



## XAFS Analysis of the Structural Change in Si-Zr-C-O Fiber Accompanied by Thermal Decomposition

As the operating gas temperature of gas turbine engines increases year by year in response to issues related to energy and the environment, the materials temperature of such high-temperature parts as the turbine blades, stator, and combustor liner are nearing the limit for adiabatic metallic materials even when cooling is applied. For this reason, there is much interest in studies on the application of ceramic materials in gas turbine engines, and continuous fiber-reinforced ceramic matrix composite (CFCMC) materials, which are expected to exhibit high damage tolerance, are highly promising (Fig. 1) [1]. An experiment has been carried out at beamline **BL01B1** [2].

Figure 2(a) is a schematic illustration of the CFCMC structure. We are now working on process development, parts fabrication technology development, and materials evaluation technology development centered around SiC-based composite materials (Si-Zr-C-O/SiC) that use Si-Zr-C-O amorphous fiber as the reinforcing fiber [3-7].

The decline in strength of Si-Zr-C-O/SiC materials in a high-temperature environment, as is shown in Fig. 2(b), is attributed mainly to the decline in fiber strength due to the thermal decomposition and crystallization of the Si-Zr-C-O fiber, which is mainly responsible for the strength of the Si-Zr-C-O/SiC composite. Also, in ambient air, embrittlement caused by fiber/matrix boundary oxidation may have an effect [4].

Figure 3 is an outline of the Si-Zr-C-O/SiC fabrication process developed by Kawasaki Heavy Industries, Ltd. The Si-Zr-C-O fiber is prepared as a woven pre-form. A thin gradient layer of C/SiC is deposited on the surface of each filament in the pre-form by the CVD method. After the pre-form is impregnated with polycarbosilane xylene solution, it is pyrolyzed to form the SiC matrix [3,4]. As shown in Fig. 3, the Si-Zr-C-O fiber is exposed to a high temperature under reduced pressure and inert gas pressure in the fabrication process. Moreover, the operating environment of gas turbines is high-pressure ambient air. For these reasons, understanding the structural changes in the Si-Zr-C-O fiber in these differing environments should provide a guideline for optimizing the process conditions so as to control the degradation of materials in the fabrication stage or for improving the materials configuration so as to increase durability.

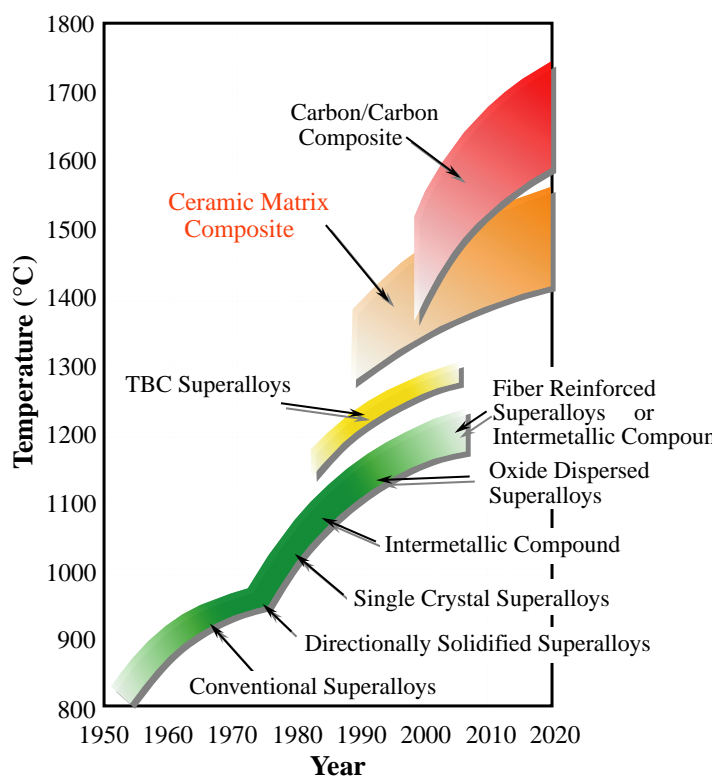


Fig. 1. Development status of heat resistant materials [1].

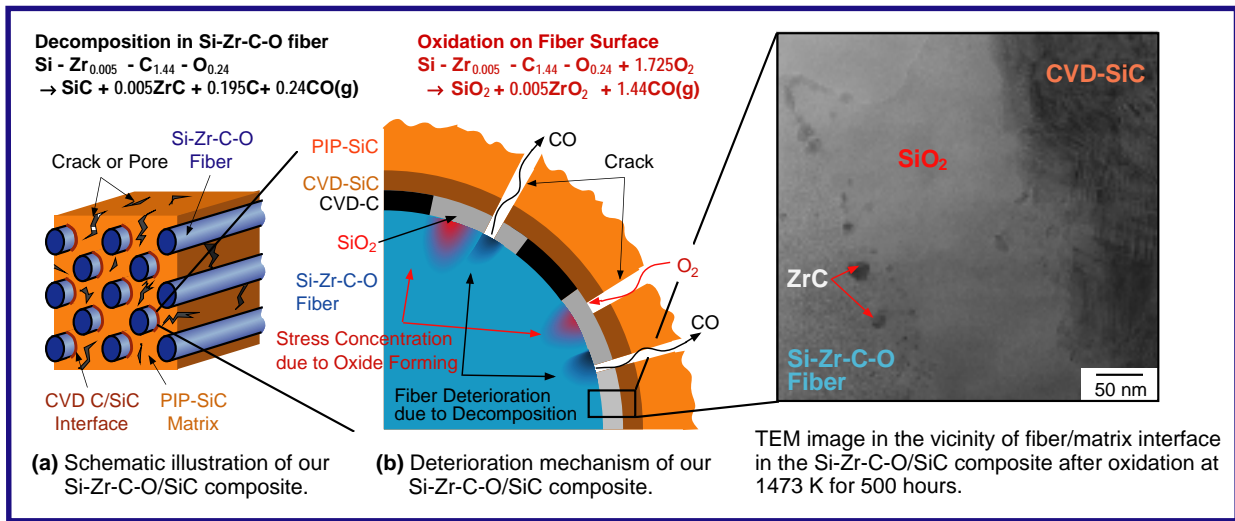


Fig. 2. Schematic illustrations of our Si-Zr-C-O/SiC composite and its deterioration mechanism in ambient atmosphere.

Figure 4 shows the XANES spectra at Zr K-edge of the Si-Zr-C-O fiber after heat treatment at 1673 K, and the zirconium foil. In the Si-Zr-C-O fiber heat-treated in ambient air and argon, the spectra were not much different from that of the as-fabricated fiber. However, in the Si-Zr-C-O fiber

heat-treated in a vacuum, the spectra differed from that of the as-fabricated fiber after just four hours, and underwent an even more pronounced change when treated for 16 hours. This indicates that some kind of the change in the electronic structure of Zr occurred for the fiber heat-treated in vacuum

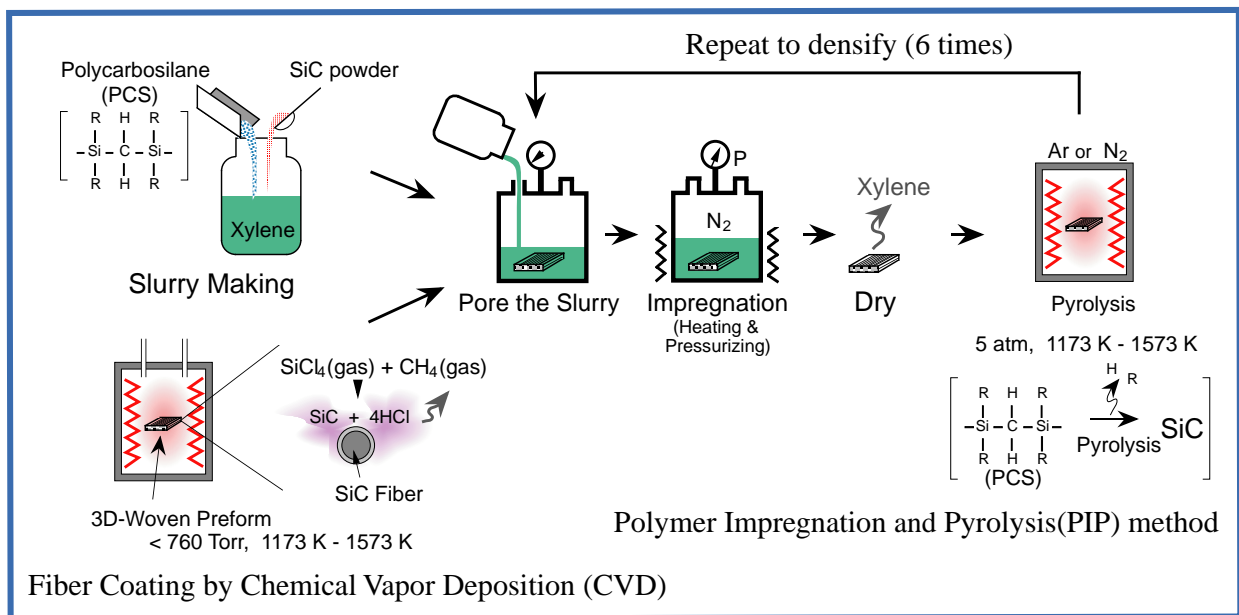


Fig. 3. Schematic illustrations of the fabricating procedure for our Si-Zr-C-O/SiC composite.

in a short time.

Figure 5 shows the Fourier transformation of XAFS spectra at Zr *K*-edge. A significant difference exists between the spectrum of the Si-Zr-C-O fiber heat-treated in ambient air and argon and that heat-treated in a vacuum. The peak near 3 Å, which is characteristic of the fiber after vacuum treatment, is believed to be zirconium because it can also be seen in metallic zirconium foil.

The peak near 4.2 Å in the sample after vacuum treatment is fairly strong despite the great distance, and it is believed to be zirconium with a higher atomic weight. These results reveal that the behavior of zirconium in the crystallization stage varies according to the heat-treatment atmosphere. Because the thermal decomposition of Si-Zr-C-O fiber is accompanied by the formation of carbon monoxide gas as shown by the equation in Fig. 2(b), the reaction can be expected to progress faster in a vacuum than in an argon atmosphere. Comparing the lower three spectrum in detail, the spectrum of the Si-Zr-C-O fiber heat-treated in ambient air and that of as-fabricated fiber are quite similar, but that heat-treated in argon is slightly different from the former two.

It has been reported that when Si-Ti-C-O fiber is heat-treated in ambient air, an oxide film formed on the fiber surface inhibits CO gas emission accompanied with the thermal decomposition of Si-Ti-C-O fiber, and consequently the thermal decomposition is controlled [8]. The same oxide film up to 0.5 μm thick on its surface was found on Si-Zr-C-O fiber heat-treated in ambient air. Therefore it can be supposed that the difference between the spectrum of the Si-Zr-C-O fiber heat-treated in ambient air and that of argon is related to the rate of the thermal decomposition, although further study will be required to conclude this.

Figure 6 shows a comparison of the Fourier transformation of XAFS spectra at the Zr *K*-edge of Si-Zr-C-O/SiC composites, containing Si-Zr-C-O

fiber at about 40 vol.%, before and after high-temperature exposure under various conditions. The spectra for those composites, even when exposed to such a high temperature as 1773 K for as long as 400 hours, exhibited no major differences, and were close to that of the Si-Zr-C-O fiber heat-treated in an argon atmosphere in Fig. 5 rather than that in ambient air. These results suggest that the CVD process, which is conducted in a reduced pressure atmosphere, or pyrolysis step in inert gas, are effective for certain structural changes of the Si-Zr-C-O fiber.

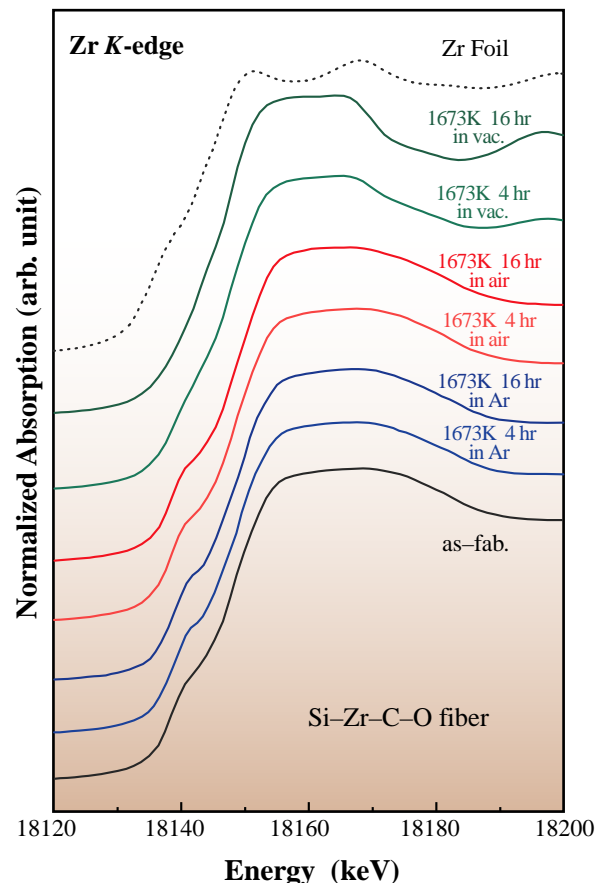


Fig. 4. XANES spectra of Si-Zr-C-O fibers after heat treatment, compared with as-fabricated fiber and Zr foil.

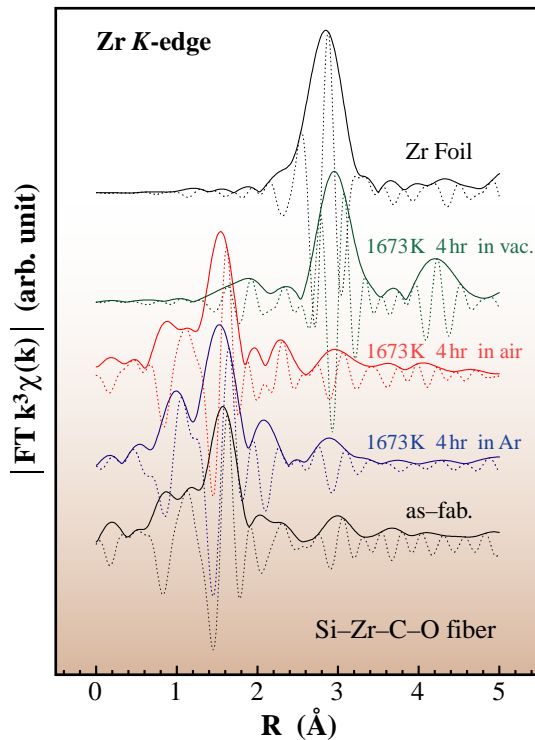


Fig. 5. Fourier transformation of XAFS spectra for Si-Zr-C-O fibers after heat treatment, compared with as-fabricated fiber and Zr foil.

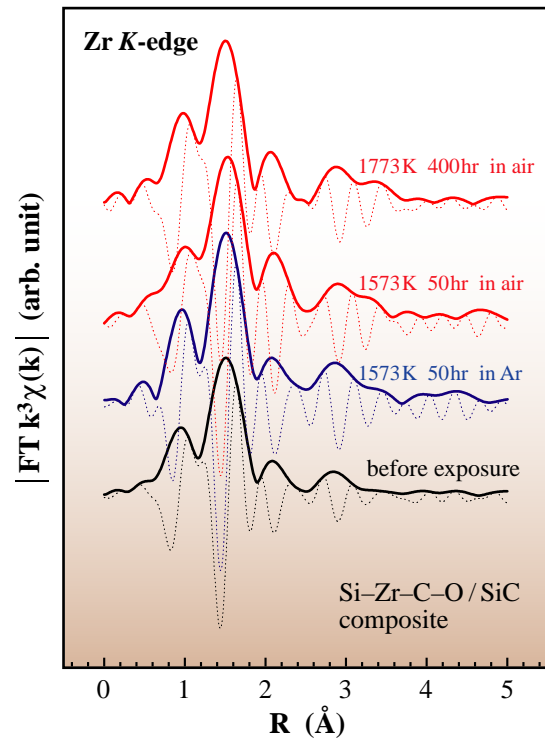


Fig. 6. Fourier transformation of XAFS spectra for Si-Zr-C-O/SiC composites before and after heat treatment.

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