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Materials

Environmental Effects on Microstructural Stability of SiC/SiC Composites

Tamaki Shibayama[1], *Guo Wei He*[1], *Heishichiro Takahashi*[1], *Yutai Katoh*[2], *Akira Kohyama*[2]

1) Center for Advanced Research of Energy Technology, Hokkaido University, Sapporo 060-8628, Japan
2) Institute of Advanced Energy, Kyoto University, Gokasho, Uji 611-0011, Japan
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Abstract: Environmental effects, especially O_2 pressure, often make SiC/SiC composites degraded. In order to investigate the effects on microstructural stability, SiC/SiC composite specimens, made of Hi-Nicalon™ SiC fibers, were annealed under a commercial grade Ar flow and an ultra-high purified Ar flow respectively. The microstructural evolution in SiC/SiC composites was examined by a field emission type high-resolution electron microscopy and a parallel electron energy loss spectroscopy. A possible mechanism for this degradation was discussed.

Key words: ceramic matrix composite; SiC; oxidation; crystallization; interface

Low Z materials have many advantages in nuclear environments, such as less production of radioactive wastes due to substantially low activation, and higher convergent efficiency due to the capability of high temperature operation. Hopkin has discussed SiC-based materials for fusion reactors for many years [1]. Because the monolithic SiC is inherently brittle, the benefit of using Continuous Fiber Ceramic Composites (CFCC) in fusion environments has been proposed in recent years [2,3]. Environmental effects, especially O_2 pressure, often make SiC/SiC composites weak. References [4–6] gave various criteria for the effects on microstructural evolution at the interfaces of SiC/SiC composites, however, there are few data for nano-structure analyses [7]. Recently, of interest is that the degradation of the composites was observed after annealed at 1 500 ℃ under an ultra-high purified Ar flow condition [8–10]. This paper examined the environmental effects on the microstructural stability of SiC/SiC composites by a high-resolution electron microscopy (HR-TEM) and a Parallel Electron Energy Loss Spectroscopy (PEELS), and proposed a possible mechanism for this degradation.

1 Experimental

Hi-Nicalon™ SiC fibers were chosen to produce two-dimensional (2D) SiC/SiC composites in this study. The sizing of SiC fibers was not removed, and 2D cloths are laid up. The SiC fiber preform which was composed of seventh cloths by a 2D woven of Hi-Nicalon™ fibers was dipped into the phenol resin solution and then rigidized prior to chemical vapor infiltration (CVI) process. Following the rigidization, the preform was heated up to 1 000 ℃ in Ar and then a carbon interface was applied to the preform by decomposition of the phenol resin. Finally, all materials for this round Robin test were fabricated by the conventional Isothermal Chemical Vapor Infiltration (ICVI) method. The typical process time for CVI was one week, because of some discontinuous internal inspection. More detailed fabrication process is reported in reference [11].

Some specimens were annealed at 1 500 ℃ for 1 h with a heating rate of 100 ℃/h under a commercial grade Ar (>99.999%) flow and an ultra-high purified Ar flow, whose O_2 contents is less than 0.2×10^{-6} and $< 0.1 \times 10^{-9}$ in mass fraction, respectively. The moisture and oxygen can electrically remove by an ultra-dry gas generator, KDG-02. It is a new principle to using an oxygen ion conductor consisted of yttria stabilized zirconia (YSZ). Kaken Co. Ltd. in Ibaraki, Japan is applying for a patent on the details of the removal mechanism for the moisture and oxygen. SiC/SiC specimens were air cooled after the heat treatment.

The density measurement and Vickers micro indentation tests of SiC/SiC specimens were also conducted. Fractography was discussed by a Scanning Electron Microscope (SEM).

The environmental effects on microstructural evolution in SiC/SiC composites were also examined by the JEOL-2010F. The FE-TEM has an electron energy loss spectrometer (Gatan model 766) and a post column energy filter (Gatan imaging filter, Gatan model 678). PEELS point analysis was also conducted to reveal the

chemical bonding state in the nano-structure between SiC fibers and SiC matrixes by FE-TEM. The spherical aberration (C_s) and the chromatic aberration (C_c) are 0.5 and 1.1 mm, respectively. The energy resolution of this microscope is 0.8 eV.

2 Results and Discussion

Figure 1 shows the HRTEM image of SiC/C/SiC layers. A bright contrast region is observed between the carbon interphase and the SiC fiber. It is 3 or 4 nm thick. In general, it is well known to distribute the oxygen-enriched phase, *e.g.* SiO_xC_y, homogeneously in the

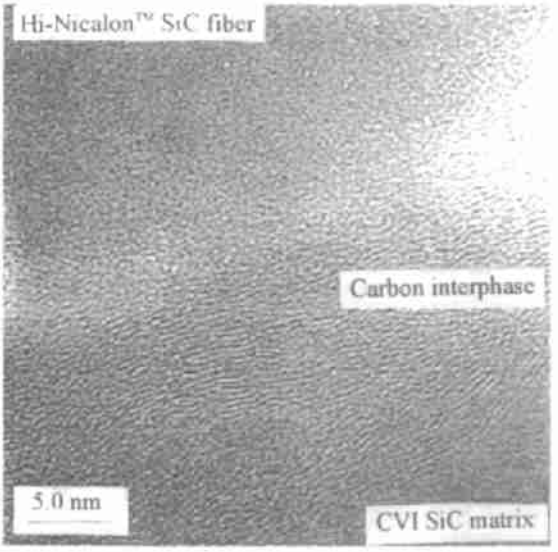

Figure 1 HRTEM photograph of SiC fiber/carbon phase/SiC matrix.

SiC fiber. However, this result suggests that a thin layer might be existed near the surface of the SiC fiber. **Figure 2** shows the PEELS spectrum of carbon interphase as received specimens. π^* peak which corresponding to π bonding orbital around 285 eV is visible. Therefore, the carbon interpahse is found to be graphite. Nevertheless, the crystallization could not be good, because the intensity of π^* peak is not so high. Hi-Nicalon™ SiC fibers show higher performance at high temperature than ceramic grade (standard) Nicalon™ fibers due to low oxygen contents, and show nano SiC crystalline structure in the SiO_xC_y fiber matrix. The tensile strength and elastic coefficient of Hi-Nicalon™ SiC fibers are higher than that of standard Nicalon™ SiC fibers. The measured density of 2D Hi-Nicalon™ SiC/CVI SiC composites was between 2.8 and 2.9 g/cm^3. **Figure 3** shows the SEM micrographs of SiC/SiC composites after Vickers micro indentation tests (a) as-received and (b) annealed at 1 500 ℃ for 1 h in an ultra-high purified Ar flow. In as-received specimens, cracks stopped at SiC/SiC interfaces, such as carbon interphases. On the other hand,

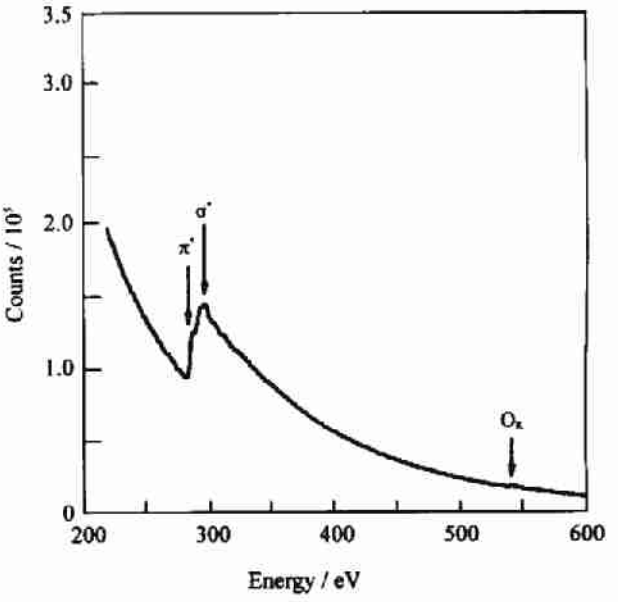

Figure 2 PEELS spectrum of carbon interphase of SiC/SiC composite as-received.

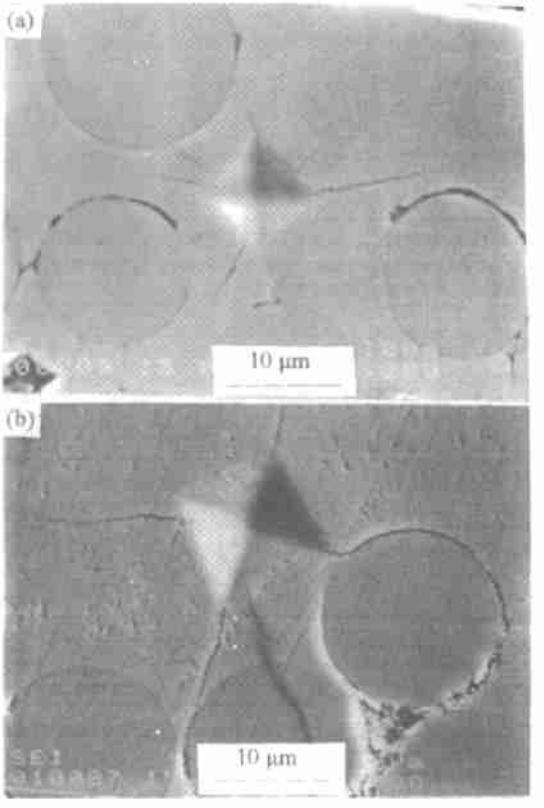

Figure 3 SEM photographs after Vickers micro indentation tests (a) as-received and (b) annealed at 1 500 ℃ for 1 h under ultra-high purified Ar flow.

cracks penetrated through carbon interphases during annealed in a high purified Ar flow. The SiC fiber was also divided two pieces in figure 3(b). One possible reason for this degradation is that the sintering occurs between SiC fibers and SiC matrixes. The other is the self-decomposition of SiC fibers for quite low O_2 partial pressure during annealing process. Hi-Nicalon™ SiC fibers are produced by electron beam curing pro-

cess. This process can effectively reduce the oxygen content in mass fraction from 10% in standard Nicalon™ fibers to the value less than 0.5% in Hi-Nicalon™ fibers. However, the siliconoxycarbide is remained in SiC fibers. Therefore, high O_2 partial pressure leads to a self-decomposition of SiO_xC_y phase in SiC fibers according to

$$SiO_xC_y + O_2 \rightarrow xSiO(g) + (x+y-1)C(s) + (1-x)SiC(s) \quad (1)$$

From equation (1), the siliconoxycarbide phase could be also decomposed by self-containing oxygen in SiC fibers. This phase would be a by-product of the oxygen cross-linking step through fibers processing by oxygen residue in raw materials. Therefore, in general, Hi-Nicalon™ contains little oxygen yet and it could be caused self-decomposition at high temperature. It is the essential procedure to reduce the oxygen to develop the improved SiC/SiC composites for near future. Free carbon in SiC fibers and carbon interface layers can be oxidized in high O_2 partial pressure environments according to

$$C + 1/2\,O_2 \rightarrow CO \quad (2)$$

While CO gas diffuses to the outer surface, some CO gas penetrates to the intra bundle porosity insides of SiC/SiC composites through microvoids and cracks.

In the commercial Ar gas flow condition, it is continued to supply oxygen to the SiC/SiC composites. However, SiC phase can be oxidized to

$$SiC + 2/3\,O_2 \rightarrow SiO_2 + CO \quad (3)$$

Then a thin SiO_2 layer forms around the surface of SiC/SiC composites. Finally, the SiO_2 layer was not completed to cover the surface and the interface of SiC/C/SiC through annealed at 1 500 ℃ for 1 h in a commercial Ar flow. On the other hand, in an ultra-high purified Ar flow, O_2 partial pressure is quite low. Therefore, it is hard to oxidize the carbon interfaces of SiC fibers and SiC matrixes. Hi-Nicalon fibers are decomposed according to the following reaction [12]:

$$SiC_xO_y \rightarrow SiC(s) + C(s) + SiO(g) + CO(g) \quad (4)$$

After the decomposition of SiC fibers, the new SiC crystalline would be grown on the surfaces of Hi-Nicalon fibers according to the following reaction [13]:

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \quad (6)$$

As mentioned above, the carbon layers disappeared and slightly sintered were occurred between SiC fibers and CVI SiC matrixes. Then carbon interface layers were missed and slightly sintering occurred between SiC fibers and CVI SiC matrixes above by-productive reaction. However, oxygen-enriched layers in SiC/C/SiC interfaces were observed by HRTEM observation. The elemental mapping images of SiC/C/SiC interfaces are shown in **figure 4**. The oxidized reaction

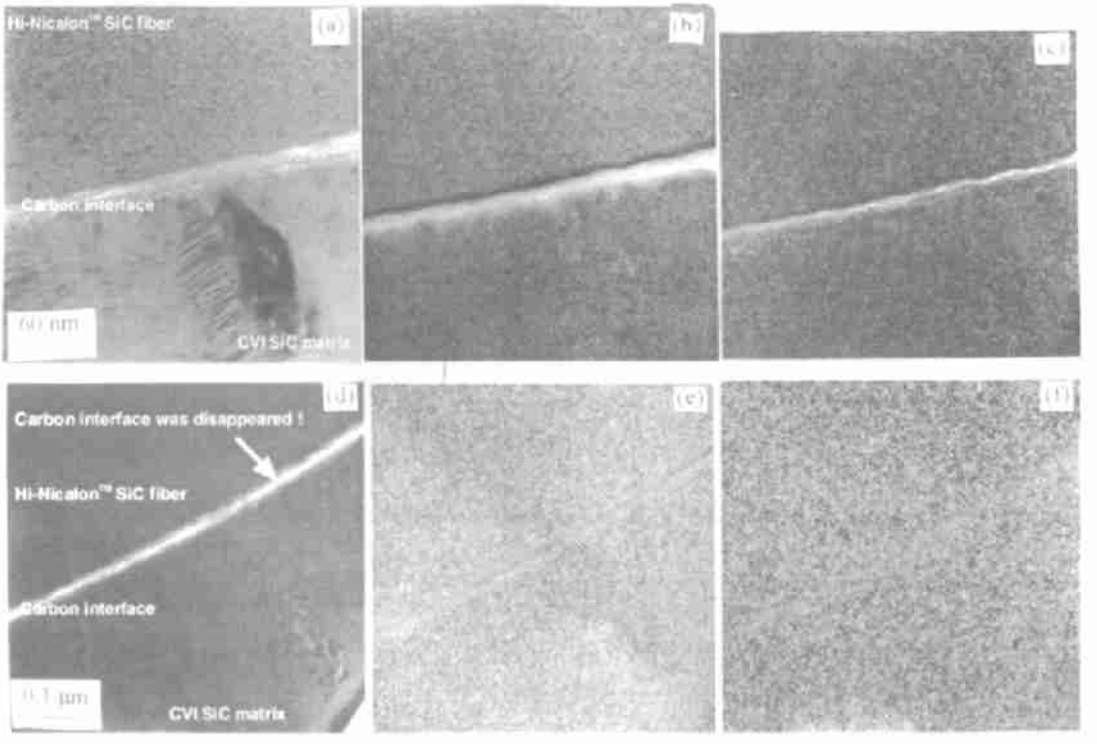

Figure 4 Elementary mapping images of ternnaly interface in SiC/SiC composites by GIF (a), (b) and (c) as received, (d), (e) and (f) annealed at 1 500 ℃ for 1 h in ultra-high purified Ar flow (the mass fraction of O_2 is less than 10^{-6}).

of SiC fibers, carbon interfaces and CVI SiC matrix were also happened in a quite low O_2 partial pressure environment due to supply oxygen from oxygen-enriched layers between SiC fibers and carbon interfaces. SiC/SiC composites were substantially degraded during annealed in the ultra-high purified Ar flow. This degradation mechanism could be supported by the microstructural observation and energy filtering technique.

3 Conclusions

(1) In a commercial Ar flow, SiC fibers, carbon interface layers and CVI SiC matrixes are oxidized. SiC fibers are also decomposed by oxygen. Therefore, slightly degradation occurs during annealing. However, it was not enough time to introduce the catastrophic degradation of SiC/SiC composites at 1 500 ℃ within 1 h.

(2) In an ultra-high purified Ar flow, none of three components is oxidized. However, SiC fibers are self-decomposed by self-containing oxygen and oxygen-enriched layers around SiC fibers. Carbon interface layers are also disappeared by reaction of oxygen from oxygen-enriched layers. Therefore, carbon interface layers are missed and slightly sintering occurs between SiC fibers and CVI SiC matrixes. Then this scenario leads to substantially the degradation of SiC/SiC composites.

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