

Electrical resistivity of Si–Ti–C–O fibres after rapid heat treatment

M. NARISAWA, Y. ITOI, K. OKAMURA

College of Engineering, University of Osaka Prefecture, Gakuencho 1-1, Sakai, Osaka 593, Japan

Two types of Si–Ti–C–O fibres were heat treated in a preheated graphite furnace at temperatures between 1273 and 1973 K, and the change in the electrical resistivity was measured after removing the fibres from the furnace. The resistivity of the fibres decreased monotonically with increasing heat-treatment temperature, but showed a significant increase of the order of 10^1 – 10^2 in the temperature range of gas evolution from the fibres. The resistivity of the fibre which has an amorphous character began to increase at a lower temperature than that of the fibre with a crystalline character. This increase in resistivity did not occur during heat treatment in a pure oxygen atmosphere, because the oxide layer formed on the fibre surface suppressed gas evolution from the fibres. The X-ray diffraction patterns of heat-treated fibres in nitrogen or oxygen atmospheres revealed that β -SiC crystals began to precipitate from the amorphous state as the heat-treatment temperature increased. The β -SiC crystal growth, however, did not always correspond with the decrease in the fibre resistivity.

1. Introduction

The processing SiC ceramic fibres from a polymer precursor has been developed and has attracted much attention. The properties of these fibres are known to depend intrinsically upon the heat-treatment process. In particular, the change in mechanical properties with heat treatment is very important [1–3], because SiC fibres are possible candidates for reinforcement in advanced intermetallic compounds or ceramic composites. Not only are the mechanical properties attracting attention, but the electrical properties of the fibres are also of current interest [4, 5]. SiC fibres are n-type semiconductors with a resistivity between 10^0 and $10^6 \Omega \text{cm}$ [6]. In recent years, the application of polymer precursor methods to the fabrication of electronic devices has been attempted [6, 7].

The effect of heat treatment on the properties of the SiC fibres have usually been investigated using samples heat treated under mild conditions. In the present study, the resistivity of Si–Ti–C–O fibres, which are known to show superior heat persistence among commercialized SiC fibres [8], was measured after rapid heat treatment in pure nitrogen or oxygen atmospheres. The fibres treated under such violent conditions are expected to exhibit a different microstructure from that of the well-known SiC fibres.

2. Experimental procedure

2.1. Materials

Two types of Si–Ti–C–O fibres commercialized by Ube Industries Ltd, were prepared for measurement. The composition, density and diameter of the fibres

are shown in Table I. The fibre which contains a large amount of oxygen was named Tyranno 1, and the fibre which contains less oxygen was named Tyranno 2. The fibres were always heat treated in an argon atmosphere up to 1073 K in order to eliminate any sizing agent on the fibres prior to the experiments.

2.2. Heat treatment of the fibres

A graphite crucible containing 0.5 g fibre, was put into a graphite furnace which has been preheated to appointed temperatures with a stream of nitrogen gas. An automatic balance (limit 200 g, sensitivity 0.1 mg) was attached to the graphite furnace in order to monitor weight loss of the fibres. For heat treatment in an oxygen atmosphere, 1.0 g fibre in a magnesia crucible was put into a furnace equipped with a silicon carbide heater with a stream of a pure oxygen gas. The weight gain caused by the oxidation reaction was monitored.

2.3. Measurements

The electrical resistivity of the fibre was measured using a two-probe direct-current method at room temperature after removing the sample from the furnace. The fibres were placed on an alumina substrate and both ends were connected to copper plates with silver paste. The distance between the copper plates was 0.8 mm. The diameters of the fibres were measured using an optical microscope just before the resistivity measurements, which were carried out ten times for one sample, and then the results averaged. In the case of oxidized fibres, the fibres were washed with

TABLE I Properties of Si-Ti-C-O fibres

	Heat-treatment temperature (K)	Composition	Diameter (μm)	Density (Mg m^{-3})
Tyranno 1	1573	$\text{SiTi}_{0.02}\text{C}_{1.40}\text{O}_{0.64}$	8.5	2.33
Tyranno 2	1573	$\text{SiTi}_{0.02}\text{C}_{1.33}\text{O}_{0.44}$	8.5	2.38

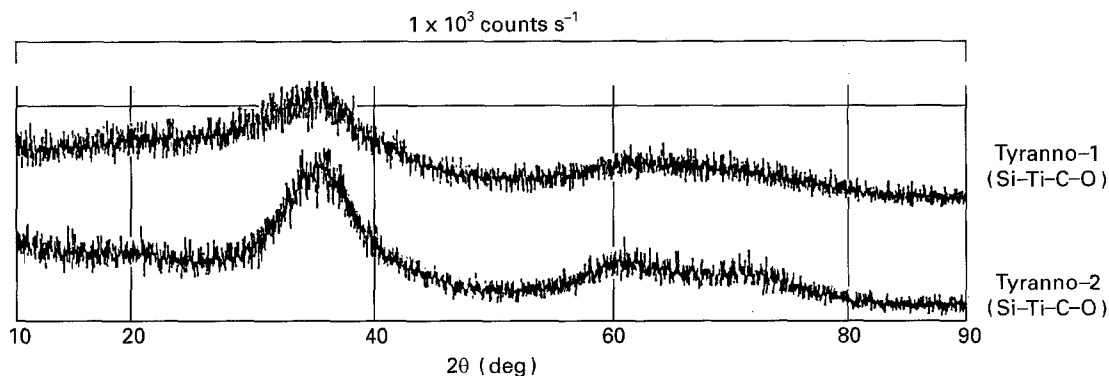


Figure 1 X-ray diffraction patterns of the original Tyranno fibres.

HF-NH₄F solution (HF:NH₄F = 10 mol:2 mol) before measurement in order to eliminate the oxide layer on the fibres.

X-ray diffraction patterns were measured with Rint-5000 using CuK_{α1} radiation at 40 kV and 20 mA. HF-NH₄F solution was used before the XRD measurement for the oxidized fibres.

3. Results and discussion

3.1. Electrical resistivity of Si-Ti-C-O fibres after rapid heat treatment in a nitrogen atmosphere

Fig. 1 shows X-ray diffraction (XRD) patterns of Tyranno 1 and Tyranno 2. The peaks of the two

samples are not sharp; however, the peak intensity of Tyranno 2, is higher than that of Tyranno 1, and the peak of Tyranno 2 at about $2\theta = 65^\circ$ is slightly split [9]. Fig. 2 represents the weight losses of Tyranno 1 and Tyranno 2 after 1 h heat treatment. The weight of Tyranno 1 began to decrease from 1600 K, and the weight of Tyranno 2 began to decrease from 1750 K. Whole weight loss after heat treatment at 1973 K is also larger for Tyranno 1. These decreases in fibre weight are considered to be caused by gas evolution, such as SiO and CO, from the fibres. The possible reaction proceeding with the weight loss is [10]

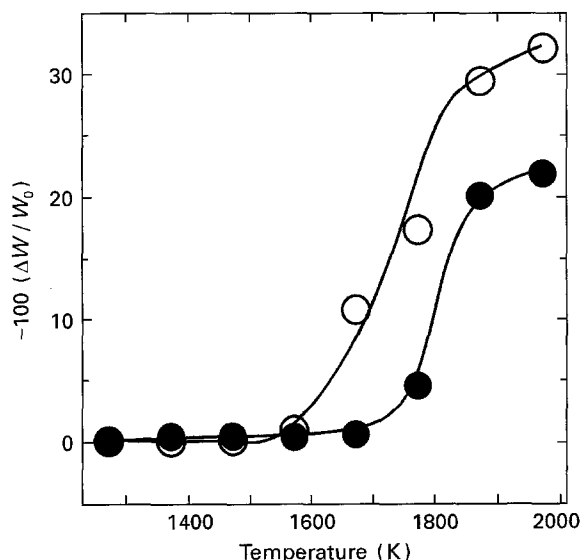
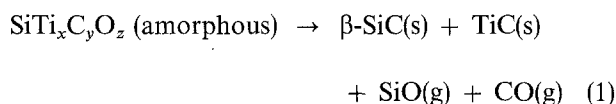


Figure 2 Weight losses of Si-Ti-C-O fibres after 1 h heat treatment in a nitrogen atmosphere.

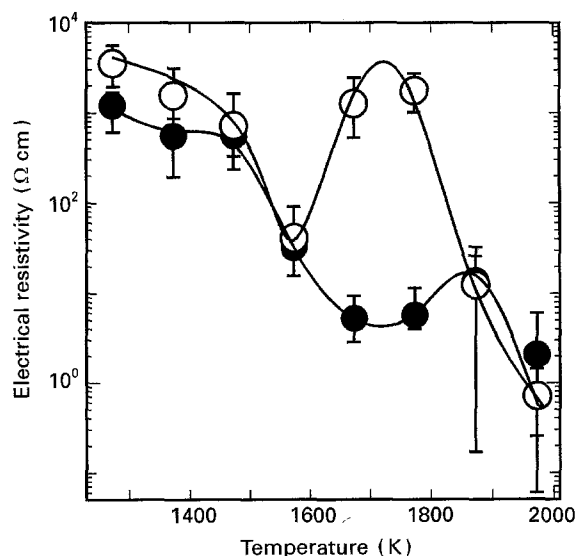


Figure 3 Electrical resistivity of Si-Ti-C-O fibres after 1 h heat treatment in a nitrogen atmosphere.

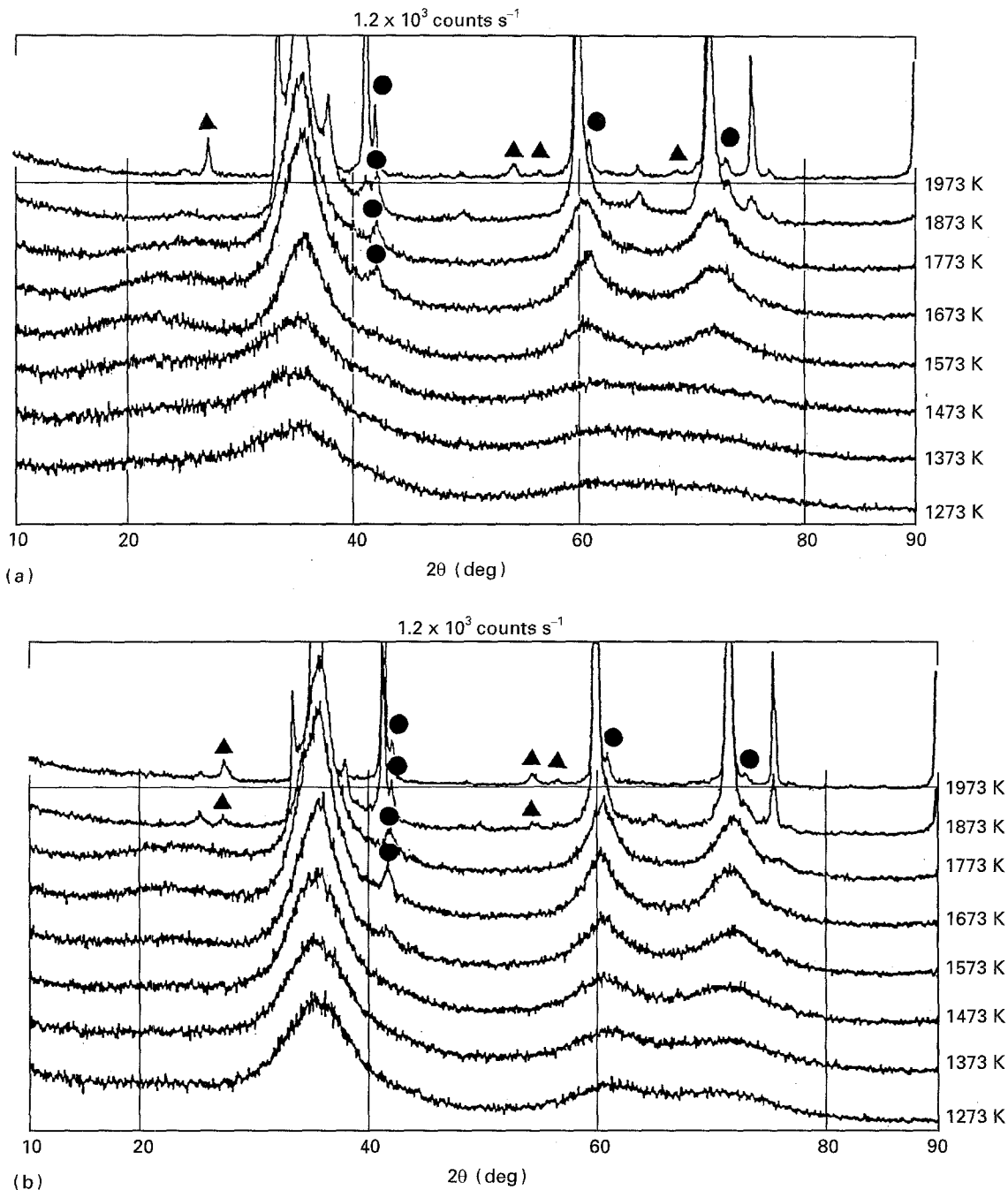


Figure 4 X-ray diffraction patterns of Si-Ti-C-O fibres after 1 h heat treatment in a nitrogen atmosphere: (a) Tyranno 1; (b) Tyranno 2. (●) TiC, (▲) TiO₂.

A small number of hydrogen atoms still remain in the fibres, and they are also possibly evolved in the form of hydrogen gas during heat treatment [11]. The evolution of hydrogen gas, however, has very little effect on the weight loss, because the hydrogen atom is light compared with other elements in the fibres. The results of the XRD studies and the weight-loss measurements reveal that Tyranno 1 has a more amorphous character than Tyranno 2.

Fig. 3 shows the results of the electrical resistivity measurements of Tyranno 1 and Tyranno 2 with varying heat-treatment temperature. For Tyranno 1, the resistivity decreases gradually up to 1573 K, and shows a 10^2 order of increase from 1573–1673 K. After that, the resistivity shows a 10^4 order of decrease, again from 1773–1973 K. For Tyranno 2, the resist-

ivity decreases up to 1673 K and shows a 10^1 order of the small increase from 1673–1873 K, after which the resistivity decreases again from 1873–1973 K. The temperature of the resistivity increase in Tyranno 1 is lower than that in Tyranno 2, and the order of increase is also larger in Tyranno 1.

Fig. 4 shows the results of XRD measurements of Tyranno 1 and Tyranno 2 with varying heat-treatment temperature. Peaks of β -SiC and TiC become clear as the temperature increases in both cases [10]. In particular, a remarkable growth of β -SiC and TiC crystals occurs at about 1873 K. The peaks of TiC in Tyranno 2 show slightly higher intensity than those in Tyranno 1 at 1873 K. No significant differences, however, are observed between the two samples over the whole temperature region, except at 1873 K, although

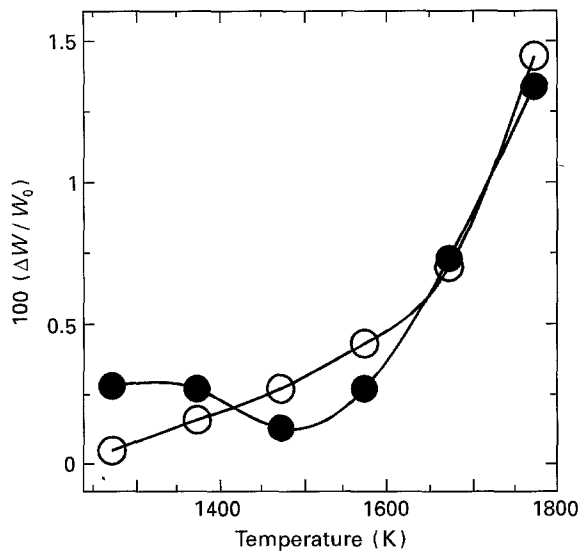


Figure 5 Weight gains of Si-Ti-C-O fibres after 1 h heat treatment in an oxygen atmosphere.

Tyranno 1 begins to release gaseous species at a lower temperature than Tyranno 2 with the change in resistivity. This fact indicates that the observed increases in resistivity are connected with some structural change in the fibres but cannot be explained solely in terms of the growth of the β -SiC and TiC microcrystals.

Such increases in the fibre resistivity have not been observed nor anticipated in former studies. Monthieux *et al.* [4, 5] however, investigated structural evolution in many types of SiC ceramics produced with polymer precursor methods, and emphasized the role of basic structure unit (BSU) stacks of carbon in the resistivity [4, 5]. They observed such BSU stacks on SiC nanocrystals even in heat-treated Si-Ti-C-O fibres [12]. The structural change of carbon during heat treatment may provide some explanation of these unexpected changes in fibre resistivity because XRD measurements are not so sensitive to the carbon structure in the temperature range of our studies.

In our system, the fibres contain a considerable quantity of oxygen and were put into a furnace which had been preheated to the appointed temperature. If the heat-treatment temperature was little different from the temperature used for the Tyranno fibre production, the development of BSU could easily catch up with the β -SiC growth. On the other hand, Raman studies of SiC fibres have revealed that the precipitation of carbon from the excess amorphous carbon competes with the loss of carbon through CO gas evolution [13]. If the heat-treatment temperature is too high to be caught up, carbon is removed from the systems during pyrolysis before BSUs make contact with each other. The SiC nanocrystals directly in contact with each other and the resistivity of SiC nanocrystals should dominate the whole resistivity of the fibres in this case. This idea has not yet been confirmed, but is still being considered as an explanation for the relationship between gas evolution and fibre resistivity.

We have found that the SiC crystals begin to be surrounded by TiC instead of carbon in Si-Ti-C-O fibres as the pyrolysis process proceeds [14]. The

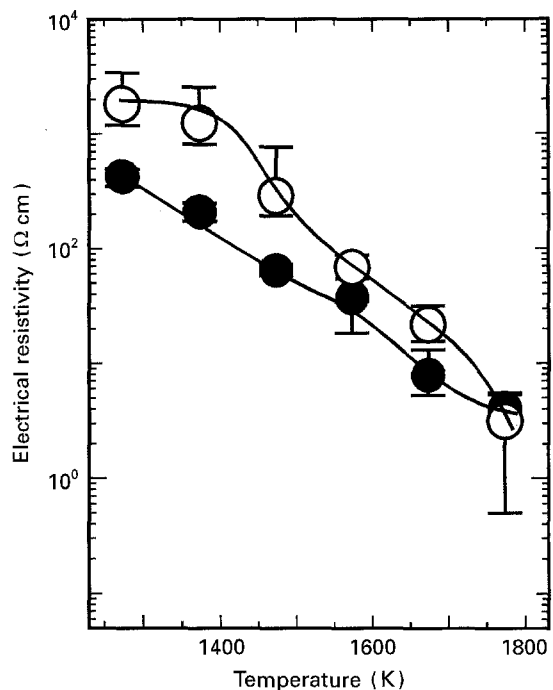


Figure 6 Electrical resistivity of Si-Ti-C-O fibres after 1 h heat treatment in an oxygen atmosphere after eliminating the oxide layers.

second decreases in the fibre resistivity shown in Fig. 3 may be caused by contacts between TiC nanocrystals instead of carbon.

3.2. Effect of oxide-layer formation on the electrical resistivity of SiC fibres

Si-Ti-C-O fibres are known to form an oxide layer on the fibre surface with the heat treatment in an oxidation atmosphere, which consists of cristobalite and rutile. This oxide layer greatly contributes to the high-temperature persistence of Si-Ti-C-O fibres, because the oxide layer suppresses gas evolution from the inner part of the fibre and extenuates the degradation progress [15]. The effect of the oxygen atmosphere on the electrical resistivity of the fibres is very interesting, if the observed increases in resistivity are truly concerned with gas evolution.

Fig. 5 shows the weight gains of Si-Ti-C-O fibres during heat treatment in a pure oxygen atmosphere. The oxide layers thicken as the temperature increases, and the fibres increase in weight. The thicknesses of the oxide layers calculated from weight gains after 1 h of heat treatment at 1773 K were about 0.3 μm in Tyranno 1 and about 0.2 μm in Tyranno 2. No gas evolution was observed up to 1773 K.

Fig. 6 shows the results of the electrical resistivity measurements of the Si-Ti-C-O fibres after 1 h heat treatment in an oxygen atmosphere with varying heat treatment temperature. The resistivity of both samples decreases monotonically as the temperature increases. The resistivity of Tyranno 1 is slightly higher than that of Tyranno 2 because Tyranno 1 retains a more amorphous character than Tyranno 2, even during oxidation. The difference between them tends to decrease as the heat-treatment temperature increases.

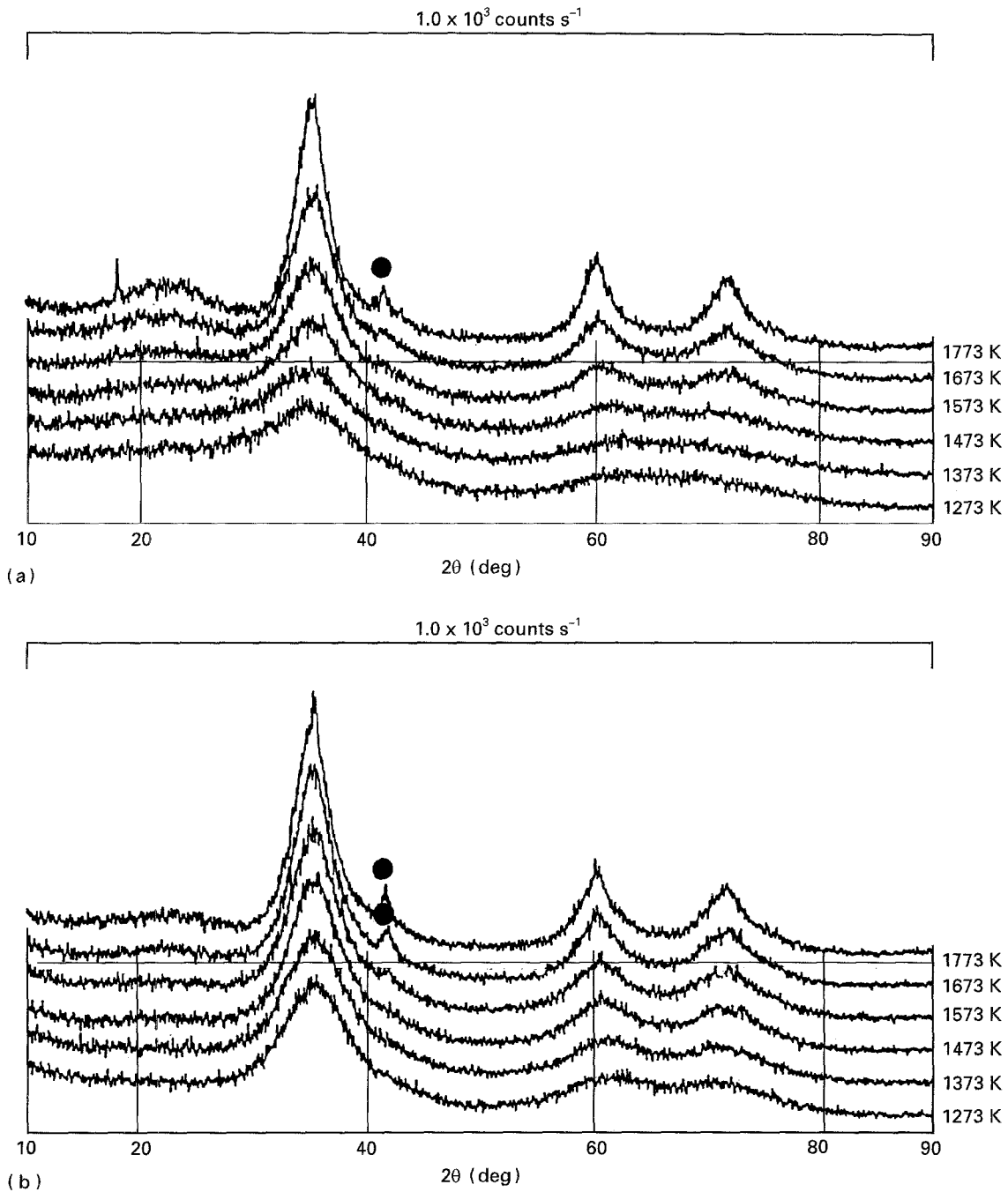


Figure 7 X-ray diffraction patterns of Si-Ti-C-O fibres after 1 h heat treatment in an oxygen atmosphere after eliminating the oxide layers: (a) Tyranno 1; (b) Tyranno 2. (●) TiC.

The region of resistivity increase has disappeared in this case.

XRD patterns of Tyranno 1 and Tyranno 2 heat treated in an oxygen atmosphere for 1 h are shown in Fig. 7. The fibres become crystalline as the heat-treatment temperature increases. The peak intensity of SiC and TiC in the fibre heat treated in an oxygen atmosphere is not much different from the fibre heat treated at the same temperature in a nitrogen atmosphere. Some structural change, however, should have already occurred in the excess amorphous carbon around SiC or TiC nanocrystals, because the oxide layer will have suppressed the elimination of carbon from the systems. Tyranno 1 heat treated at 1773 K in an oxygen atmosphere appears to have a slightly clearer peak at about 23° compared with the fibre heat treated at the

same temperature in a nitrogen atmosphere. This difference may reflect the difference in BSU stacks in Tyranno 1.

4. Conclusion

In the measurements of the electrical resistivity of Si-Ti-C-O fibres subjected to a rapid heat treatment, temperature regions of increasing resistivity were found. These regions depend on the composition of the fibres and correspond to regions of gas evolution from the fibres. During heat treatment in an oxygen atmosphere, gas evolution was suppressed by the oxide layer formed on the fibre surface and the resistivity monotonically decreases as the temperature increases. XRD patterns of the fibres showed that they become

more crystalline as the heat-treatment temperature increases, but the degree of the SiC or TiC precipitation does not directly correlate with the change in resistivity. The contacts between BSUs of carbon around SiC nanocrystals are probably important in the resistivity of Si-Ti-C-O fibres.

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