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Preparation and properties of continuous Al-containing silicon carbide fibers①

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Abstract: Continuous SiC(OAl) fibers, named KD-A fibers, were prepared by the melt-spinning of ceramic precursor polyaluminocarbosilane, air-curing, and pyrolizing at 1 300 ℃. These fibers contained small amount of aluminum and 7%－9% oxygen. The KD-A fibers were converted into sintered SiC(Al) fibers, named KD-SA, by sintering at 1 800 ℃. The fibers were characterized by chemical analysis, tensile strength test, SEM and XRD. The tensile strength, elastic modulus and diameter of the KD-A fibers are 2.6 GPa, 210 GPa, 12－14 μm, respectively. The KD-A fibers have higher thermal stability, more excellent oxidation resistance than the Nicalon fibers. The properties of the KD-A fibers have reached the level of Hi-Nicalon fibers. The tensile strength, elastic modulus and diameter of the KD-A fibers are 2.1 GPa, 405 GPa, 10－12 μm, respectively. The KD-SA fibers with nearly stoichiometric component have stable performance at high temperature, and better creep resistance than the Tyranno SA fibers.

Key words: continuous silicon carbide fibers; polyaluminocarbosilane; polymer pyrolysis
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1 INTRODUCTION

Among inorganic fibers, SiC fibers have special advantage of oxidation resistance at high temperature over carbon fibers. Applications envisaged are in gas turbines, both aeronautical and ground based, heat exchangers, first containment walls for fusion reactors[1-4]. However, the mechanical properties of the common SiC fibers, especially Nicalon, are degraded above 1 200 ℃ due to the crystal coarseness and the release of gases (SiO, CO). This limits SiC fibers applications in the fields of ceramic matrix composite (CMC) and metal matrix composite (MMC)[1, 5]. In order to overcome the drawbacks of the Nicalon fibers, the Hi-Nicalon, Hi-Nicalon S fibers produced by Nippon Carbon have a low oxygen content and improved thermal resistance at high temperature (1 400 ℃)[6, 7]. More recently, Ube Industries had developed a super high temperature-resistant Tyranno SA fiber made from a polyaluminocarbosilane (PACS), which was produced by introducing hetero-element aluminum into polycarbosilane (PCS). The Tyranno SA fibers showed excellent heat-resistance (up to 2 000 ℃), high strength (over 2.5 GPa) and modulus (over 300 GPa), superior creep resistance, and prominent alkali resistance[8]. Up to date, these fibers exhibit the best performance in all SiC-based ceramic fibers. In this work, super high temperature-resistant continuous SiC fibers are prepared by the method of polymer pyrolysis in our laboratory. The properties of the continuous SiC fibers are described, and compared with the Nicalon, Hi-Nicalon and Tyranno SA fibers.

2 EXPERIMENTAL

Polysilacarbosilane (PSCS) was converted from polydimethylsilane and was a viscous polymer with the basic structure —SiH(CH_3)—CH_2—Si(CH_3)$_2$—. The precursor PACS was synthesized by the catalystic reaction of aluminum acetylacetonate (Al(AcAc)$_3$) with PSCS[9, 10]. Continuous SiC(OAl) fibers, named KD-A fibers, were prepared by the melt-spinning of PACS, air-curing, and pyrolizing at 1 300 ℃. These fibers contained small amount of aluminum and 7%－9% oxygen. The KD-A fibers were converted into a sintered SiC(Al) fibers, named KD-SA, by sintering at 1 800 ℃, which contained aluminum and small amount of oxygen.

The tensile strength and tensile modulus of a fiber were measured by the single filament method of GJB 1871－94. Every data point is the average value of 25 monofilaments. Fiber morphology was studied by scanning electron microscopy (SEM,

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JEOL JSM-6300). X-ray diffraction (XRD) spectra (Cu K_α/ Siemens D500 diffractometer, Germany) were obtained from powdered fiber. The apparent mean grain size of the β-SiC crystalline phase present in the sample was calculated from the width of the (111) diffraction peak at mid-height, according to the Scherrer equation[11]. Elemental analyses (Si, C, Al) were performed on the samples by a chemical-analysis process. Oxygen contents were determined by a nitrogen/oxygen analyzer (TC-436, LECO, America).

3 RESULTS AND DISCUSSION

Fig. 1 shows the photo of winded continuous thin diameter KD-A fibers. The surface of black lustrous KD-A fibers looks very smooth.

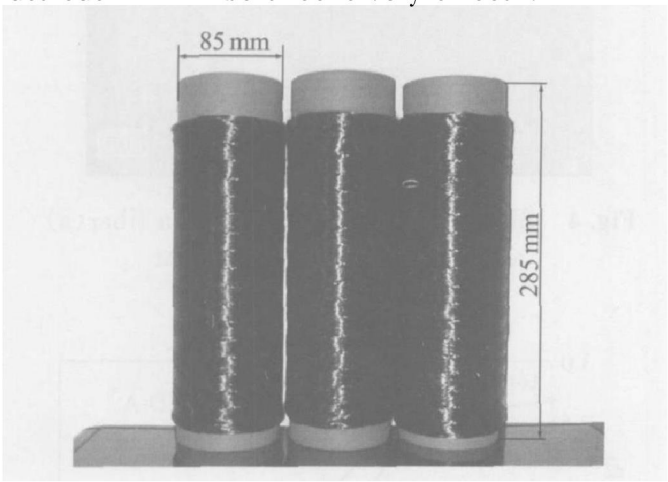

Fig. 1 Winded continuous thin diameter KD-A fibers

3.1 Typical properties and chemical composition

Table 1 shows the typical properties and chemical compositions of the KD-A fibers and KD-SA fibers, in comparison with Nicalon fibers and Tyranno SA fibers. Oxygen concentration of the KD-A fibers is less than that of the Nicalon fibers. However, the most significant difference between KD-A fibers and Nicalon fibers in terms of their components is that the former contains aluminum. The tensile strength, elastic modulus and diameter of the KD-A fiber are 2.6 GPa, 210 GPa, 12-14 μm, respectively. The KD-SA fibers, which are crystalline SiC fiber, have a nearly stoichiometric composition (C/Si atomic ration is 1.07). The tensile strength, elastic modulus and diameter of the KD-SA fiber are 2.1 GPa, 405 GPa, 10-12 μm, respectively.

3.2 Fiber structure

Fig. 2 shows XRD patterns of fibers. In case of the KD-A and Nicalon fibers, the XRD patterns are broad, which shows that these fibers have the amorphous structure. The XRD spectrum of the Nicalon fibers shows three main peaks at 36.5°, 60.1° and 73°, assigned to the (111), (220) and (311) reflections of β-SiC. However, the XRD pattern of the KD-A fibers shows broad peaks at 60.1° and 73°, which indicates that the crystallinity of the KD-A fibers is inferior to that of the Nicalon fibers. On the other hand, the XRD pattern of the KD-SA fibers exhibits sharp peaks corresponding to those of β-SiC, which shows that this fiber has high crystalline structure. The mean grain sizes of the Nicalon, KD-A, and KD-SA fibers determined by Scherrer line broadening method[11] using the (111) reflection are about 2.1, 1.3 and 40 nm, respectively. The crystallinity of the fibers is closely related to the pyrolizing temperature and the inside composition of fibers. When the pyrolizing temperature is the same, the crystallinity is mainly controlled by the composition of fibers[13]. At 1 300 ℃, the high content of oxygen and carbon can prevent the nucleation and growth of SiC phase in fibers. However, the content of oxygen and free carbon in KD-A fibers are lower than those of the Nicalon fibers. Therefore, that the KD-A fibers have small grain size is because the KD-A fibers contain small amount of aluminum, which congregates at interphase and restrains crystal. The large grain size of the KD-SA fibers is due to the high temperature sintering.

Fig. 3 shows the typical SEM surface micrographs of the KD-A fiber and the KD-SA fiber. Fig. 4 shows the SEM photographs of the Nicalon fiber and the sintered Nicalon fiber. After treatment at 1 800 ℃, it can be observed that the Nicalon fiber without aluminum has an extremely rough surface, on which many particles of 0.5 μm in size,

Table 1 Typical properties and chemical composition of fibers

Trade name	Composition(mass fraction)/%				C/Si (atomic)	Density/ (g·cm^{-3})	Diameter/ μm	Strength/ GPa	Elastic modulus/ GPa	Structure
	Si	C	O	Al						
Nicalon[1]	57	31	12		1.34	2.55	14	2.9	220	Amorphous
Tyranno SA[1]	67.8	31.3	0.3	< 2.0	1.08	3.02	10	2.8	420	Crystalline
KD-A	60.2	31.6	7.1	1.1	1.23	2.5	12-14	2.6	210	Amorphous
KD-SA	66.51	30.3	1.09	1.56	1.07	2.95	10-12	2.1	405	Crystalline

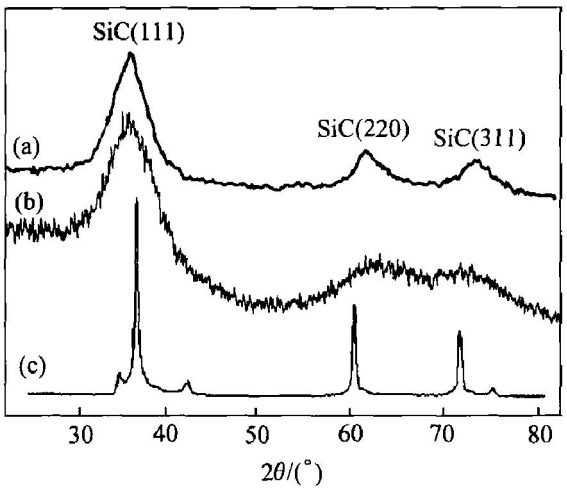

Fig. 2 XRD patterns of Nicalon(a), KD-A(b) and KD-SA(c) fibers

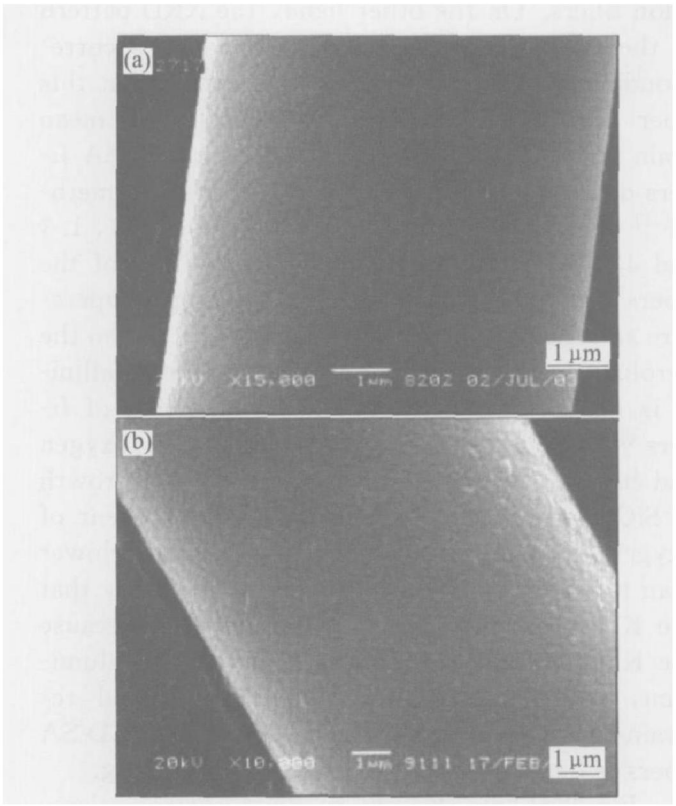

Fig. 3 SEM photographs of KD-A(a) and KD-SA(b) fiber

presumably crystalline SiC, have grown excessively during treatment[14]. Conversely, the KD-A fiber and the KD-SA fiber have very smooth surface without any observable flaws. This suggests that pores and defects formed by the removal of oxygen and excess carbon may be efficiently healed by sintering in the presence of aluminum.

3.3 Heat resistance

Fig. 5 shows the tensile strength of the fibers after heat treatment in Ar for 1 h. The tensile strength of the Nicalon fibers degrades drastically above 1 300 ℃ and becomes unmeasurably weak at 1 600 ℃. On the other hand, the tensile strength

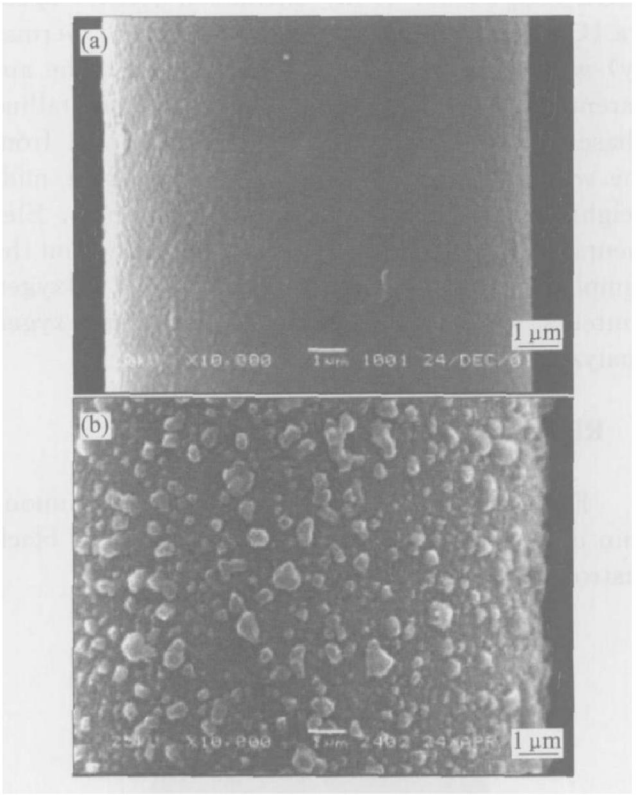

Fig. 4 SEM photographs of Nicalon fiber(a) and Nicalon fiber sintered at 1 800 ℃ for 1 h (b)

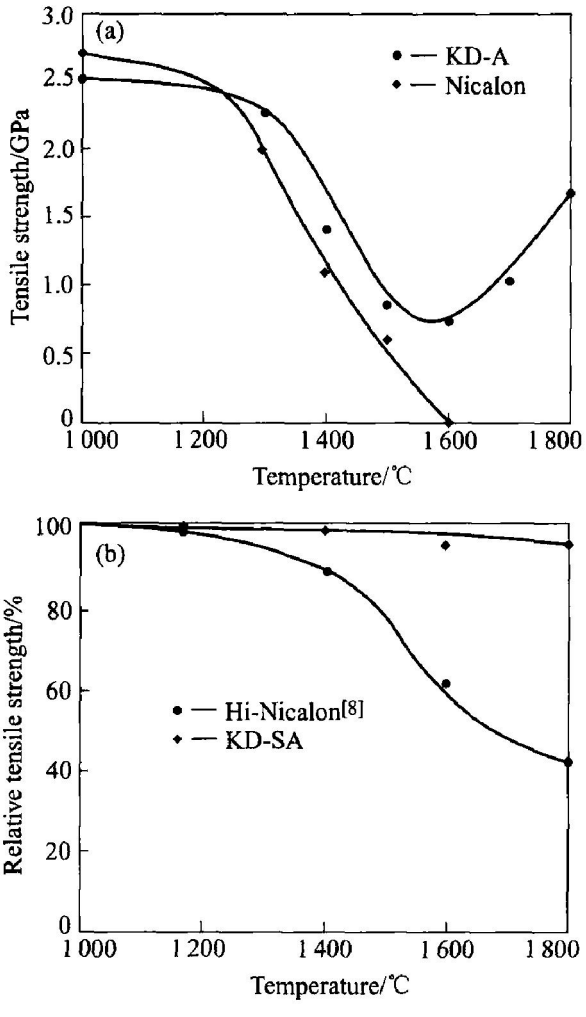

Fig. 5 Tensile strength changes of fibers after heat treatment in Ar for 1 h

of the KD-A fibres decreases slowly above 1 300 ℃ and shows about 0.6 GPa at 1 600 ℃, but rapid recovery of the tensile strength at 1 700 ℃ occurs, which may be due to the occurrence of sintering of the fiber, after thermal exposure at 1 800 ℃ 62% of the initial tensile strength is preserved. Therefore, it is considered that the aluminum constituent in the KD-A fibers plays a role as sintering aid to densify the fibers at high temperature. In contrast, the strength of a representative commercial SiC fiber Hi-Nicalon is reduced to 40% of the initial strength by heating in Ar for 1 h at 1 800 ℃[8]. So, the KD-A fibers have better high-temperature resistance than the Hi-Nicalon fibers. In case of the KD-SA fibers, the tensile strength is almost retained up to 1 800 ℃. The high observed tensile strength retention is believed to be due to its oxygen free composition and its compact structure. The aluminum constituent in the KD-SA also can prevent SiC crystal coarseness at high temperature.

Fig. 6 shows the tensile strength change of fibers after heat treatment at temperatures between 1 000 ℃ and 1 300 ℃ in air for 1 h. Fig. 7 shows the tensile strength change of the KD-A and the Nicalon fibers after heat treatment at 1 000 ℃ in air. The strength of both fibers degrade with increasing exposure temperature and heat treatment time. However, the KD-A fibers maintain higher strength in these fibers. Therefore, the KD-A fibers have better oxidation resistance than the Nicalon fibers. On the other hand, the relative strength of the KD-A and the KD-SA fibers exposed in air at 1 000 ℃ for 100 h is 69% and 94%, respectively, whereas that of Nicalon and Hi-Nicalon fibers exposed under the same test condition is 35% and 74%[8], respectively. When exposed in air at 1 300 ℃ for 100 h, the KD-A and the KD-SA fibers maintain 41% and 68% of the initial strength, respectively, however, the Hi-Nicalon fiber only preserves 23% of the initial strength[8].

From above results, the KD-A and the KD-SA fibers are found to show excellent heat resistance and oxidation resistance compared to the Nicalon and Hi-Nicalon fibers.

3.4 Creep resistance

The creep resistance of ceramic fibers was determined using the bending stress relaxation (BSR) method which was recommended by Dicarlo[15]. In this method, ceramic fibers were wound around a graphite rod of radius R_0 (8 mm) and put it in a programmable furnace, set at different preselected temperatures (1 000, 1 200, 1 400, 1 500, 1 600, 1 800 ℃) which were attained at a rate of 50 ℃/min, and the maximum temperatures reached were held for 1 h in Ar. The stress relaxation, m,

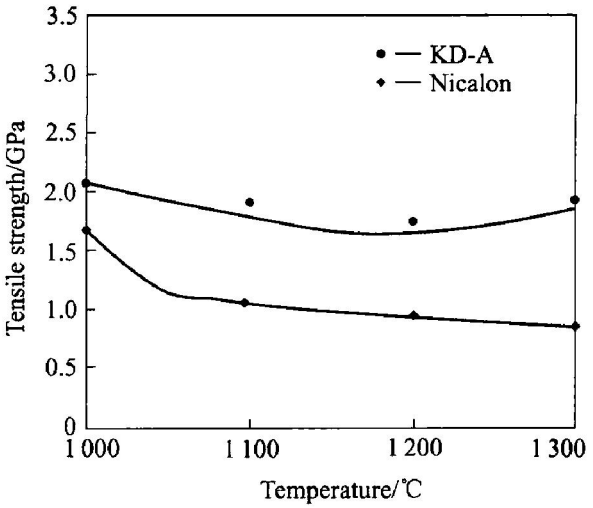

Fig. 6 Tensile strength change of fibers after exposed in air for 1 h

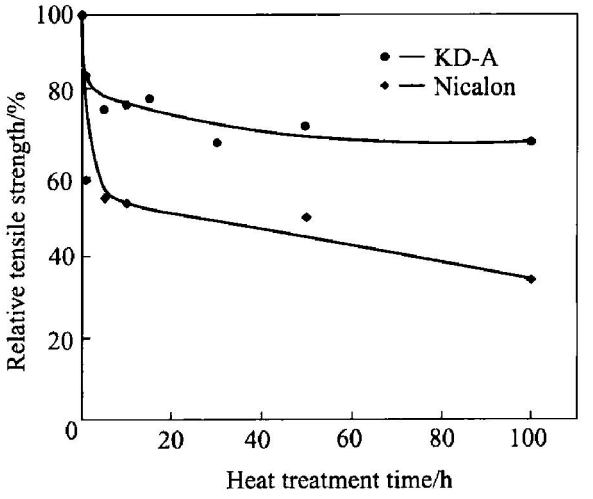

Fig. 7 Relative strength change of fibers after exposed in air at 1 000 ℃

was calculated using the remaining radius, R, of the relaxed fiber at room temperature from the following equation:

$$m = 1 - (R_0/R) \quad (1)$$

Therefore, the value of m is between 0 and 1, and the higher the m value, the more excellent the creep resistance.

The creep resistance of the ceramic fibers is shown in Fig. 8. It is clear that the KD-SA fibers show a higher value of m than any other SiC-based fiber. Moreover, in the case of the KD-SA fibers, very little creep is observed at 1 300 ℃, even at 1 800 ℃ the value of m is 0.33. However, at 1 800 ℃ Tyrano SA fiber entirely creep, i.e. m= 0. We note that commercial Tyranno SA fiber is well-known SiC-based fibers with very high heat resistance, however, our KD-SA fiber is found to show better creep resistance than Tyranno SA fiber. On the other hand, the KD-A and Hi-Nicalon fibers have similar creep resistance performance. The Nicalon fibers have entire creep at 1 300 ℃.

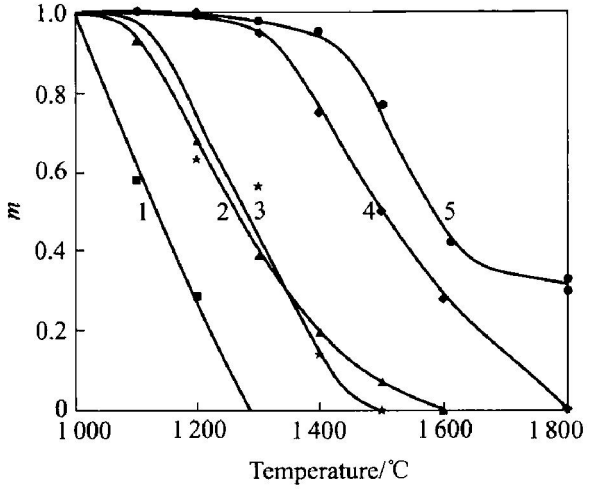

Fig. 8 Creep-resistance of KD-A fiber and KD-SA fiber in comparison with other SiC fibers
1—Nicalon[8]; 2—Hi-Nicalon[8]; 3—KD-A; 4—Tyranno-SA[8]; 5—KD-SA

4 CONCLUSIONS

The KD-A fibers were prepared by the melt-spinning of ceramic precursor PACS, air-curing, and pyrolizing at 1 300 ℃. These fibers contained a small amount of aluminum and 7% - 9% oxygen. The KD-A fibers were converted into the KD-SA fibers by sintering at 1 800 ℃, which contained aluminum and a small amount of oxygen. The tensile strength, elastic modulus and diameter of the KD-A fiber are 2.6 GPa, 210 GPa, 12 - 14 μm, respectively. The KD-A fibers have amorphous structure, which have higher thermal stability, more excellent oxidation resistance than the Nicalon fibers. The properties of the KD-A fibers have reached the level of Hi-Nicalon fibers. The tensile strength, elastic modulus and diameter of the KD-A fiber are 2.1 GPa, 405 GPa, 10 - 12 μm, respectively. The KD-SA fibers with nearly stoichiometric component have stable performance at high temperature, and better creep resistance than the Tyranno SA fibers.

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