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# Excellent heat resistance of Si-Zr-C-O fibre

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In order to obtain the high heat-resistant fibre, Si-Zr-C-O fibre has been developed. Si-Zr-C-O fibre was produced by the use of polyzirconocarbosilane as the precursor polymer. In this paper, the difference in heat-resistance between Si-Ti-C-O and Si-Zr-C-O fibres was clarified. Si-Zr-C-O fibre showed excellent heat resistance (up to 1773 K) compared with Si-Ti-C-O fibre (up to 1573 K). Generally speaking, decomposition reaction of this type of fibre proceeds accompained by the release of CO gas which was formed by the reaction between excess carbon and oxygen included in the fibre. In the case of Si-Zr-C-O fibre, Zr can strongly capture the oxygen atoms, so that the aforementioned decomposition hardly proceeds up to 1873 K ($ZrO_2 + 3C = ZrC + 2CO$; $\Delta G < 0$ at over 1906 K). © *1999 Kluwer Academic Publishers*

## 1. Introduction

Continuous fibre-reinforced ceramic matrix composites (CMCs) have been widely studied for the purpose of applications in aerospace and general industrial fields [1, 3]. Generally speaking, the reinforcements should not have only high heat-resistance and excellent oxidation resistance, but also have good processing ability into complex weave.

Si-C-O fibres [4] synthesized from an organic silicon polymer as a precursor, and Si-Ti-C-O fibres [5] containing Ti as a crystallization inhibitor, have been the advantageous candidate for the reinforcement with respect to the required characteristics. However, the heat-resistance of these fibres has not been always sufficient at very high temperature. It is well known that pyrolysis of these fibres at very high temperature proceeds with the release of CO and/or SiO accompanied by crystal grain growth of $\beta$-SiC [6]. The heat-resistance of these fibres has surely been improved by reducing the oxygen content in the fibre by the use of an electron beam in a curing process [7, 8]. This process is very expensive, though. Using another approach, we have developed a new type of highly heat-resistant Si-Zr-C-O fibre, in which the Zr plays an important role in increase in pyrolysis temperature. In this study, in order to clarify its heat-resistant mechanism, we investigated the fibre's pyrolysis behavior at high temperatures.

## 2. Experimental

### 2.1. Synthesis of Si-Ti-C-O and Si-Zr-C-O fibres

Si-Ti-C-O fibre was synthesized according to the method written in other paper [5]. Si-Zr-C-O fibre was prepared by the use of polyzirconocarbosilane (PZC) which was synthesized by the reaction between polycarbosilane and ziroconiumacetylacetonate at 573 K. PZC was continuously melt-spun and then cured in air by heating up to 443 K. By pyrolysis at 1573 K of the cured PZC fibre, Si-Zr-C-O fibre was obtained.

### 2.2. Chemical analysis

Determination of silicon, titanium, zirconium, carbon and oxygen present in the fibres was carried out by the following methods. For silicon determination, a fibre sample was decomposed by means of a fused alkali salt, and then neutralized in hydrochloric acid. The sample was then evaporated to obtain dry $SiO_2$ and analyzed by gravimetry. For titanium and zirconium determination, following decomposition of the fibres by means of the same fused alkali salt, hydrochloric acid was added and the sample was then filtered. The filtrate was subjected to titanium and zirconium determination by an inductivity coupled plasma (ICP) method. Carbon and oxygen were determined by means of a combustion volumetric method with C-LECO and O-LECO analyzers.

### 2.3. X-ray diffraction

For X-ray powder diffraction measurement, the fibre sample was pulverized and the powder was subjected to X-ray diffractometry (Rigaku X-ray diffractometer) with $CuK_\alpha$ characteristic X-ray and a Ni filter. The apparent size of the $\beta$-SiC crystals was calculated using the following equation derived by Scherrer with a half-bandwidth of $\beta$-SiC (111) diffraction peak in the diffraction diagram.

$$L_{111} = 1.0\lambda/\beta\cos\theta$$

where, $\lambda$ is the X-ray wavelength, $\theta$ is the angle of diffraction and $\beta$ is the half-bandwidth.

### 2.4. Pyrolysis of fibres

The fibre sample, from which a sizing agent had already been removed by 15 minutes heat treatment in air at 873 K, was heated under an Ar gas flow in a tube-type electric furnace at each designated temperature in the range of 1573 to 2173 K for 1 hour. The fibres were weighed before and after each heat treatment, and the difference between the weight before and that after treatment was calculated for each designated temperature.

### 2.5. Tensile strength of fibres

The tensile strength of the fibres was measured by the single filament method using an Orientec UTM-20 with a gauge length of 25 mm and cross-head speed of 2 mm/min.

## 3. Results and discussion

Table I shows the results of chemical analysis of the fibres used in this study.

Oxygen concentration of the Si-Zr-C-O fibre is 1 wt % less than that of the Si-Ti-C-O fibre. However, the most significant difference between these fibres in terms of their components is that the former contains Zr and the latter contains Ti.

Fig. 1 shows the weight loss of the fibres upon 1 hour heat treatment at each designated temperature in the range of 1573 to 2173 K. In the case of the Si-Ti-C-O fibre, a significant weight loss was observed at a temperature over 1573 K, and maximum weight loss was recognized at 1773 K. In contrast, in the case of the Si-Zr-C-O fibre, no weight loss was observed upon heat treatment below 1773 K, indicating that this fibre is very stable at high temperature. A significant weight loss of the Si-Zr-C-O fibre was recognized at 1873 K. The whole weight decreases of the Si-Ti-C-O and Si-Zr-C-O fibres were 20.6% and 17.7%, respectively. These values are slightly higher than those calculated under the assumption that all the oxygen contained in each fibre was released in the form of CO gas. This is probably because release of SiO also occurred simultaneously.

TABLE I Chemical composition of Si-Zr-C-O and Si-Ti-C-O fibre

| | Chemical composition (wt %) | | | | | |
|---|---|---|---|---|---|---|
| Fibre | Si | C | O | Zr | Ti | Chemical formula |
| Si-Zr-C-O fibre | 55.3 | 33.9 | 9.8 | 1.0 | — | $SiZr_{0.01}C_{1.43}O_{0.31}$ |
| Si-Ti-C-O fibre | 55.4 | 32.4 | 10.2 | — | 2.0 | $SiTi_{0.02}C_{1.37}O_{0.32}$ |

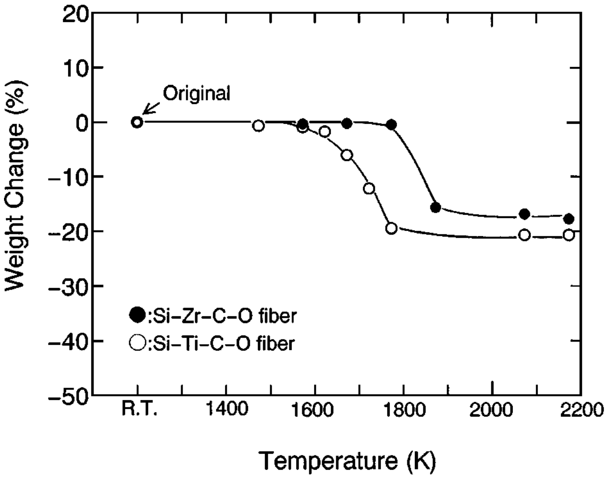

*Figure 1* Weight change of the fibres upon 1 hour heat treatment in a stream of Ar gas at each designated temperature.

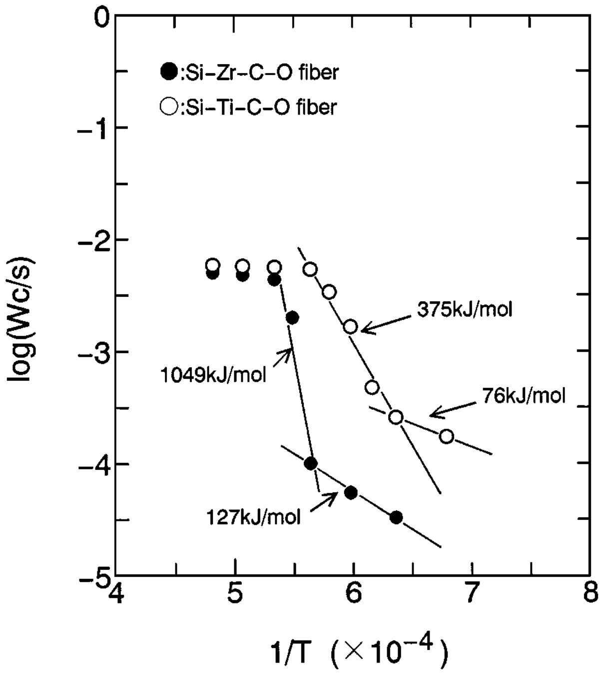

*Figure 2* Arrhenius plots of apparent pyrolysis rate of the fibres.

Fig. 2 shows Arrhenius plots of the apparent pyrolysis rate of each fibre. The activation energy of the pyrolysis for the Si-Ti-C-O fibre was calculated from the rate of weight loss between the heat treatment temperatures of 1573 K and 1773 K to be 375 kJ/mol. This value is within the reported range of activation energies of 302 to 586 kJ/mol for when bulk diffusion of carbon occurs in the SiC phase [9, 10]. During pyrolysis of the Si-Ti-C-O fibre, grain growth of $\beta$-SiC accompained by CO gas desorption was observed. Based on this, and from the results of other studies, it is concluded that the reaction below is the main one occurring in the pyrolysis. In addition, from the above results, the rate of this reaction is considered to be determined by the rate of carbon diffusion in the SiC phase.

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (1)$$

On the other hand, for the Si-Zr-C-O fibre, the activation energy for the pyrolysis calculated from the rate of weight loss between the heat treatment temperatures of 1773 and 1873 K was 1049 kJ/mol, which is remarkably large. Therefore, in this case, reaction (1) should not proceed at a rate determined by the rate of carbon diffusion, and is unlikely to occur under the conditions used in these experiments.

Figs 3 and 4 show X-ray powder diffraction patterns for Si-Ti-C-O and Si-Zr-C-O fibres after 1 hour heat treatment at each designated temperature in the range of 1573 to 2073 K. Both fibre samples gave broad diffraction patterns before the heat treatments, and thus, from the point of view of X-ray powder diffraction measurement, are considered to be noncrystalline. In the diffraction pattern of the Si-Ti-C-O fibre heated at 1673 K, a diffraction peak with $2\theta = 42°$ is observed. Peak of both (200) TiC and (200) $\beta$-SiC may appear in this region. However, as described later, based on the change of standard free energies of formation of these compounds, TiC is more easily formed than $\beta$-SiC at temperatures of around 1673 K, and therefore the above diffraction peak was assigned to (200) TiC. Furthermore, in the diffraction pattern of other specimens heat-treated at temperatures over 1773 K, sharp diffraction peaks with $2\theta = 35.6°$, 60° and 71.8° are observed, corresponding to (111), (220) and (311) $\beta$-SiC, respectively. This illustrates that the crystallization of $\beta$-SiC proceeds with the progress of pyrolysis of the fibres. On the other hand, the diffraction patterns for the

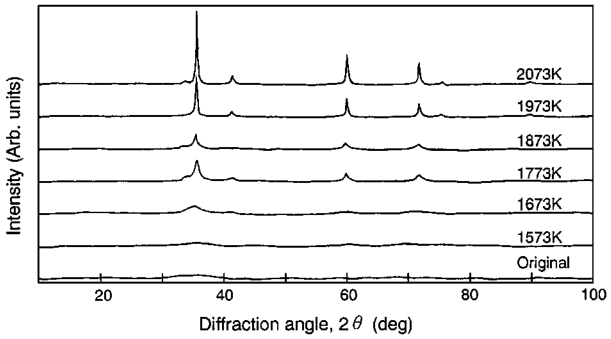

*Figure 3* X-ray diffraction patterns for Si-Ti-C-O fibre after 1 hour heat treatment in a stream of Ar gas at each designated temperature.

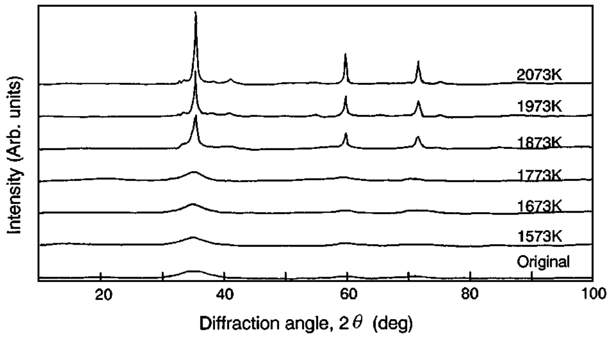

*Figure 4* X-ray diffraction patterns for Si-Zr-C-O fibre after 1 hour heat treatment in a stream of Ar gas at each designated temperature.

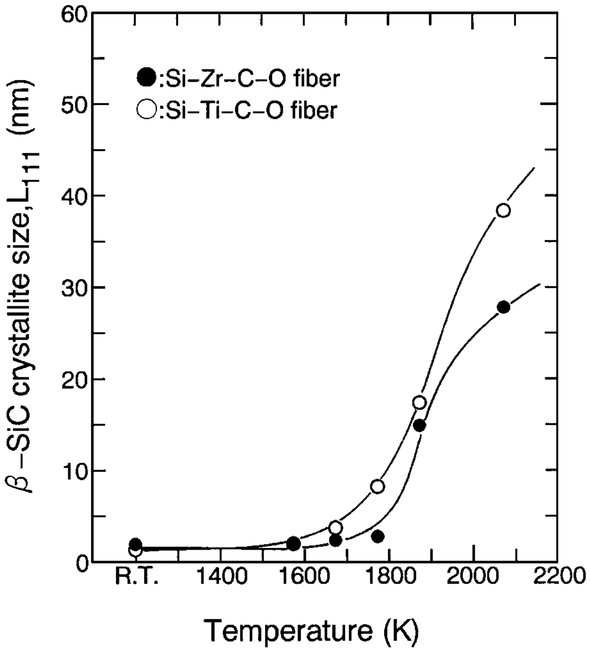

*Figure 5* Changes in the $\beta$-SiC crystallite size of the fibres after 1 hour heat treatment in a stream of Ar gas at each designated temperature.

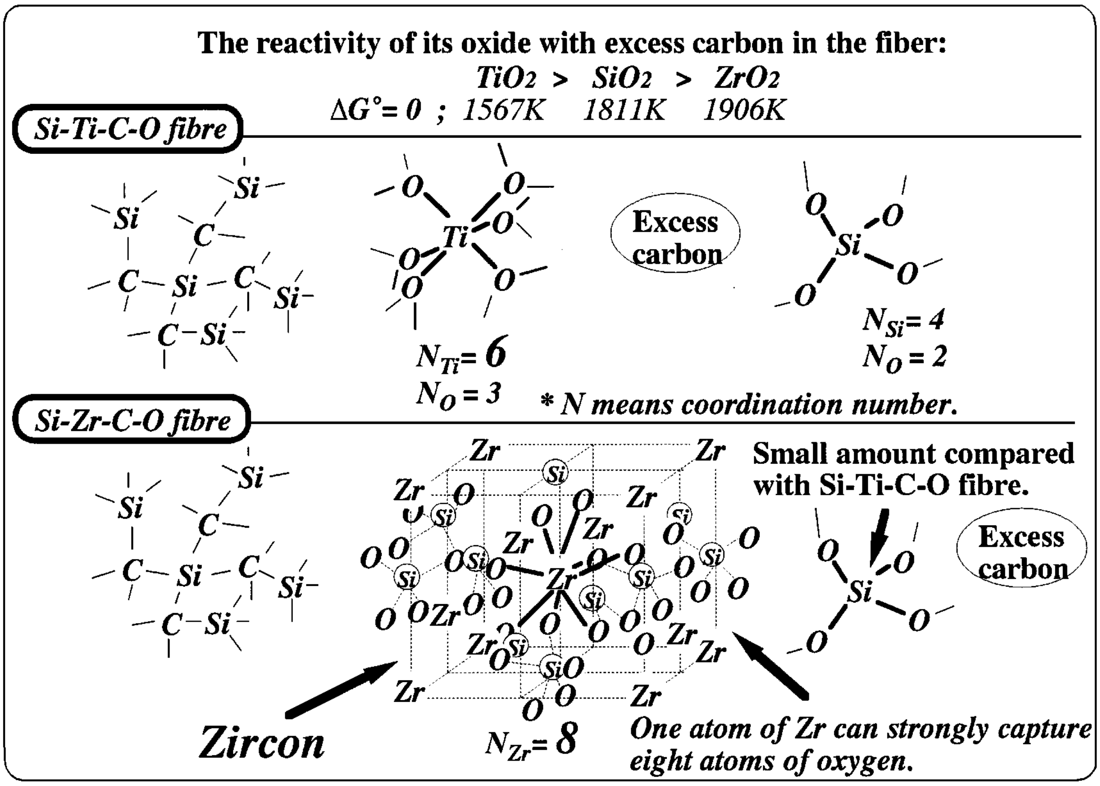

*Figure 6* The structural differences between the Si-Ti-C-O and Si-Zr-C-O fibres.

Si-Zr-C-O fibres heated at less than 1773 K are broad. In the diffraction patterns for the fibres heated at 1873 K or higher, the above-described diffraction peaks corresponding to $\beta$-SiC are sharp, indicating the occurrence of crystallization in the fibre. However, the ZrC peak does not appear in the diffraction patterns for the fibres heated at less than 1973 K. These results agree with those shown in Fig. 1, and indicate that the pyrolysis of these fibres proceeds via reaction (1). Fig. 5 shows the change in apparent crystal size observed on the $\beta$-SiC (111) surface.

To clarify the differences in the changes described above, we discuss a state of the oxygen and carbon contained in each fibre, and the free energy changes for the reactions which are considered to occur during pyrolysis of the fibres.

In the Si-Ti-C-O fibre, with respect to the stability of the chemical bonds, oxygen must be bonded to Ti and/or Si. As shown in Table I, nonstoichiometric excess carbon also exists in the fibre. $TiO_2$ and $SiO_2$, examples of compounds produced by bonding of oxygen to Ti or Si, respectively, cannot easily form a stable solid solution under the production condition of the fibre and therefore these compounds exist separately in the fibre. Ti and Si are considered to form a stable structure in the fibre with coordination numbers of 6 and 4, respectively.

On the other hand, the oxygen present in the Si-Zr-C-O fibre must be bonded to Zr and/or Si. Zr can form

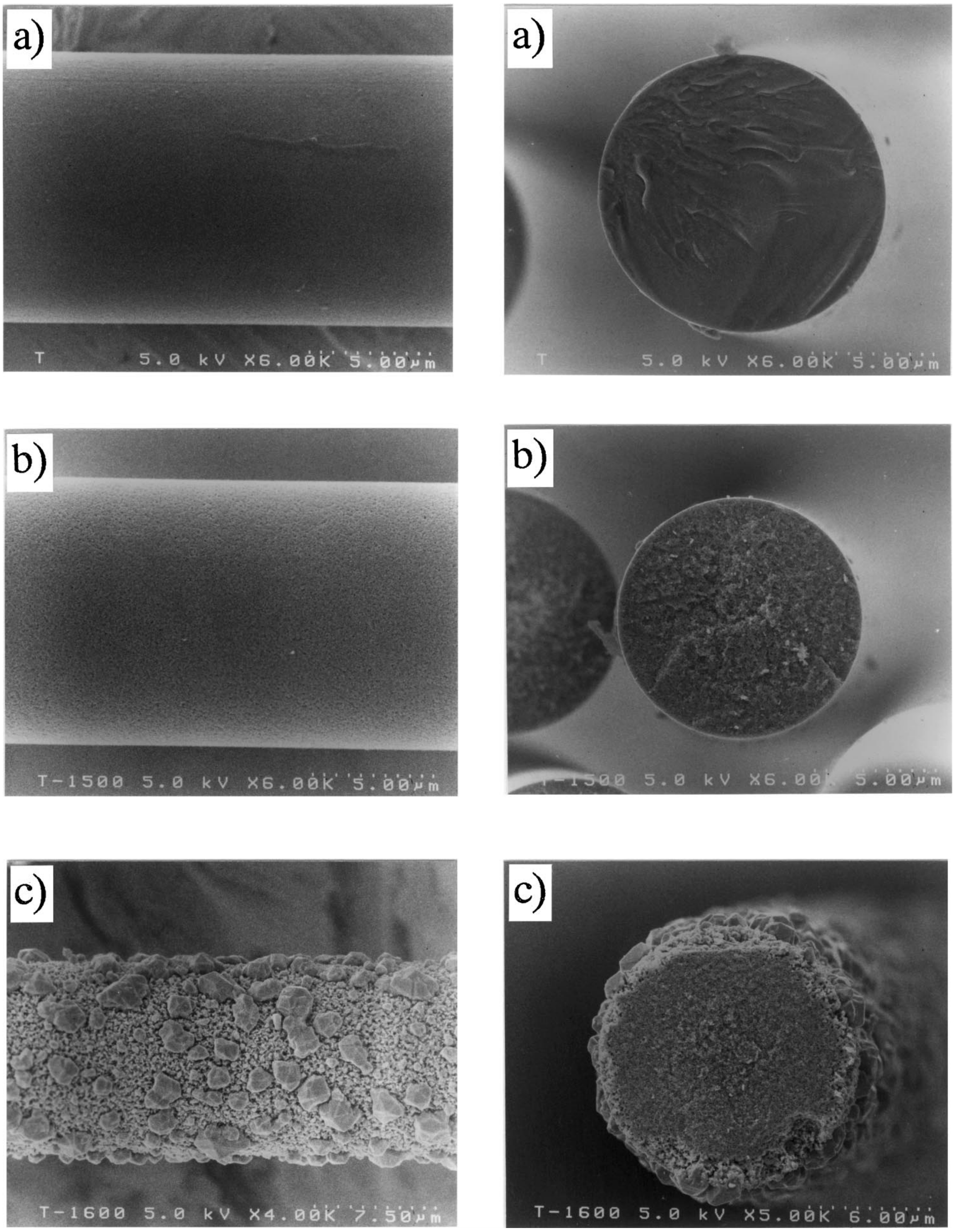

*Figure 7* SEM photographs of Si-Ti-C-O fibres after 1 hour heat treatment in a stream of Ar gas at each designated temperature: (a) before heat treatment; (b) 1773 K; (c) 1873 K.

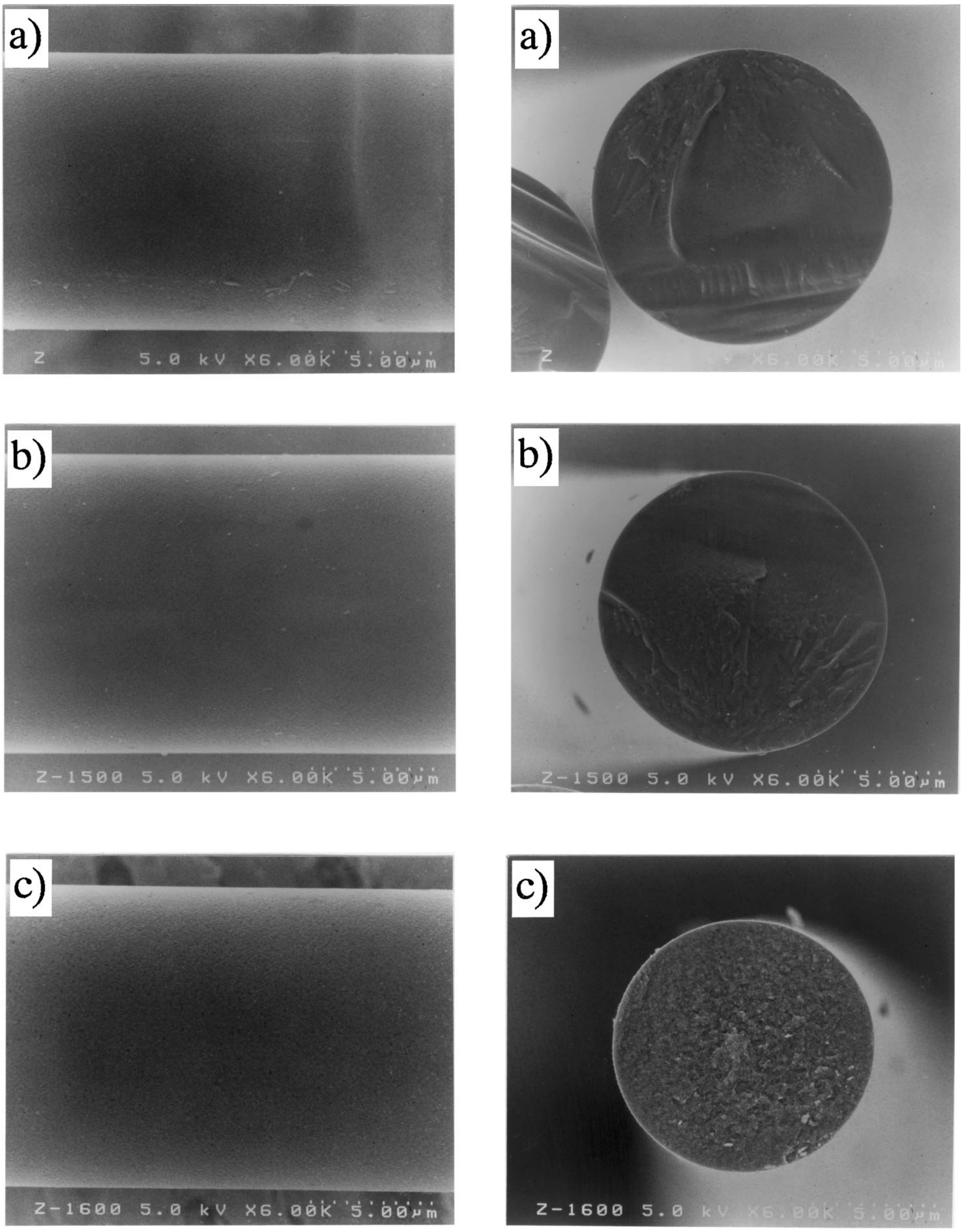

*Figure 8* SEM photographs of Si-Zr-C-O fibres after 1 hour heat treatment in a stream of Ar gas at each designated temperature: (a) before heat treatment; (b) 1773 K; (c) 1873 K.

a stable structure in the fibre with eight oxygen atoms per one zirconium atom, and can also form thermodynamically stable solid solutions with silicon oxides. An example of a solid solution is zircon. In zircon, Zr with a coordination number of 8 is bonded to oxygen and exists among four $SiO_2$ compounds. In any case, we assume that the Zr in the Si-Zr-C-O fibres strongly captures oxygen, forming thermally stable structure.

Based on the above considerations, we estimate the structural differences between the Si-Ti-C-O and Si-Zr-C-O fibres to be as shown in Fig. 6.

The formation of carbides by reaction of oxides of Ti, Si and Zr with nonstoichiometric excess carbon, accompained by the release of CO gas, should also be considered in discussions of the mechanism of pyrolysis of these fibres. Typical examples of these reactions include reaction (1) and the following ones.

$$TiO_2 + 3C \rightarrow TiC + 2CO \tag{2}$$

$$ZrO_2 + 3C \rightarrow ZrC + 2CO \tag{3}$$

The temperatures at which these reactions occur spontaneously, or at which the standard free energy changes of these reactions become negative, are 1811, 1567 and 1906 K for reactions (1), (2) and (3), respectively. As indicated by these temperatures, reaction (2) is the most likely to occur at the lowest temperature. This temperature is also consistent with the fact that the diffraction peak of (200) TiC was observed when the sample was heated at over 1573 K. Accordingly, in the pyrolysis of the Si-Ti-C-O fibre, TiC formation occurs before the other reactions, and the TiC produced acts as a crystallization nucleus. It is therefore considered that the SiC formation represented by Equation 1 also occurs at a comparatively low temperature. We assume that this is the cause if the significant weight loss which occurred upon pyrolysis of the Si-Ti-C-O fibre at temperatures of over 1573 K.

On the other hand, from the temperatures calculated on the basis of the free energy changes of the above reactions, it is understood that, in the case of the Si-Zr-C-O fibre, the ZrC formation represented by Equation 3 occurs at a higher temperature than that at which reaction (1) occurs. As previouly mentioned, Zr can exist as an atom with a coordination number of 8, forming stable structures by trapping and bonding strongly with oxygen or $SiO_2$. Therefore, we speculate that the SiC formation represented by Equation 1 does not occur easily in the Si-Zr-C-O fibre. These considerations also are consistent with the weight loss of the Si-Zr-C-O fibre which occurred upon pyrolysis at temperatures over 1773 K.

Figs 7 and 8 show SEM images of Si-Ti-C-O and Si-Zr-C-O fibres heated for 1 hour at 1773 and 1873 K, respectively. The structure observed in the cross section of the Si-Ti-C-O fibre heated at 1773 K is remarkably porous, and contains $\beta$-SiC crystals. It also can be observed that the $\beta$-SiC crystals in the sample heated at 1873 K are larger than those in the sample heated at 1773 K. On the other hand, in the cross section of the Si-Zr-C-O fibre heated at 1773 K, mirror, mist and hackle are observed, and the structure in the cross section is well ordered. The structure in the cross section of the sample heated at 1873 K is slightly porous, and $\beta$-SiC crystals can be recognized in it, however, no evidence of grain growth of $\beta$-SiC crystals, which can be observed in the Si-Ti-C-O fibre, is detected. These morphological differences between the two fibres agree well with the weight changes shown in Fig. 1 and the X-ray diffraction results shown in Figs 3 and 4.

Fig. 9 shows the tensile strength of the Si-Ti-C-O and Si-Zr-C-O fibres heated for 1 hour at each designated temperature in the range of 1573 to 2073 K. The tensile strength of both of these fibres before the heat treatment was approximately 3.5 GPa. The tensile strength of the Si-Ti-C-O fibre decreased upon heat treatment at over 1573 K and became unmeasurable upon heat treatment at 1873 K. The tensile strength of the Si-Zr-C-O fibre after heating at 1773 K was higher than 2 GPa. Furthermore, even after heat treatment at over 1873 K, at which the pyrolysis of the fibre is completed, the fibre had a tensile strength of approximately 1 GPa, proving the excellent heat stability of the Si-Zr-C-O fibre. In order to aid in the understanding of the thermal stability of each fibre, the changes in the tensile strengths of the fibres by heat-treatment at high temperatures are summarized in Table II.

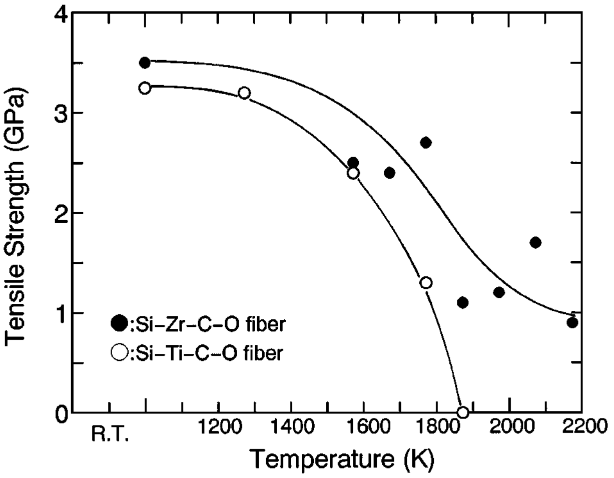

*Figure 9* The tensile strength of the fibres after 1 hour heat treatment in a stream of Ar gas at each designated temperature.

TABLE II The tensile strengths of each fibre after heat-treatment at various temperatures for 1 hour in Ar

| Treatment temperature | Tensile strengths (GPa) (at R.T.) | | | | |
|---|---|---|---|---|---|
| | R.T. | 1573 K | 1773 K | 1873 K | 2173 K |
| Si-Zr-C-O fibre | 3.49 | 2.53 | 2.72 | 1.11 | 0.9 |
| | (2.0) | (2.0) | (2.5) | (15.1) | — |
| Si-Ti-C-O fibre | 3.15 | 2.43 | 1.30 | ~0 | ~0 |
| | (1.8) | (2.0) | (8.2) | (17.7) | — |

*( ): Apparent crystalline grain size of $\beta$-SiC (111) ⟨unit: nm⟩.

## 4. Conclusions

We studied the behavior of a Si-Zr-C-O fibre during pyrolysis in comparison with that of a Si-Ti-C-O fibre, and obtained the following results.

1. The activation energy for pyrolysis of the Si-Zr-C-O fibre was 1049 kJ/mol, which is extremely high compared to that of the Si-Ti-C-O fibre, 375 kJ/mol.
2. The X-ray diffraction pattern for the Si-Ti-C-O fibre heated at 1673 K or higher had a TiC diffraction peak, and in the same sample, $\beta$-SiC crystal grain growth occurred. In contrast, in the Si-Zr-C-O fibre sample, a significant weight loss and crystal grain growth of $\beta$-SiC were recognized at 1873 K. In addition, a ZrC diffraction peak was only observed in the case of heat treatment at 1973 K or higher.
3. The tensile strength of Si-Zr-C-O fibre was approximately 1 GPa even after heat treatment at 1873 K, at which pyrolysis of the fibre was completed, proving the excellent heat stability of this fibre.
4. It is considered that the excellent heat stability of the Si-Zr-C-O fibre is due to the presence of Zr, which can strongly capture eight oxygen atoms per one zirconium atom, forming thermally stable structure.

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