning of the SiC crystals [29,34].

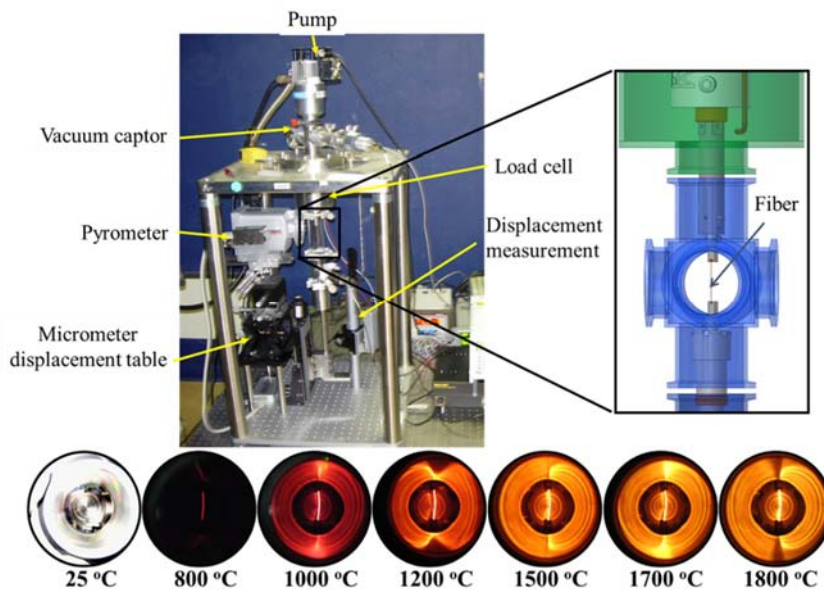


Fig. 1. MecaSiC apparatus and photographs of single fibers heated to 25–1800 °C.

3. Results

3.1 High-temperature *in situ* measurements of AM fiber modulus and conductivity

3.1.1 Measurements performed during heating to 1900 °C

Table 1 lists the average ($n = 20$) tensile properties, such as tensile strengths, moduli, and elongations

of different fibers in the EX-LZ instrument. Figure 2 presents the stress–strain curves recorded at 0–200 MPa during the *in situ* tensile tests of AM fibers, revealing that they remained linearly elastic up to 1300 °C and became inelastic above 1350 °C.

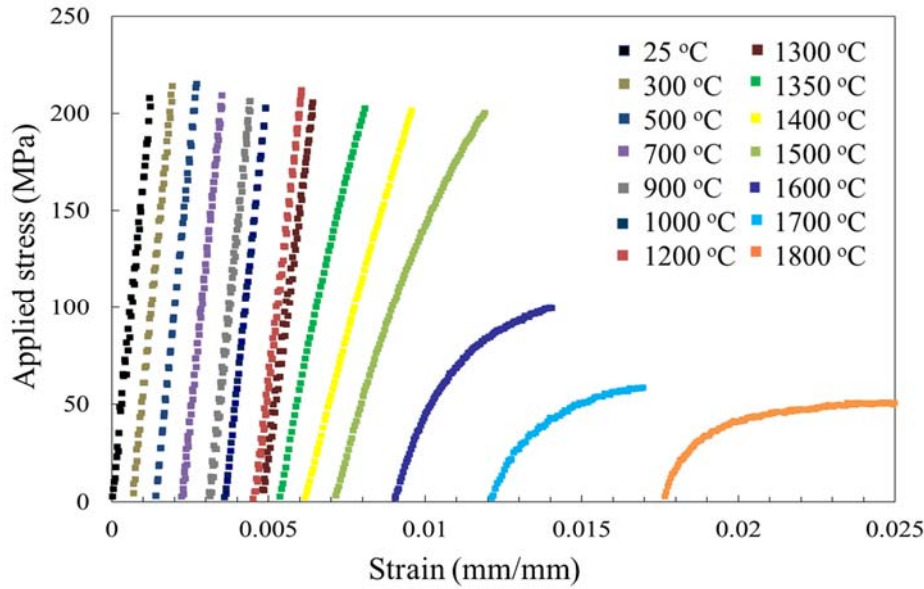


Fig. 2. Stress–strain curves of AM fibers heated from 25 to 1800 °C.

Figure 3 presents the effects of temperature on the (non)normalized elastic moduli of different SiC fibers using the MecaSiC instrument, showing that at 25 °C, AM, N, HNS, and SA3 fibers showed elastic moduli of 179 ± 10 , 186 ± 8.9 , 346 ± 5.0 , and 400 ± 3.8 GPa, respectively. There were no significant differences in elastic moduli between MecaSiC and EZ-LZ instruments. The elastic modulus of AM fibers behaved similarly to that of N fibers, i.e., started to decrease at 1200 °C and experienced a rapid decline at 1300–1400 °C. However, compared with N fibers, which experienced complete failure at ~1400 °C, AM fibers exhibited a slower elastic modulus decrease above 1400 °C and did not fail even at 1900 °C. The elastic moduli of HNS and SA3 fibers remained at $\geq 90\%$ of the corresponding room-temperature values up to 1400 °C but decreased at higher temperatures. Figure 4 presents the effects of temperature on the (non)normalized electrical conductivities of different SiC fibers using the MecaSiC instrument, showing that the conductivities of AM, N, HNS, and SA3

fibers at 25 °C equaled 9.5 ± 7.6 , 11 ± 1.1 , 54 ± 0.12 , and $290 \pm 0.99 \text{ S m}^{-1}$, respectively. The relatively wide scatter in electrical conductivity of AM fibers came from the fiber diameter, which was $9.5 \pm 1.5 \text{ }\mu\text{m}$. The conductivity of AM fibers behaved similarly to that of N fibers, slowly increasing with temperature up to 1200 °C and rapidly increasing above 1300 °C. However, compared with N fibers, which exhibited complete failure at ~1400 °C, AM fibers exhibited a dramatic increase in conductivity at 1400–1900 °C, reaching that of SA3 fiber. Specifically, the conductivity of AM fibers at 1900 °C (3280 S m^{-1}) was 347 times that at 25 °C. The normalized conductivity of third-generation (HNS and SA3) fibers was considerably smaller than that of AM fibers within the examined temperature range.

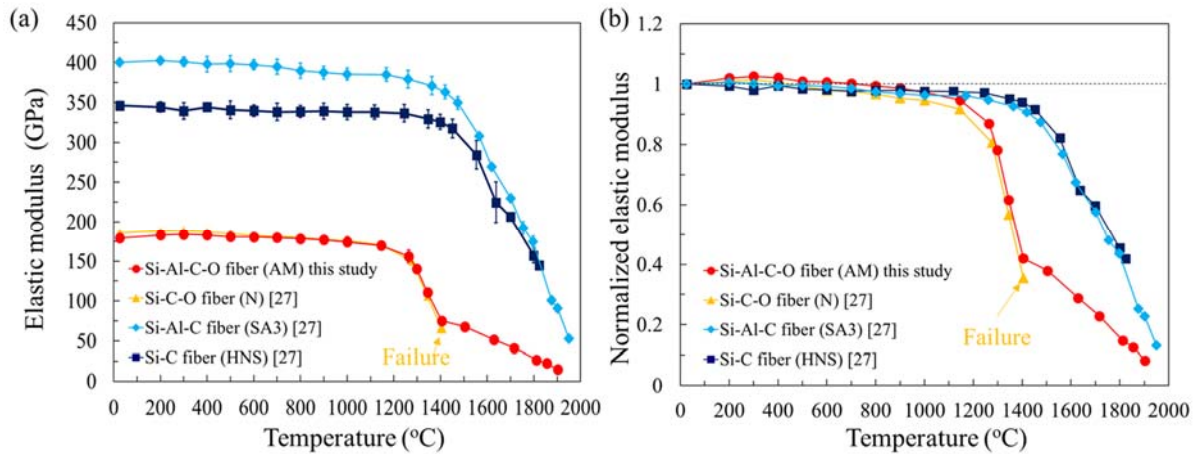


Fig. 3. (a) Nonnormalized and (b) normalized elastic moduli of different SiC fibers as functions of temperature.

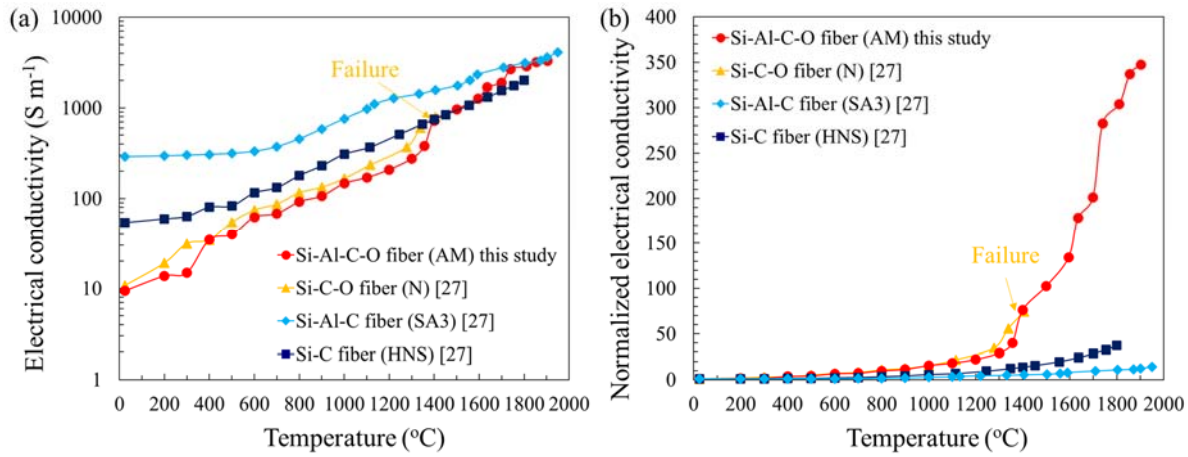


Fig. 4. (a) Nonnormalized and (b) normalized conductivities of different SiC fibers as functions of temperature.

3.1.2 Measurements performed during heating to/cooling from maximum temperatures of 1200–1900 °C

Figure 5 presents the changes in the (non)normalized elastic moduli of AM fibers during heating to/cooling from maximum temperatures of 1200–1900 °C. In the case of 1200 °C, the elastic moduli observed during cooling were almost identical to those observed during heating, which indicated reversibility. In contrast, irreversibility was observed above 1500 °C. The elastic moduli of the samples heated to and cooled from 1500 and 1700 °C were lower than those of the pristine sample (25 °C), which implied that heating/cooling resulted in mechanical property degradation. The elastic moduli of the samples heated to/cooled from 1800 and 1900 °C exceeded that of the pristine sample (25 °C), which implied mechanical property enhancement. In particular, the elastic modulus of the sample heated to/cooled from 1900 °C (288 GPa) exceeded that of the pristine sample 1.6-fold.

Figure 6 presents the changes in the (non)normalized conductivities of AM fibers during heating to/cooling from maximum temperatures of 1200–1900 °C. At 1200 °C, the conductivities obtained during cooling were almost identical to those obtained during heating, which indicated reversible behavior, as in the case of the elastic modulus. Above 1500 °C, the process became irreversible.

Heating to/cooling from 1800 and 1900 °C resulted in conductivities considerably exceeding those observed after heating to/cooling from 1500 and 1700 °C. In particular, the value obtained after heating to/cooling from 1900 °C (2245 S m^{-1}) exceeded that of the pristine sample (25 °C) 129-fold.

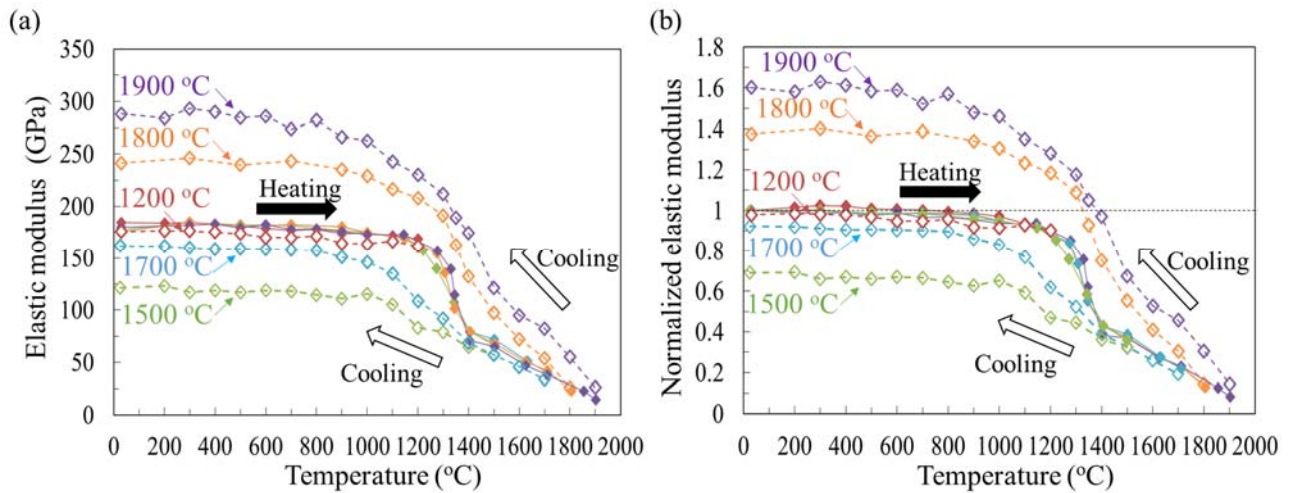


Fig. 5. (a) Nonnormalized and (b) normalized elastic moduli of AM fibers recorded during heating to (solid symbols, solid line) and cooling from (open symbols, dashed line) maximum temperatures of 1200–1900 °C.

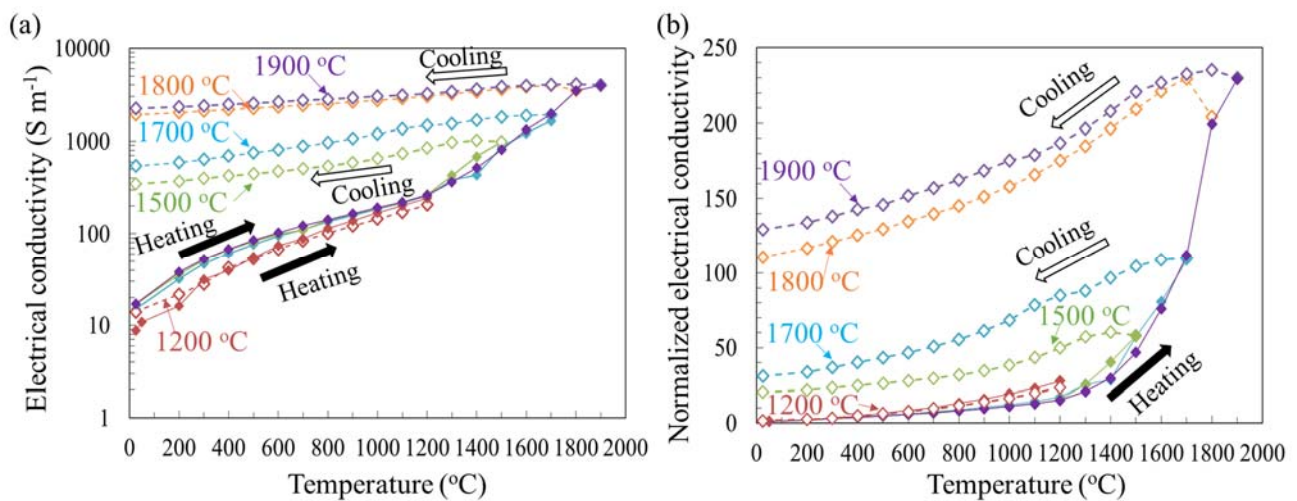


Fig. 6. (a) Nonnormalized and (b) normalized conductivities of AM fibers recorded during heating to

(solid symbols, solid line) and cooling from (open symbols, dashed line) maximum temperatures of 1200–1900 °C.

3.2 Characterization of AM fibers after heating to maximum temperatures of 1200–1900 °C

3.2.1 Weight and tensile strength changes

Figure 7 shows the weight change of AM fibers as a function of the maximum exposure temperature, revealing that the weight loss after heating to 1200 °C (1.68%) was almost identical to that observed for N fibers under the same conditions. The weight loss of AM fibers (19%) after heating to 1500 °C was considerably smaller than that observed for N fibers (26%). The weight loss of AM fibers gradually increased with temperature in the range of 1500–1700 °C and reached 34% above 1800 °C, whereas third-generation (HNS and SA3) fibers showed almost no change after heating to 1500 °C and exhibited considerable weight loss at 1800 °C (~20%). Figure 8 presents the (non)normalized tensile strengths of the different fibers as functions of the maximum exposure temperature, showing that the room-temperature (25 °C) nonnormalized values of AM, N, HNS, and SA3 fibers equaled 2.84 ± 0.48 , 2.75 ± 0.44 , 2.62 ± 0.37 , and 2.21 ± 0.38 GPa, respectively. Figure 8 also lists the previously reported (non)normalized tensile strengths of AM fibers heated in Ar for 60 min [26]. The tensile strength of AM fibers initially decreased upon heating, reaching ~37% of the room-temperature value at 1500 °C, subsequently increasing to ~63% of the room-temperature value at 1900 °C. The HNS and SA3 fibers showed high strength retention up to 1500 °C. At 1800 °C, the tensile strength of HNS fibers marginally exceeded that of SA3 fibers.

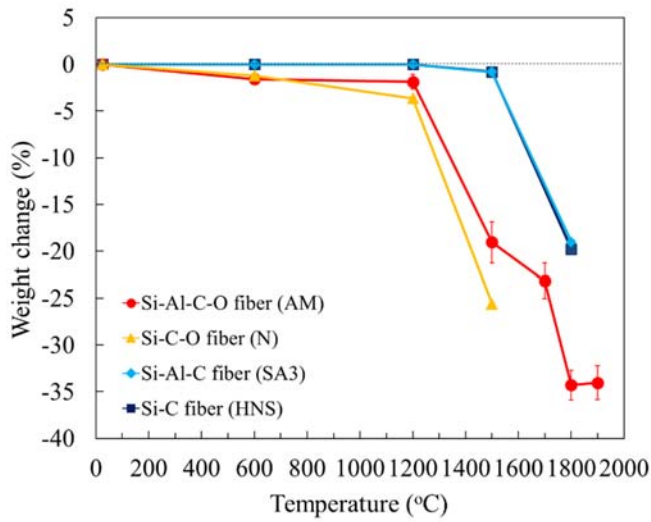


Fig. 7. Weight changes of different fibers as functions of the maximum exposure temperature.

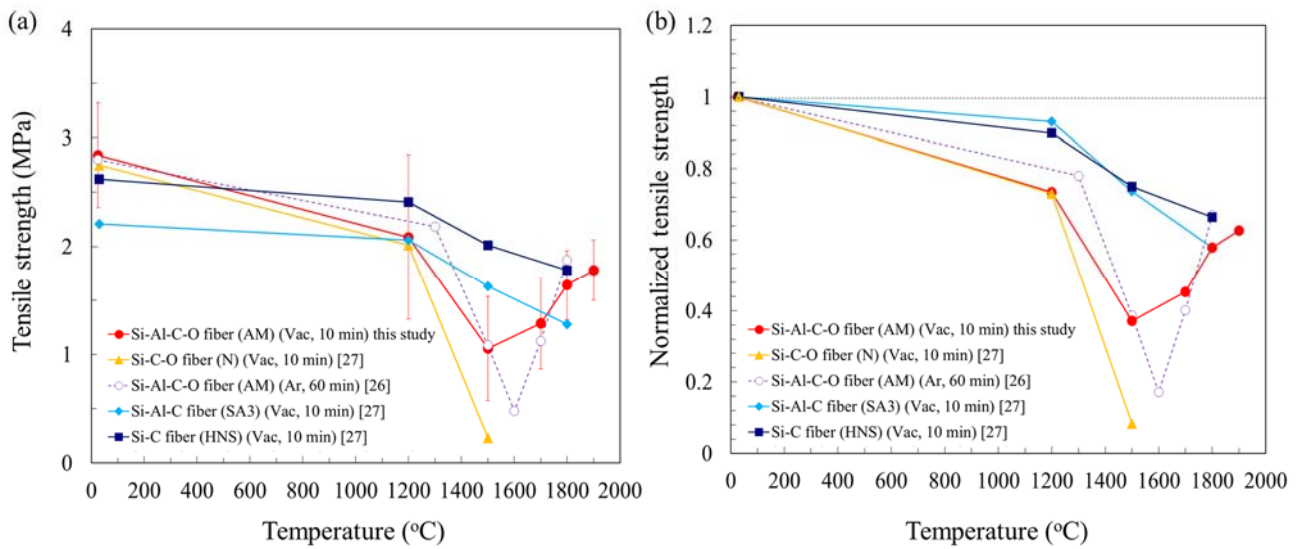


Fig. 8. (a) Nonnormalized and (b) normalized tensile strengths of AM fibers as functions of the maximum exposure temperature.

3.2.2 Crystalline phases

Figure 9 shows the XRD patterns of AM fibers before (at 25 °C) and after exposure to maximum temperatures of 1200–1900 °C: (a) overall and (b) zoom at 30–45° of 2θ . The pattern of pristine AM fibers featured broad peaks and indicated high oxygen content, thus implying a low crystallinity and

large content of the amorphous phase—like first-generation N fibers. Thus, pristine AM fibers comprised fine β -SiC nanocrystals (apparent crystallite size = 2.0 nm), free carbon, and an amorphous phase. The diffraction peaks at 35.6° , 41.4° , 60.0° , 71.8° and 75.5° were assigned to the (111), (200), (220), (311), and (222) planes of β -SiC (3C), respectively. The patterns of AM fibers heated to $>1500^\circ\text{C}$ featured stronger and sharper peaks of β -SiC with stacking faults. According to Tateyama et al., the XRD pattern analysis of β -SiC nonsymmetric reflection (prism reflection) near $2\theta=33.6^\circ$ and (200) reflection profile near $2\theta=41.4^\circ$ is closely related to stacking faults; the intensity of prism reflection increases and the (200) reflection peak becomes broader as the fault density increases [33]. The X value itself therefore was regarded as qualitatively representing the stacking fault density. The X values were calculated since 1500°C , where the peak of 33.6° (2θ) appeared. The X values decreased with an increase in the temperature of exposure, from 1.73 at 1500°C to 0.49 at 1900°C . This indicated that stacking fault density decreased with an increase in exposed temperature. There is, however, another point of view in which the prism reflection corresponds to the existence of the 2H polytype in SiC. If the 2H polytype is present, a much stronger reflection peak near $2\theta=38.3^\circ$ would be observed, but no such peak was seen in diffraction patterns of all exposed fibers (Fig. 9(b)). The patterns of AM fibers heated to $>1500^\circ\text{C}$ featured stronger and sharper peaks of β -SiC with stacking faults, composed of twins and deformation faults, which indicated a higher crystallinity [35,36]. Exposure to temperatures above 1800°C resulted in the emergence of a peak at 26.4° , which was indexed to (002) plane of carbon and became sharper with increasing temperature, which was attributed to Si sublimation from the fiber surface, as reported previously [29,37–39]. Figure 10 shows the apparent size of β -SiC (111) crystallites of different fibers as a function of the maximum exposure temperature, revealing that above 1200°C , AM and N fibers experienced considerable growth in apparent size of β -SiC crystallites. For AM fibers, the increase in the apparent size of β -SiC crystallites at 1500 – 1700°C was slow, accelerating above 1800°C . The apparent size of β -SiC crystallites in HNS and SA3 fibers stayed nearly constant

below 1500 °C, whereas exposure to higher temperatures caused a continuous increase in the case of HNS fibers and hardly affected the crystallite size of SA3 fibers. The apparent size of β -SiC crystallites in AM fibers heated to 1800 °C (37 nm) was almost identical to that in SA3 fibers.

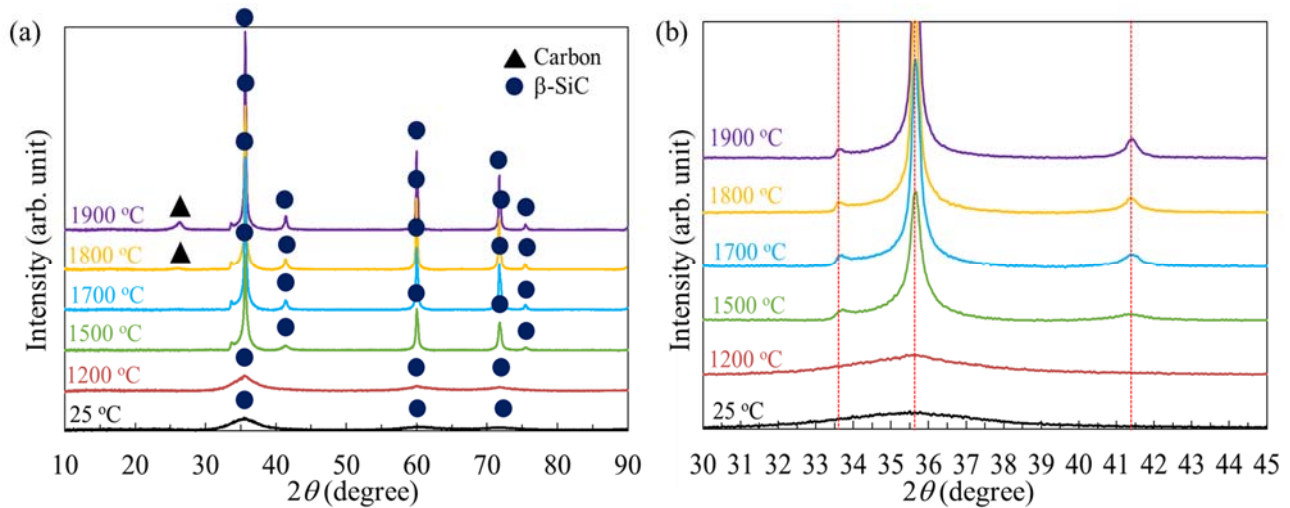


Fig. 9. X-ray diffraction patterns of the AM fibers heated to different temperatures: (a) overall and (b) zoom at 30-45° of 2θ .

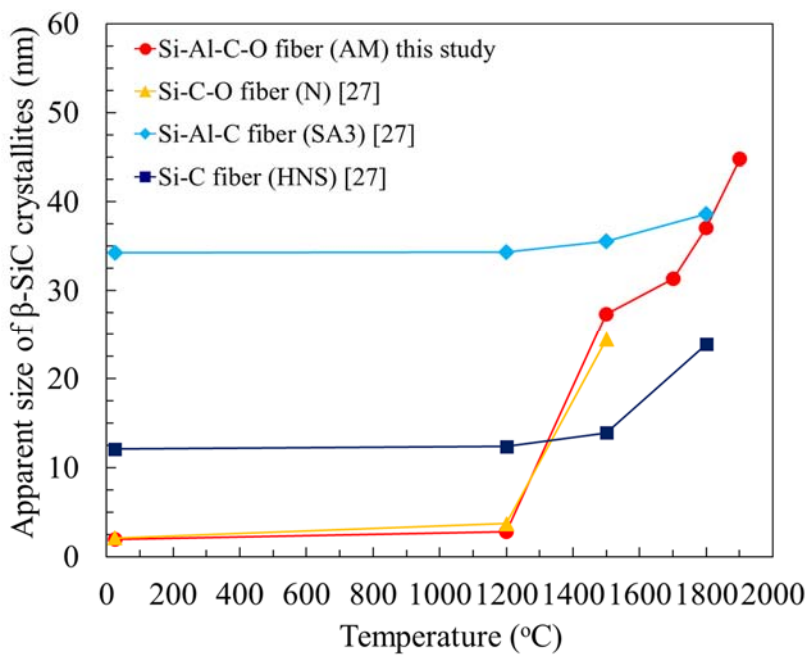


Fig. 10. Apparent size of β -SiC crystallites of different fibers as a function of the maximum exposure

temperature.

3.2.3 Microstructural changes

Figure 11 shows cross-sectional and surface FE-SEM images of (a, b) pristine AM fibers and AM fibers heated to (c, d) 1200, (e, f) 1500, (g, h) 1700, (i, j) 1800, and (k, l) 1900 °C. Figure 12 shows magnified FE-SEM images of the central and near-surface regions of AM fibers heated to (a, b) 1500, (c, d) 1700, (e, f) 1800, and (g, h) 1900 °C. Figures 11a and b present the cross-sectional and surface FE-SEM images of pristine AM fibers, showing that these fibers had smooth surfaces, which were preserved after heating to 1200 °C (Figs. 11c and d). Moreover, cross-sectional imaging revealed the absence of obvious defects, pores, and grains. However, heating to 1500 °C resulted in the development of a porous microstructure with a fine-grained core and coarse surface observed by the high-magnification FE-SEM image (Figs. 11e, 11f, 12a and 12b). Moreover, some SiC crystals were observed on the fiber surface (Fig. 11f). The coarse surface and nanopores were considered to result in decreased tensile strength. After heating to 1700 °C (Figs. 11g, 11h, 12c and 12d), the fiber surface was no longer smooth and exhibited coarsening and SiC crystals, although the internal microstructure was more tightly bonded by the fine grains. Heating to 1800 °C (Figs. 11i, 11j, 12e and 12f) resulted in further surface coarsening and the formation of a thin carbon layer (~100 nm), although the fiber interior had a porous structure despite the occurrence of nanograin growth. Heating to 1900 °C (Figs. 11k, 11l, 12g and 12h) resulted in the formation of a core-shell cross-sectional morphology. The carbon layer became thicker (~1 μm) and was uniformly distributed on the fiber surface, featuring an almost constant thickness. Figures 13a and b present the EDS elemental mapping and Raman spectra, respectively, of AM fibers heated to 1900 °C. These analyses confirmed the presence of the abovementioned 1 μm thick carbon layer and revealed the formation of SiC grains and carbon pockets in the core. The sharp Raman peaks around 1345 and 1600 cm⁻¹, observed both for the surface and core regions, were attributed to C_{sp3}-C_{sp3} (diamond type) and C_{sp2}-

C_{sp2} (graphite type) bonds. The core-region spectrum featured two additional Raman peaks around 795 and 970 cm^{-1} , which were assigned to the transverse optical (TO) and longitudinal optical (LO) phonons, respectively, corresponding to crystalline β -SiC.

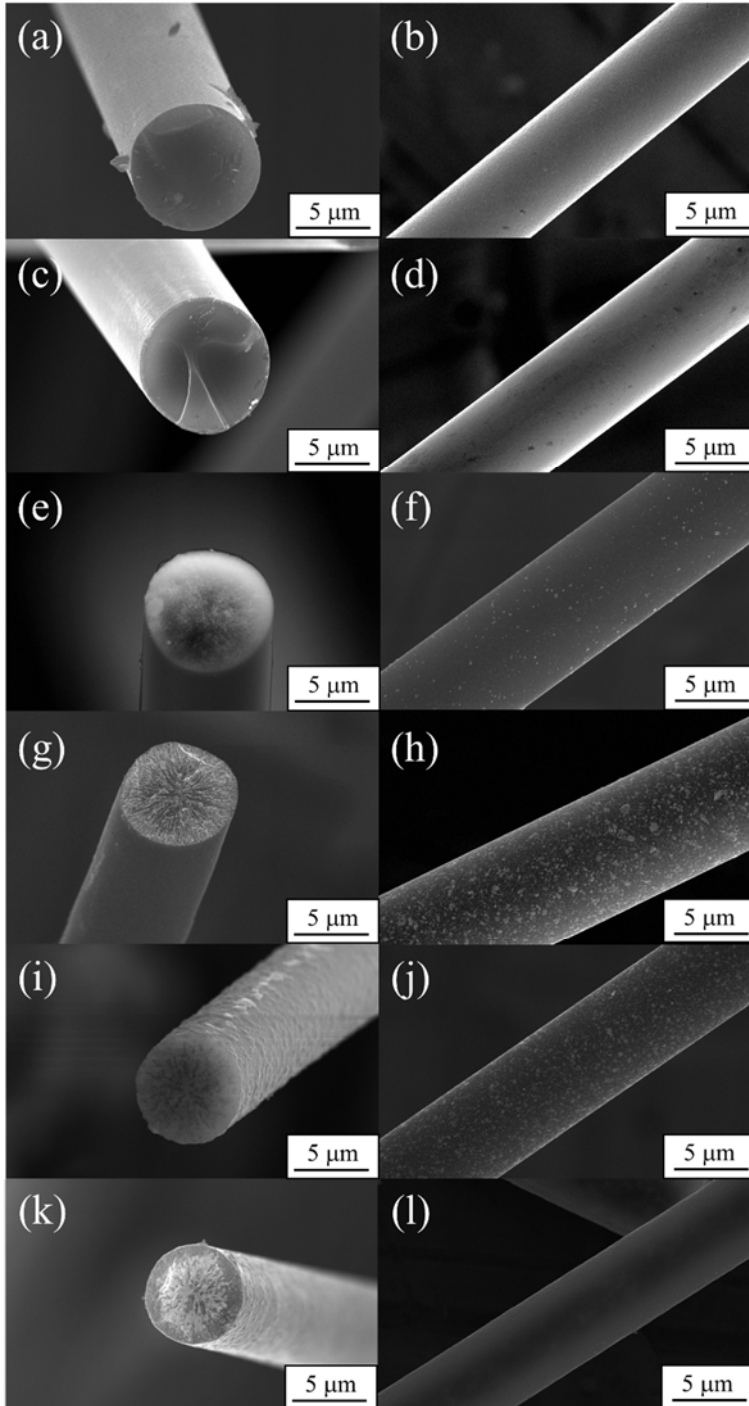


Fig. 11. Cross-sectional and surface field-emission scanning electron microscopy (FE-SEM) images of (a, b) pristine AM fibers and AM fibers heated to (c, d) 1200, (e, f) 1500, (g, h) 1700, (i, j) 1800,

and (k, l) 1900 °C.

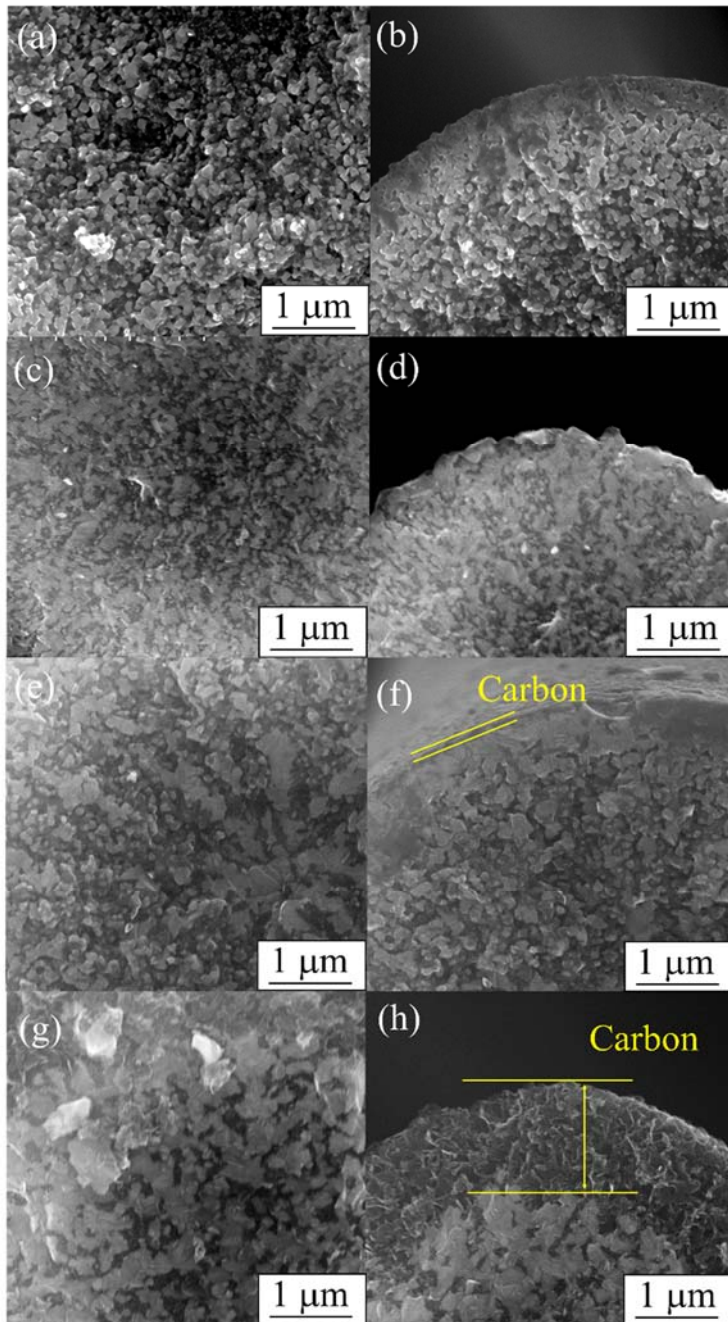


Fig. 12. Magnified FE-SEM images of the central and near-surface regions of AM fibers heated to (a, b) 1500, (c, d) 1700, (e, f) 1800, and (g, h) 1900 °C.

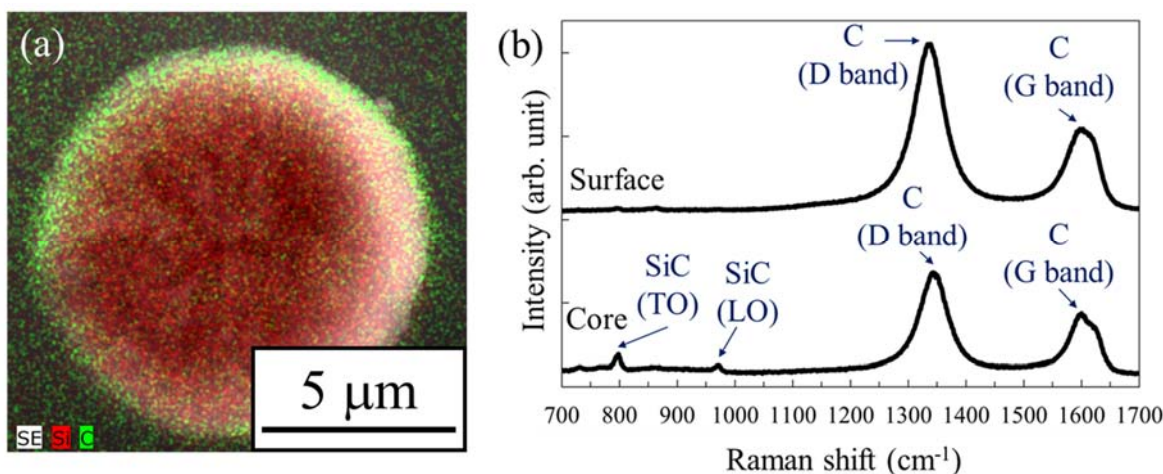


Fig. 13. (a) Energy-dispersive X-ray spectroscopy (EDS) elemental mapping and (b) Raman spectra of AM fibers heated to 1900 °C.

4. Discussion

The currently available SiC fibers (first, second, and third generations) have different heat resistances, which depend on chemical and structural properties such as oxygen content, crystallinity, and chemical composition, as described above. The low heat resistance of the first-generation SiC fibers is mainly due to the presence of the thermally unstable amorphous oxygen-rich SiC_xO_y phase [14–16]. The degradation of this phase is accompanied by the formation of numerous defects and release of gaseous products, thus considerably decreasing fiber mechanical strength and even causing complete failure below 1500 °C, as exemplified by the failure of N fibers at ~1400 °C (Figs. 3 and 4). Ishikawa et al. [6] solved the problem of the SiC_xO_y phase by heating polyaluminocarbosilane-derived amorphous Si–Al–C–O fibers to >1800 °C to obtain polycrystalline Si–Al–C fibers. The degradation of the amorphous SiC_xO_y phase in the former fibers afforded crystalline β -SiC, which was sintered and densified in the presence of a small amount of Al. The obtained Si–Al–C fibers had high heat resistance and retained their strength upon heating to 2200 °C in an inert atmosphere. However, the degradation of SiC_xO_y is difficult to control because of its sensitivity to several factors, including the oxygen and Al content of Si–Al–C–O fibers, heating rate, temperature, atmosphere,

and total pressure in the furnace [6,23,24,40,41]. Herein, we examined the changes in the thermomechanical and thermoelectrical properties due to the heating-induced conversion of first-generation AM fibers to third-generation fibers. The N fibers became porous and experienced thermomechanical and thermoelectrical property degradation above 1200 °C because of the decomposition of the SiC_xO_y phase, failing at ~1400 °C because of structural instability. The Al-doped AM fibers showed thermomechanical and thermoelectrical property degradation similar to that observed for N fibers but did not fail even at 1900 °C. In particular, a considerable decrease in elastic modulus and increase in conductivity were observed above 1300 °C; above 1500 °C the decrease in elastic modulus slowed down, whereas the increase in conductivity accelerated. This behavior was attributed to the degradation of the SiO_xC_y phase and/or sintering of β -SiC grains. The weight change of N fibers (Fig. 7) suggested that their degradation started above 1200 °C and was almost complete at 1500 °C. This conclusion was confirmed by the effect of oxygen content on the weight change of first-generation (Si–C–O) fibers reported previously [40,41]. However, the weight loss of AM fibers (19.0%) at 1500 °C was smaller than that of N fibers (25.6%), as shown in Fig. 7. Thus, the addition of Al may have had a stabilization effect, minimally delaying the degradation of the SiC_xO_y phase. Quyang et al. used a thermogravimeter mass spectrometer analysis to demonstrate that the thermal degradation of the SiC_xO_y phase in Si–Al–C–O fibers could occur above 1500 °C and be accompanied by a minimal weight loss [40]. This behavior was also reported for Zr-containing Si–C–O fibers [26,42]. Consequently, the stabilization effect of Al was expected to prevent a significant decrease in the tensile strength of AM fibers after heating to 1500 °C (Fig. 8). Heating to 1700 °C may result in the complete termination of the SiC_xO_y phase degradation and trigger the initial stage of nano-SiC sintering in the thus produced porous structure (Figs. 11g, 11h, 12c, and 12d). Tensile strength after heating at 1700 °C was minimally higher than that after heating at 1500 °C despite the lower weight loss (Fig. 7) and larger crystallite size (Fig. 10) in the former case. This finding was supported by the results of heating and cooling experiments (Fig. 5). The recovery of elastic modulus

during cooling after heating at 1700 °C exceeded that observed during cooling after heating at 1500 °C. Above 1800 °C, the sintering of nano-SiC was accelerated, and the elastic moduli observed during cooling exceeded those observed during heating (Fig. 5). As a result, AM fibers heated at 1900 °C exhibited good mechanical properties (tensile strength = 1.78 ± 0.28 GPa, elastic modulus = 288 ± 21 GPa). In particular, the normalized tensile strength of AM fibers after heating at >1800 °C was similar to that of third-generation (HNS and SA3) fibers (Fig. 8). Microstructural analysis indicated that the sintering of nano-SiC at the fiber core became more pronounced above 1800 °C because of the significant grain growth of β -SiC under these conditions (Figs. 12e and g). SiC is a promising high-power semiconductor because of its wide band gap and high electron mobility [43,44]. The conductivity of SiC fibers negligibly depends on the electron transfer inside the SiC grains but may be affected by the amorphous phase within the fibers, grain boundaries, and/or free carbon networks. In fact, the conductivities observed during heating to 1200 °C almost fully matched those observed upon subsequent cooling, whereas above 1500 °C, i.e., in the region corresponding to the degradation of the SiC_xO_y phase and large weight loss, the conductivities in the cooling branch considerably exceeded those in the heating branch (Fig. 6). The significant difference between conductivities observed after heating at 1500, 1700, 1800, and 1900 °C was rationalized in terms of microstructure and crystallinity changes. Heating at 1500 and 1700 °C caused the decomposition of the amorphous SiC_xO_y phase, a considerable weight loss, and an increase in the apparent size of β -SiC crystallites, resulting in a porous structure. Heating at 1800 and 1900 °C resulted in sintering, which promoted densification, increased crystallinity, and triggered a transition from the porous structure of nano-SiC to a rigid structure due to the concomitant growth of β -SiC crystallites. This transition may be the reason for the gradual increase in conductivity during heating and marginal increase in conductivity during cooling after heating at >1800 °C (Fig. 6). In addition, heating at 1900 °C resulted in the surface degradation of AM fibers (Figs. 11k and 12h). The microstructure at the fiber core was unaffected, and EDS and Raman spectroscopy revealed that the annular region

was composed of an approximately 1 μm -thick carbon layer (Fig. 13). The formation of this layer may explain the marginal increase in conductivity during cooling after heating at 1900 $^{\circ}\text{C}$, as carbon is more conductive than SiC. XRD, SEM, EDS, and Raman analyses confirmed the formation of the carbon layer in the annular region after heating at 1800 and 1900 $^{\circ}\text{C}$. These findings indicated the occurrence of Si volatilization, which resulted in an additional large weight loss ($\sim 15\%$, Fig. 7). Heating was carried out at a pressure of $<10^{-4}$ Pa, which was lower than the vapor pressure of Si above 1400 $^{\circ}\text{C}$ [45]. In fact, some SiC crystals, formed by the reaction of excess carbon on the surface with SiO gas, were observed after heating at 1500 and 1700 $^{\circ}\text{C}$ (Figs. 11f and h). The carbon layer was not detected by EDS in the annular region after heating at 1500 and 1700 $^{\circ}\text{C}$, probably because of the short holding time of 10 min. The strength retention of AM fibers after 10 min heating in vacuum was considerably limited in relation to that after 1 h heating at >1800 $^{\circ}\text{C}$ in Ar [26], which may be due to the formation of carbon in the annular region (largely caused by the volatilization of Si from the fiber surface). The diameter of AM fibers after heating at 1900 $^{\circ}\text{C}$ was 8.1 ± 0.46 μm . Based on FE-SEM imaging results (Figs. 11k and 12h), the cross-sectional area ratio of SiC to C was 69:31, and the theoretical elastic modulus corresponding to this composition ($0.69 \times$ modulus of SiC for SA3 (~ 400 GPa [27]) + $0.31 \times$ modulus of C for carbon (graphene) fibers (~ 23 GPa[39]) = 283 GPa) was close to the experimental value of 288 GPa. However, the elastic modulus of AM fibers after heating at 1800 $^{\circ}\text{C}$ (241 GPa) was significantly smaller than the theoretical elastic modulus calculated using the cross-sectional area ratio of SiC to C (98:2). This may be because the fiber interior had a porous structure despite the occurrence of nanograin growth, as shown in Figs. 12e and f. Thus, the high elastic modulus (approximately 400 GPa) corresponding to dense and crystalline SiC like SA3 was not fully achieved. SiC fibers have been extensively characterized to analyze the effects of temperature, holding time, atmosphere, and other factors on composition, microstructure, and other properties [46–50]. Vacuum is considered a special condition for testing the changes in SiC fiber properties [37–40,50]. Zhang et al. synthesized carbon (graphene) fibers by heating SiC fibers

in vacuum at 1800 °C for 5 h or 2000 °C for 1 h [39], showing that this transformation occurs in the direction from the fiber surface to the core. Zhang et al. also reported that heating in vacuum caused the desorption of Si from the SiC fiber surface and carbon formation [50], claiming that pure graphene fibers can be produced by increasing the heating temperature and holding time.

Although the heating temperature >1900 °C or holding time >10 min were not mentioned in this study, it would be important to investigate a type and thickness of carbon layer on the surface of SiC fibers quantitatively as future work. In addition, it would be key to investigate the effects of stacking faults in β -SiC (3C) on the mechanical and electrical properties of SiC fibers during conversion from amorphous to polycrystalline fibers for optimal heat treatment conditions. The findings of this study are valuable for the future high-quality design and wide range application of SiC/SiC and provide valuable insights into the strength and microstructure of first generation SiC fibers with the addition of Al as a sintering additive at elevated temperatures.

5. Conclusions

The thermal conversion of amorphous Si–Al–C–O (AM) fibers to Si–Al–C polycrystalline fibers was evaluated using a single tensile test device (MecaSiC) in the temperature range of 25–1900 °C under vacuum ($<10^{-4}$ Pa). The changes in elastic modulus and conductivity during heating to/cooling from temperatures of up to 1900 °C for 10 min in vacuum were monitored using *in situ* measurements to investigate the thermomechanical and thermoelectrical properties of AM fibers. In addition, the thermal conversion of AM fibers was discussed based on weight and tensile strength changes and their correlation with fiber crystallinity and microstructural changes after heating at 1200–1900 °C for 10 min in vacuum. The key findings of this study are as follows.

- The thermomechanical and thermoelectrical property degradation of the Al-containing AM fibers resembled that observed for N fibers. However, the former fibers did not fail even at 1900 °C,

whereas the latter fibers failed above ~ 1400 °C.

- The Al in AM fibers delayed the thermal degradation of the SiC_xO_y phase and the associated large weight loss (19%), which was smaller than that observed for N fibers (25.6%) after heating at 1500 °C, thus helping avoid significant strength degradation.
- Heating at 1700 °C resulted in the complete termination of the SiC_xO_y phase degradation and the onset of nano-SiC sintering in the thus produced porous structure.
- Heating at 1800 and 1900 °C induced sintering and resulted in densification and a crystallinity increase, triggering a transition from the porous nano-SiC structure to a rigid structure due to the increase in the apparent size of β -SiC crystallites. Consequently, the normalized tensile strength of AM heated to >1800 °C was similar to that of third-generation SiC fibers, such as HNS and SA3. The surface degradation of AM fibers, which featured a surface carbon layer with a thickness of ~ 1 μm , was observed upon heating at 1900 °C.

The findings of this study are valuable for the future of high-quality design and the wide range of applications of SiC/SiC and provide valuable insights into the strength and microstructure of first generation SiC fibers with the addition of Al as a sintering additive at elevated temperatures.

CRedit authorship contribution statement

Kazuya Shimoda: Conceptualization, Resources, Methodology, Investigation, Formal analysis, Funding acquisition, Writing – original draft, review & editing. **Christian Colin:** Conceptualization, Resources, Methodology, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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