Effect of CO$_2$ partial pressure on oxidation of low-oxygen SiC fibers (Hi-Nicalon) in Ar-CO$_2$ gas mixtures

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The oxidation behavior and thermal stability of Si–C fibers (Hi-Nicalon) in Ar-CO$_2$ gas mixtures were investigated at 1773 K, through mass change determination, XRD analysis, resistivity measurement, SEM observation and tensile tests. Mass gain and cristobalite formation were observed at $p_{\text{CO}_2} \geq 10^3$ Pa, showing the occurrence of passive-oxidation of the fibers. On the other hand, the active-oxidation was characterized by the mass loss, no formation of SiO$_2$ film and a marked increase in resistivity at $p_{\text{CO}_2} \leq 5 \times 10^2$ Pa. The oxygen potential for the active-to-passive oxidation transition in Ar-CO$_2$ gas mixtures was nearly identical to that in Ar-O$_2$ gas mixtures. About 50% of the strength in the as-received state was retained after the active-oxidation in Ar-CO$_2$ gas mixtures.

1. Introduction

Polycarbosilane-derived silicon carbide fibers are of great importance as reinforcing materials of ceramic matrix composites (CMC) for high-temperature applications. The high-temperature stability and oxidation resistance are required for fabrication and service of such fiber-reinforced CMC. Therefore, the microstructure, microchemistry, mechanical properties and thermal stability have been extensively investigated for the silicon carbide fibers after high-temperature exposure in inert environments (Ar, N$_2$ and vacuum) and oxidizing environments (O$_2$ and air). The combustion environments have been changed over a wide range of oxygen potentials. As a result, silicon carbide fibers can be oxidized in either the passive-oxidation regime or the active-oxidation regime. Since the passive-oxidation allows the surface of silicon carbide fibers to be coated with a stable SiO$_2$ film under high oxygen potential, further oxidation can be retarded. On the other hand, the active-oxidation causes the evaporation of SiC in the fibers producing SiO gas under a low oxygen potential, resulting in a marked degradation of fiber strength. While there were numerous reports on the passive-oxidation of silicon carbide fibers [1–21], there was little information on the active-oxidation of silicon carbide fibers. The authors have investigated the oxidation behaviors for various types of polymer-derived silicon carbide fibers in Ar-O$_2$ gas mixtures ranging from active-oxidation to passive-oxidation region [22–24]. CO$_2$ gas is necessarily present in the combustion environments. Therefore, further investigations of the oxidation of silicon carbide fibers throughout a wide range of CO$_2$ concentrations are important. Therefore, the oxidation of Nicalon and Hi-Nicalon fibers (Nippon Carbon Co., Japan) has been studied in pure CO$_2$ gas [25, 26]. The exposure of the fibers at 1773 K in CO$_2$ gas showed the mass gain and silica formation which are characteristic of passive-oxidation. The reduction in CO$_2$ partial pressure appears to cause the transition from passive-oxidation to active-oxidation. In the present work, the CO$_2$ partial pressures were controlled by diluting CO$_2$ gas with Ar gas. The oxidation behavior of Hi-Nicalon fibers at 1773 K under CO$_2$ partial pressures from $10^2$ to $10^3$ Pa was studied through mass change determination, X-ray diffraction analysis, resistivity measurements, scanning electron microscopic observation and tensile tests. The CO$_2$ partial pressure for the active-to-passive oxidation transition was determined for Hi-Nicalon in Ar-CO$_2$ gas mixtures. These results were compared with those for the oxidation of Hi-Nicalon in Ar-O$_2$ gas mixtures [23].

2. Experimental method

The samples employed in this study were Si–C fibers (Hi-Nicalon) manufactured by Nippon Carbon Co. (Tokyo, Japan). Hi-Nicalon fibers have a molar composition of SiC$_{1.39}$O$_{0.01}$ and a mean diameter of 14 µm. 500 mg of fibers, 3 cm in length, were charged in a high-purity alumina boat and then were placed in a alumina tube of an SiC resistance furnace. After evacuation, an Ar-CO$_2$ gas mixture was allowed to flow in to the tube at a flow rate of 100 cm$^3$/min. The partial pressure of carbon dioxide was changed over a range from
10^2 to 10^5 Pa (p_N2 = 0 Pa). The sample was heated at a rate of 300 K/min and after holding of 36 ks at 1773 K, it was cooled to room-temperature at 600 K/h.

The mass change of the fibers was determined by weighing before and after oxidation in Ar-CO2 gas mixtures. The existing phases and β-SiC crystallite size of the fibers were determined by X-ray diffraction (XRD). Before the specific resistivity measurements and tensile tests, SiO2 film was removed with NH4OH + HF solution. The fibers oxidized in the active-oxidation region, as it was, were subjected to resistivity measurement and tensile test. The resistivity measurements were performed at room temperature by applying a direct current to a single fiber. Both ends of a fibers were attached, with an electroconductive resin, to copper electrode plates spaced 0.8 mm apart. Ten fibers were tested to determine the average resistivity. Room-temperature tensile tests were conducted using a 10 mm gauge length and a crosshead speed of 2 mm/min. The average of 10 tensile tests was taken as the tensile strength under each oxidation. Morphology of as-oxidized fibers and SiO2-removed fibers were examined by field-emission scanning microscopy (FE-SEM).

3. Results

3.1. Mass change

Fig. 1 shows the mass changes for Hi-Nicalon fibers oxidized for 36 ks at T = 1773 K and p_{CO2} = 10^5–10^7 Pa. There were the mass gains of +5–+7% at p_{CO2} = 10^3 Pa. Hi-Nicalon fibers were oxidized in the passive-oxidation regime in pure CO2 gas (at p_{CO2} = 10^5 Pa) [25]. Therefore, the observed mass gains show the occurrence of passive-oxidation as well. On the other hand, the mass losses of about −0.5% after exposure of 36 ks at T = 1773 K and p_{N2} = 10^5 Pa (in pure Ar gas). Furthermore, they were roughly double the mass loss of −2.3% for compete decomposition of amorphous silicon oxycarbide (SiC_{x}O_{y}) phase in Hi-Nicalon fibers [13]. This result implies that the high-temperature exposure in Ar-CO2 gas mixtures with low CO2 partial pressures caused the thermal decomposition of SiC_{x}O_{y} phase and the subsequent active-oxidation of SiC grains, as well as the exposure in Ar-CO2 gas mixtures of p_{CO2} ≤ 10 Pa [23].

3.2. X-ray diffraction analysis

Fig. 2 shows the X-ray diffraction patterns for the fibers oxidized for 36 ks at T = 1773 K and p_{CO2} = 0–10^3 Pa. The sharp X-ray diffraction peak at 2θ = 2θ reveals that Hi-Nicalon fibers were passively oxidized at p_{CO2} ≥ 10^3 Pa, resulting in the formation of a cristobalite film on the fiber surface. On the other hand, in view of the mass loss (Fig. 1), no detection of cristobalite phase implies the occurrence of active-oxidation at p_{CO2} ≤ 5 × 10^2 Pa.

The apparent crystallite size of β-SiC, D_{lc} was calculated from the half-width value of (111) peak using Scherrer’s formula. Fig. 3 shows the value D_{lc} shows a function of p_{CO2}. The fibers after oxidation at 1773 K have three times larger β-SiC crystallite size (D_{lc} = 14 nm) than the as-received fibers, independently on p_{CO2}. The grain growth β-SiC is thought to be mainly caused by the crystallization of uncrystallized SiC phase in Hi-Nicalon fibers (T ≥ 1473 K) [27]. Thus, Fig. 3 reveals that the oxidation temperature is a controlling factor in the grain growth of β-SiC.

3.3. Fiber morphology

Fig. 4 show the morphologies of the fibers oxidized for 36 ks at 1773 K. All the fibers oxidized in the passive-oxidation region were coated with thick cristobalite film (A–F). The cristobalite film is known to crack during cooling, owing to a large volume shrinkage associated to the cristobalite β → α transition (A and C). Therefore, it is noted that no crack was observed in the cristobalite film formed at p_{CO2} = 10^3 Pa (E). On the other hand, the fracture appearance of unoxidized cores is smooth and glassy (B, D and F). The fiber surface is slightly roughened after exposure at p_{CO2} = 5 × 10^2 Pa (G, H). A further reduction in p_{CO2} value (p_{CO2} = 10^2 Pa) results in a peculiar appearance on fiber surface. As a consequence of active-oxidation, the grooves are deeply scooped in the surface of fiber (I, J). The fiber core displays a glassy fracture surface, as well as that oxidized in the passive-oxidation region, showing that the active-oxidation advances from the surface to the interior.

SEM photos at high magnification are shown in Fig. 5, for the fibers in the as-received state and after active-oxidation. The irregularity of the surface is very weak in the as-received state (A). The active-oxidation, as a consequence of the gasification of SiC grains, causes serious unevenness of fiber surface (B, C).

3.4. Specific resistivity

Fig. 6 shows the specific resistivity of the fibers oxidized for 36 ks at T = 1773 K as a function of p_{CO2}. For the fibers oxidized at p_{CO2} ≥ 10^3 Pa, a cristobalite