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# Effects of residual radicals on compositional and structural stability of silicon nitride fibers

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## A R T I C L E   I N F O

## A B S T R A C T

In this study, amorphous silicon nitride fibers were prepared through the nitridation of cured polycarbosilane fibers. It was observed that their composition and properties can be controlled by adjusting the flow of $NH_3$ during the nitridation process. Based on their compositional and structural stability, the samples could be divided into two classes: stable fibers and unstable fibers. As indicated by the electron spin resonance spectra, the amount of the residual free radicals in the unstable fibers was significantly higher than that in the stable fibers. Because of the reactions of the radicals with the moisture in the air, the oxygen content of the unstable fibers increased day by day until the residual radicals were exhausted. Thus, to develop silicon nitride fibers with both low oxygen content and low carbon content, the amount of $NH_3$ used should be optimized to eliminate the free radicals. These results suggest that it is possible to tailor the nitridation conditions for preparing high-purity silicon nitride materials so that they exhibit desirable properties, such as compositional and structural stability, good mechanical properties, and high electrical resistivity.

## 1. Introduction

Silicon nitride materials have been studied intensively for several decades because of their desirable structural properties, such as high tolerance to mechanical stress, good thermal stability, and excellent oxidation resistance. Owing to their low dielectric constant and high electrical resistivity, silicon nitride ceramics are considered a superior wave-transparent and electrically insulating material that can be used in high-temperature applications [1,2]. Several types of silicon nitride fibers have been developed for use as reinforcements for ceramic-matrix composites. These include the silicon nitride fibers developed by Tonen Corp. [3], and the Si-C-N fibers developed by Domaine University [4]. The preparation of silicon nitride fibers from polycarbosilane (PCS) had been reported by K. Okamura et al. [5] at about thirty years ago. Following the same route, Sinber® fibers developed by Japan Atomic Energy Research Institute [6] as well as the Si-C-N fibers [7] and Si-N-O fibers [8] reported by our group have been developed. However, few of these fibers meet the requirements for high-temperature wave-transparent applications. One the one hand, Sinber® and other Si-C-N fibers cannot be employed in wave-transparent applications because of their relatively high carbon content. On the other hand, Si-N-O fibers cannot be used in high-temperature environments, since the oxygen in the fibers adversely affects their thermal resistance [6,9]. Therefore, it is essential to develop silicon nitride fibers that have low carbon and oxygen contents and are thus suitable for use in harsh environments.

However, the nitride products obtained from polycarbosilane usually have a high oxygen content, especially those with a low carbon content. Kamimura et al. [6] reported that, when PCS fibers were heated to 1000 °C in $NH_3$, the resulting fibers contained oxygen in a large amount. Shi et al. [10] reported that the oxygen content of mesoporous silicon nitride fibers obtained through the nitridation of an oxygen-free PCS precursor was 11 wt%. Li et al. [11] prepared silicon nitride fibers with an oxygen content of more than 16 wt% by the nitridation of γ-ray-cured PCS fibers.

In this study, to elucidate the cause of the high oxygen content, which was not known previously, we prepared five types of silicon nitride fibers using different $NH_3$ flows. For the first time, the presence of free radicals in nitride fibers was confirmed. Further, it was shown that they are responsible for the high oxygen content of the fibers. Finally, a probable mechanism to explain the generation and conversion of the free radicals was proposed.

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## 2. Materials and methods

### 2.1. Preparation of silicon nitride fibers

The starting material, PCS, was synthesized by the decomposition and condensation of polydimethylsilane. The obtained PCS was then melt-spun into green fibers, which were cross-linked through curing in He gas atmosphere by 2 MeV electron beams (EB) from an electron accelerator (Beam current: 2–5 mA; Time: 5–10 h). The dose was 15 MGy and the temperature was kept below 100 °C. After irradiation, the fibers were annealed in situ for a short period at 400 °C. The annealing treatment was a very important step because it could help diminish the active residual free radicals trapped in the fibers. A lot of free radicals remain in cured polycarbosilane fibers after electron irradiation in inert atmosphere and react with oxygen and moisture in air easily, introducing much oxygen in fibers [12]. Therefore, to eliminate the active species through heat treatment contributes to oxygen control of the raw material. In our research, EB-cured PCS fibers were contained oxygen of only 1.5 wt%.

The EB-cured PCS fibers were a strand of 1000 individual filaments with an average diameter of 12.5 μm. Next, the irradiated fibers were placed in a graphite furnace and ammoniated in a flow of $NH_3$ at temperatures of 400–1000 °C at 1–2 °C min$^{-1}$. This was followed by heating to 1300 °C in a $N_2$ atmosphere for densification. Five fiber samples were prepared for different $NH_3$ flows. The ammonia and nitrogen gases used were obtained commercially and had a purity of 99.9999%.

### 2.2. Characterization

The tensile strength and tensile modulus of the fibers were measured using an Instron-type test machine (Micro-350, Testometrix), with a gauge length of 25 mm and a crosshead speed of 5 mm min$^{-1}$. The average tensile strength was obtained from the measured results of 24 filaments. The electrical resistivity, ρ (Ω cm), was measured using a high resistance meter (Model 6517B, Keithley). Silver paste was put on the fiber bundle for two point contacts and then the resistance between the two silver electrodes which were 25 mm apart in distance was measured. The electrical resistivity was calculated with the following equation [13]: ρ=RT*10$^{-4}$/dl, where R is the resistance (Ω), d is the density of the fiber (g cm$^{-3}$) measured by the Archimedes method using ethanol, l is the length of the electrodes (mm), and T is the tex (weight per yarn length) of the fiber bundle (g km$^{-1}$). The $^{29}$Si nuclear magnetic resonance with cross polarization-magic angle spinning ($^{29}$Si CP/MAS-NMR) spectrum was measured on a Bruker AV 300 spectrometer. The spinning rate was 5 kHz and the chemical shifts were reported in parts per million (p.p.m.) relative to tetramethylsilane (TMS). Analysis of the phase composition of the silicon nitride fibers was performed by X-ray diffraction (XRD, D8 Advance, Bruker), using Cu Kα irradiation (λ = 1.54 Å) at a scanning rate of 2θ = 0.15° per step. Fourier transform infrared spectra (FTIR, Nicolet Avatar 360, America) were acquired in the scanning range of 400–4000 cm$^{-1}$. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher) spectra were recorded using Al Kα as the excitation source to detect the surface compositions and chemical bonding states in a few atomic layers. The fibers were cleaned prior to XPS analysis by argon ion bombardment.

Quantitative analysis of nitrogen and oxygen was carried out using a N/O analyzer (EMGA-820, Horiba), and carbon was measured using a C/S analyzer (EMIA-320V2, Horiba). Hydrogen was detected by an element analyzer (vario EL cube, Elementar). Pore size distribution of as-prepared fibers was performed by Barrett-Joyner-Halenda (BJH) model, which is based on Kelvin equation, using an automated volumetric sorption analyzer (autosorb-iQ2-

MP, Quantachrome). The microstructure was observed by scanning electron microscopy (SEM, S-4800, Hitachi).

The electron spin resonance (ESR) spectra of the fiber samples were measured using a Bruker E 500 system at a frequency of 9.858 GHz. To prevent radical consumption, the as-prepared fibers were collected as soon as the furnace had cooled to room temperature and were packed in an atmosphere of a shielding gas ($N_2$) in ESR quartz tubes for storage until the tests.

## 3. Results

### 3.1. Characterization of as-prepared fibers

In this work, in order to investigate the effect of the nitridation conditions on the properties of silicon nitride fibers, we varied the $NH_3$ flow rate during the nitridation process. As shown in Table 1, fibers with a tensile strength of 790 MPa and Young's modulus of 118 GPa (labeled as SN-A) were obtained for an $NH_3$ flow rate of 8 L min$^{-1}$. As the $NH_3$ flow rate was decreased, the electrical resistivity, tensile strength, and elastic modulus of the fibers increased. Moreover, the fibers became darker, turning from colorless to black.

Further, the prepared fibers exhibited markedly higher resistivities as compared to those of SiC fibers ($10^{-1}$ to $10^1$ Ω cm) fabricated in a flow of pure $N_2$ using the same precursor [7]. This was because the nitridation process significantly reduces the carbon content of the fibers as well as the amount of free carbon present within them. It has been reported that the electrical resistivity of silicon nitride fibers is affected by the amount and texture of the free carbon in the fibers through a percolation effect [14]. As shown in Table 2, the carbon content indeed decreased with a decrease in the $NH_3$ flow rate. Thus, it can be concluded that the mechanical and electrical properties of the fibers were related to their carbon content and so was their color.

The $^{29}$Si NMR spectra of the various fiber samples are shown in Fig. 1a. All the fibers exhibit the characteristic peak of $SiN_4$ centered at −45 ppm [15]; however, the peak related to the $SiC_4$ phase is not observed at −15 ppm. In addition, the peaks related to $Si_2N_2O$ and $SiO_2$ [7] are not observed at −63 and −105 ppm in the case of the SN-C, SN-D, and SN-E fibers. Meanwhile, small peaks confirm the existence of silicon oxide phases in the case of samples SN-A and SN-B. Based on the above results, it can be concluded that all the fibers were primarily composed of silicon nitride, with tiny amounts of silicon oxide phases being present in the case of SN-A and SN-B.

The crystalline structures of the fibers were investigated by XRD analysis, as shown in Fig. 1b. No distinct peaks are present in any of the spectra, confirming that all the fibers were amorphous.

Fig. 2 shows the FT-IR spectra of the fabricated silicon nitride fibers. The small peaks appearing at 1400 and 1600 cm$^{-1}$ can be assigned to trace C—N and C=N bonds [16,17]. Kaufman et al. suggested that these bands correspond to the D and G bonds, respectively, of pure amorphous carbon, which become infrared-active because of the incorporation of nitrogen atoms into the carbon network [18]. Meanwhile, a very weak CN band can be observed at approximately 2130 cm$^{-1}$; this is probably related to the nitrile group or to the sp$^2$-type carbon that binds to nitrogen in different chemical environments. Thus, the FT-IR analysis showed that the signals of the carbon-related bonds increased in intensity with an increase in the bulk C content. The band observed at wavenumbers of 3500–3000 cm$^{-1}$ in the case of the SN-A and SN-B fibers can be attributed to the N—H and O—H vibrations. This band is also observed in the spectrum of the SN-C fibers but is very weak. In addition, an Si—N—Si asymmetric stretching band is observed at 900 cm$^{-1}$ [19,20] for all the samples.