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Characterization of the medium-range structure of Si-Al-C-O, Si-Zr-C-O and Si-Al-C Tyranno fibers by small angle X-ray scattering

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The medium-range structures of Si-Al-C-O, Si-Zr-C-O and Si-Al-C Tyranno fibers, which were prepared by pyrolysing polymetalocarbosilane organic fibers, were observed by means of small angle X-ray scattering using a point-collimated Cu K_α incident beam and a two-dimensional imaging plate detector. Single Si-Al-C-O and Si-Zr-C-O Tyranno fibers of a few μm in diameter have an anisotropic structure comprising thousands of fine filaments of about 10 nm in diameter bundled together along with the long axis of the fibers. The anisotropic structure is not sensitive to the pyrolysing temperature during the organic-to-inorganic conversion process. However, the anisotropic structure of the Si-Al-C-O fibers is totally modified to an isotropic one in Si-Al-C fibers prepared by heating the Si-Al-C-O fibers above 1700°C in an argon gas stream, because of the formation of an aluminum oxide-rich phase at the grain boundaries of β-SiC nanoclusters.

1. Introduction

Si-Ti-C-O Tyranno fibers have been prepared by using the Yajima method [1], in which precursor polytitanocarbosilane organic fibers are pyrolysed to give Si-Ti-C-O inorganic fibers at temperatures above 1000°C in inert gas atmospheres. The inorganic fibers thus obtained have a typical chemical composition of $Si_{40}Ti_{1}C_{50}O_{10}$ and have been marketed commerically as Tyranno fibers. The structural evolution during the organic-to-inorganic conversion during processing of Si-Ti-C-O Tyranno fibers has been studied by means of small angle X-ray scattering (SAXS) measurements [2–5].

The medium-range structure of the Si-Ti-C-O Tyranno fibers is characterized by two spatially distinct contributions, on a length scale of 1 to 100 nm, as illustrated in Fig. 1 [2, 3]. One comes from an isotropic SAXS intensity measured over a high scattering vector range $Q > 1\ \mathrm{nm}^{-1}$, and the other contribution is from an anisotropic variation in the SAXS intensity in a low scattering vector range $Q < 0.5\ \mathrm{nm}^{-1}$, which depends on whether the direction of Q is perpendicular or parallel to the long axis of the fiber. The scattering vector Q is defined as $Q = 4\pi \sin\theta/\lambda$, where λ is the X-ray wavelength and 2θ is the scattering angle.

The isotropic SAXS intensity profiles observed in the high Q range are drastically modified during the conversion process from polytitanocarbosilane organic precursors to Si-Ti-C-O inorganic fibers and show the formation of nanometer-sized clusters of crystalline β-SiC [4] surrounded by carbon-rich shell and embedded in the Si-C-O amorphous matrix of the inorganic fibers [5, 6]. The formation of these β-SiC clusters results in a very high mechanical strength of Si-Ti-C-O inorganic fibers.

On the other hand, the anisotropic SAXS intensity profiles appearing in the low Q range suggest that a single Si-Ti-C-O Tyranno fiber, a few μm in diameter, is formed by bundling together thousands of fine filaments of about 10 nm diameters, as shown in Fig. 1 [2, 3]. This anisotropic structure is not sensitive to the pyrolysing temperature during the organic-to-inorganic conversion

TABLE I Physical properties, chemical composition and structure of Si-M-C-O inorganic fibers

		Si-Ti-C-O (LoxM)	Si-Zr-C-O (ZMI)	Si-Al-C-O (AM)	Si-Al-C (SA)	Si-C-O Nicalon NL-201
Fiber	(μm)	11	11	11	10	14
Number of filaments	(fil./yarn)	800	800	800	800	500
Tex	(g/1000 m)	200	200	200	160	210
Tensile strength	(GPa)	3.3	3.4	2.8	2.8	2.9
Tensile modulus	(GPa)	187	200	180	420	205
Elongation	(%)	1.8	1.7	1.6	0.7	1.4
Density	(g/cm^3)	2.48	2.48	2.42	3.02	2.55
Specific heat	(J/gK)	0.735	0.709	–	0.669	0.732
Thermal conductivity	(W/mK)	1.35	2.52	–	64.6	1.45
Coefficient of thermal expansion	(10^{-6}/K)	–	4.0	–	4.5	–
Chemical composition						
Si	(wt%)	55.4	56.6	53.4	67.8	57.2
C		32.4	34.8	33.8	31.3	32.7
O		10.2	7.6	12.0	0.3	10.1
Ti		2	–	–	–	–
Zr		–	1	–	–	–
Al		–	–	≦2	≦2	–
C/Si (atomic)		1.37	1.44	1.48	1.08	1.34
Structure		Amorphous	Amorphous	Amorphous	Crystalline	Amorphous

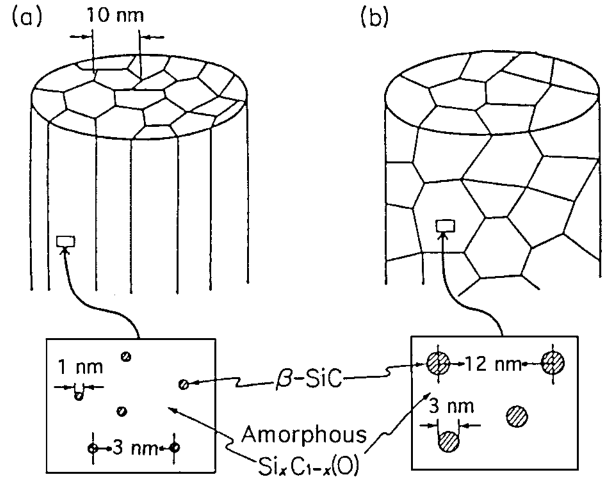

Figure 1 A model proposed for the medium-range structure of Si-Ti-C-O inorganic fibers pyrolysed at (a) 1100°C and (b) 1500°C.

process, but is lost after a long time heat treatment at temperatures above 1500°C [2, 3].

Recently, Si-Al-C-O [7] and Si-Zr-C-O [8] Tyranno fibers have been prepared by the organic-to-inorganic conversion process starting from polymetalocarbosilane organic precursor fibers including Al or Zr. These new fibers often show superior thermal stability, chemical corrosion resistance and mechanical strength to the conventional Si-Ti-C-O Tyranno fibers.

In this study the SAXS intensity profiles for both the Si-Al-C-O and Si-Zr-C-O Tyranno fibers in a low scattering vector range, $Q < 0.5$ nm^{-1}, are reported. A very drastic change in the anisotropic medium-range structure, particularly in the Si-Al-C-O pyrolysed at temperatures above 1600°C, has been observed. The anisotropic medium-range structures of the Si-Al-C-O and Si-Zr-C-O Tyranno fibers and the structural origin for the superior properties of these new Tyranno fibers are discussed.

2. Experimental procedure

Polymetalocarbosilane organic precursor fibers containing Al or Zr were cured by heating at 250°C in air and then pyrolysed at temperatures above 1300°C in a nitrogen gas stream to form Si-Al-C-O or Si-Zr-C-O inorganic fibers. Oxygen-free Si-Al-C fibers, having a near-stoichiometric β-SiC polycrystalline matrix, were obtained by heating the Si-Al-C-O fibers at temperatures above 1700°C in an argon gas stream. The wide-angle X-ray diffraction patterns, as shown in Fig. 2, suggest that the Si-Al-C-O and Si-Zr-C-O inorganic fibers are substantially amorphous structures, but that the Si-Al-C fibers are crystalline. The details of the preparation, chemical composition, thermal stability and mechanical strength of these fibers have been described previously [6, 7]. The physical and chemical properties of the Si-M-C-(O) Tyranno fibers used for the SAXS measurements are summarized in Table I.

All the SAXS measurements in this study were carried out by using a point-collimated incident X-ray beam emitted from a rotary anode and a two-dimensional imaging plate detector at room temperature. A monochromatized incident X-ray beam ($\lambda = 0.154$ nm, Cu K$_\alpha$) was reflected by a Pt-coated silica mirror and collimated with two pinhole-apertures

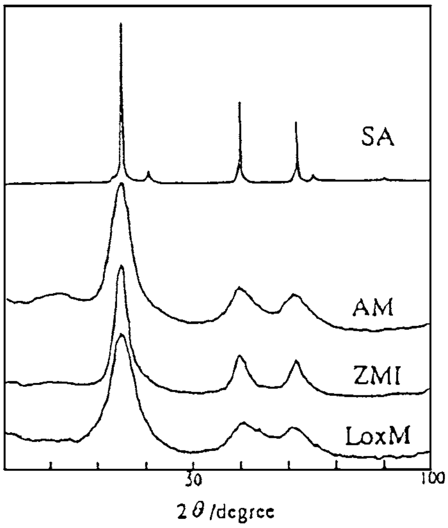

Figure 2 X-ray diffraction patterns of Si-M-C-O inorganic fibers.

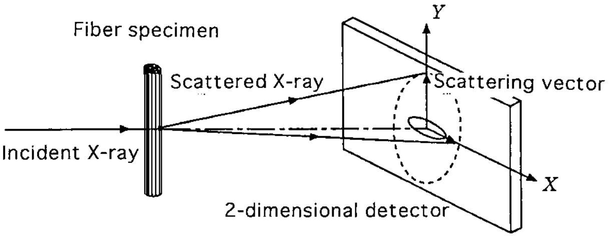

Figure 3 Experimental arrangement of small-angle X-ray scattering (SAXS) Spectrometer.

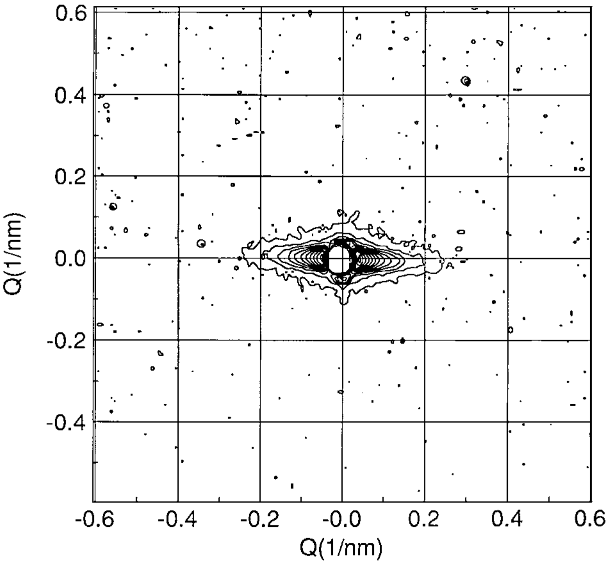

Figure 4 Isointensity contour map for two-dimensional SAXS profile of Si-Al-C-O inorganic fibers.

(0.5 mm × 0.5 mm) separated by 800 mm. The X-rays scattered from the sample were recorded as two dimensional data (pixel size: 0.5 mm × 0.5 mm) on the imaging plate fixed by a beam-stop in a vacuum chamber. All the flight paths, including the sample chamber, were evacuated to a pressure of 10^{-2} Torr. The experimental arrangement used is illustrated in Fig. 3.

The SAXS intensity profiles obtained by circular- or sector-averaging the measured two-dimensional data were converted into relative units after making corrections for background and sample absorption. Statistical errors of the SAXS intensity profiles are almost less than the size of the symbols used for the data points in the figures. The resolution of the scattering vector Q for the SAXS spectrometer is $\Delta Q_{\mathrm{FWHM}} = 0.055\ \mathrm{nm}^{-1}$. The specification of the SAXS spectrometer and the procedure of data analysis used in this study have been fully described previously [9].

3. Results

The two-dimensional SAXS data for the Si-Al-C-O fibers are shown in the form of an isointensity contour map with logarithmic spacing in Fig. 4, where the scattering vector Q on the longitudinal axis is parallel to the long direction of a fiber and the Q on the horizontal axis is parallel to the cross section (perpendicular to the long axis) of the fiber. There is a very distorted SAXS intensity profile in the central area, corresponding to the low Q region, but a circular profile in surrounding high Q region. This means that an extremely anisotropic structure exists over a length scale of 10 to 100 nm in this fiber. Such a great anisotropy between the two directions is more obvious in Fig. 5 by sector-averaging the two-dimensional data within ±15° around the both directions.

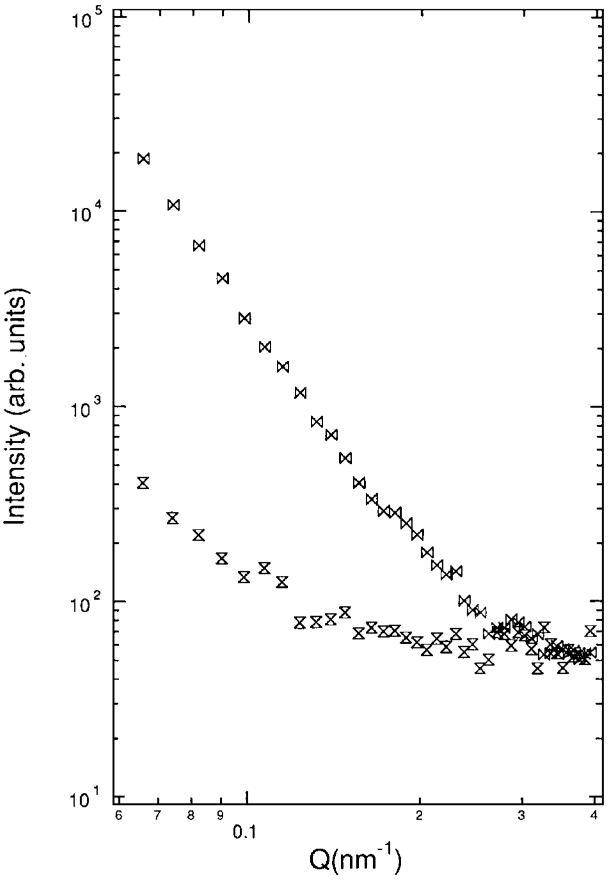

Figure 5 Anisotropic SAXS profiles sector-averaged within ±15° of the two-directions parallel (⊠) and perpendicular (⋈) to the long fiber axis of Si-Al-C-O inorganic fibers.

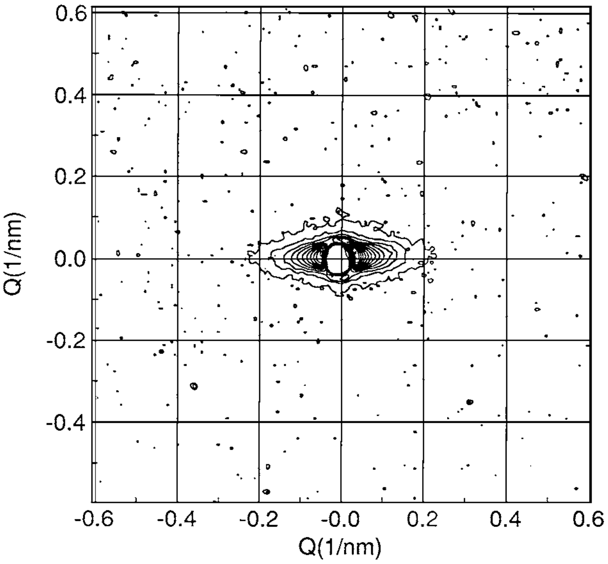

Figure 6 Isointensity contour map for two-dimensional SAXS profile of Si-Zr-C-O inorganic fibers.

The anisotropic structure observed for the Si-Al-C-O fibers is also observed for conventional Si-Ti-C-O fibers. Similar behaviors are also found for the Si-Zr-C-O fibers. Fig. 6 shows the isointensity contour map of

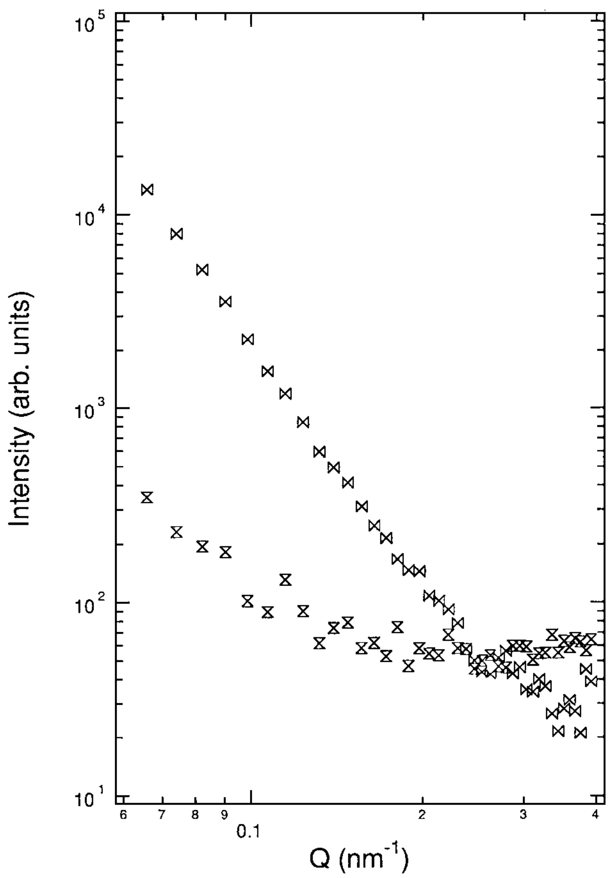

Figure 7 Anisotropic SAXS profiles sector-averaged within ±15° of the two-directions parallel (⧗) and perpendicular (⋈) to the long fiber axis of Si-Zr-C-O inorganic fibers.

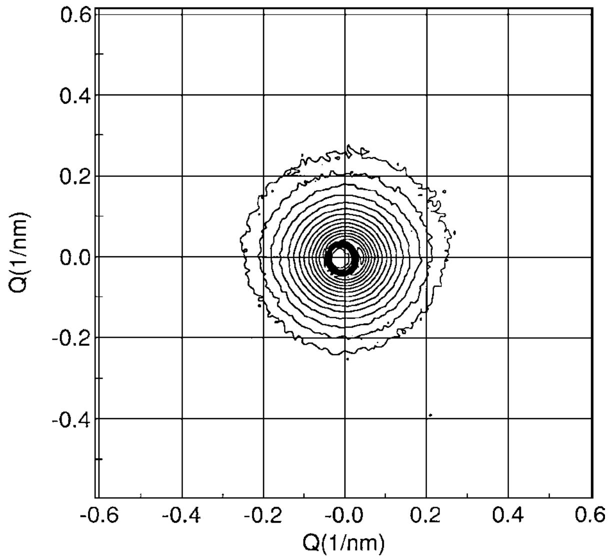

Figure 8 Isointensity contour map for two-dimensional SAXS profile of Si-Al-C inorganic fibers.

the two-dimensional SAXS intensity profile and Fig. 7 shows the sector-averaged profiles along the two directions parallel and perpendicular to the long fiber axis.

By heating the Si-Al-C-O fibers at temperatures above 1700°C in an argon gas stream, as mentioned above, oxygen-free Si-Al-C fibers consisting of nanocrystalline near-stoichiometric β-SiC clusters could be prepared. The Si-Al-C fibers thus obtained exhibit a very high tensile strength, density and thermal conductivity; the values are close to those for a high purity, bulk SiC material.

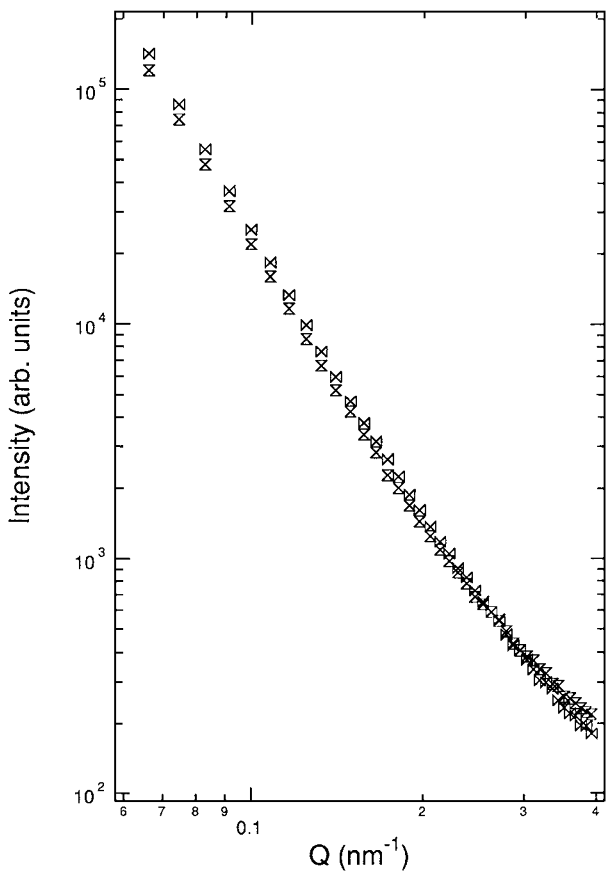

Figure 9 Anisotropic SAXS profiles sector-averaged within ±15° of the two-directions parallel (⧗) and perpendicular (⋈) to the long fiber axis of Si-Al-C inorganic fibers.

The two-dimensional SAXS profile for the Si-Al-C fibers is illustrated in Fig. 8, which surprisingly shows a very isotropic pattern in contrast to those of the other fibers. This is confirmed by sector-averaging the two-dimensional SXAS data within ±15° around the two directions perpendicular and parallel to the long axis of the fiber (see Fig. 9). Thus, there is a drastic change from an anisotropic structure to an isotropic one in the medium-range structure over a length scale of 10 to 100 nm in the fibers.

4. Discussion

The anisotropic medium-range structure extending over a length scale of about 10 nm in the cross section of the single Tyranno fiber is originally formed in the polymetalocarbosilane organic precursor fibers and is retained in the inorganic fibers after pyrolysing at temperatures above 1000°C. However, this anisotropic structure is destroyed and converted to an isotropic structure in the cases of the Si-Ti-C-O and Si-Zr-C-O Tyranno fibers pyrolysed at temperatures above 1500°C, even in an inert gas atmosphere. Also, the very high tensile strength of the fibers is drastically reduced after the high temperature heat treatment.

Si-Al-C-O Tyranno fibers are changed into Si-Al-C fibers by heating above 1600°C in an argon gas stream. The Si-Al-C fibers thus obtained are nanocrystalline β-SiC fibers containing no oxygen. The very high

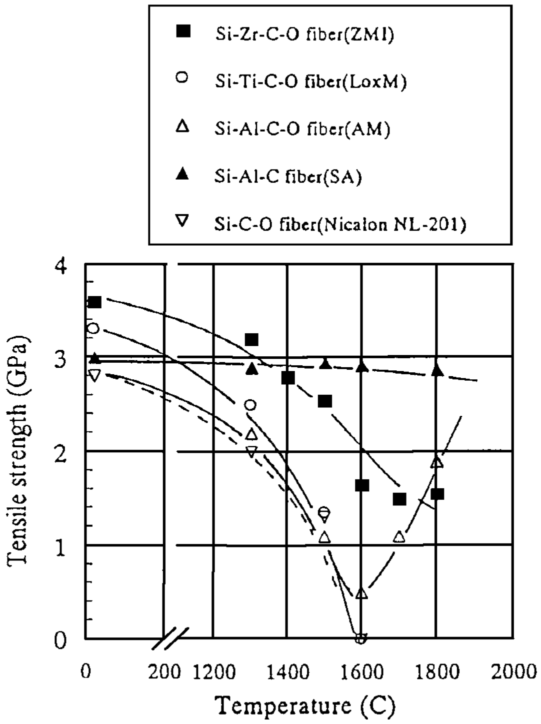

Figure 10 Tensile strength of Si-M-C-O inorganic fibers measured at room temperature after heating in an Ar gas stream for 1 hour.

tensile strength is not reduced even though an anisotropic medium-range structure is converted into an isotropic one. Such a characteristic structure change may be caused by the redistribution of aluminum oxide in the fiber. Therefore, rapid recovery of the tensile strength at temperatures above 1600°C occurs, as shown in Fig. 10 [7].

High-resolution transmission electron microscopy [10] shows that an aluminum oxide-rich phase precipitates at the triple points of the β-SiC nano-clusters and forms a three-dimensional network in the Si-Al-C fibers. The oxygen atoms existing in the amorphous matrix of the Si-Al-C-O fibers are mostly lost as CO gas and the remaining oxygen atoms form the aluminum oxide at the grain boundary triple points. During the conversion from the Si-Al-C-O fibers to the Si-Al-C fibers, the formation of the aluminum oxide and the modification of the medium-range structure occur simultaneously. Such a drastic structure change results in the destruction of the anisotropic structure of the Si-Al-C-O Tyranno fibers and the recovery of the high tensile strength in the Si-Al-C fibers.

5. Conclusion

The medium-range structures of Si-Al-C-O, Si-Zr-C-O and Si-Al-C inorganic fibers, which were prepared by pyrolysing polymetalocarbosilane organic fibers in inert gas streams, were characterized by the measurement of small angle X-ray scattering. The conclusions of this study are summarized as follows:

1. Single Si-Al-C-O and Si-Zr-C-O fibers, a few μm in diameter, have an anisotropic structure comprising thousands of fine filaments, of about 10 nm in diameter, are bundled together along with the long axis of the fibers.
2. The anisotropic structure mentioned above is not sensitive to the pyrolysing temperature during the organic-to-inorganic conversion and is preserved until very high temperatures, at which the fibers lose their mechanical strength.
3. The Si-Al-C fibers prepared by heating the Si-Al-C-O fibers above 1700°C in an argon gas stream are modified to have an isotropic medium-range structure over the length scale of 10 to 100 nm. The formation of an aluminium oxide network along the grain boundaries of β-SiC clusters, results in the high mechanical strength being regained.

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