Key Engineering Materials *Online: 2008-02-11*
ISSN: 1662-9795, Vols. 368-372, pp 1639-1641
doi:10.4028/www.scientific.net/KEM.368-372.1639

Effect of Heat Treatment on Specific Surface Area of Si-C-O Fibers

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Keywords: Si-C-O fiber; Specific surface area; Heat treatment

Abstract. In this paper, effect of heat treatment on the SSA of Si-C-O fibers was investigated and morphologies of the treated fibers were studied using SEM. The results revealed that weight loss was proportional to the treatment time at 1573K and the specific surface area (SSA) increased sharply when the weight loss reached above 6wt%. A rough and porous ceramic fiber with SSA of 23.76m^2/g could be obtained at the weight loss of 9.1wt%, as a result of the treatment at 1573K for 32h.

Introduction

Polycarbosilane-derived SiC fibers are good reinforcement materials for ceramic-matrix composites (CMCs) [1]. They contain oxygen in an amorphous oxycarbide ($Si_xC_yO_z$) phase. When exposed to elevated temperatures, the $Si_xC_yO_z$ phase crystallizes to β-SiC and generates silicon monoxide (SiO) and carbon monoxide (CO) gas [2-4]. Such thermal decomposition leads to the degradation of fiber strength due to grain growth and porosity increase.

However, the porous SiC fibers may find some special applications in the field gas separation and storage, which requires a much high specific surface area (SSA) with little demand for material strength. Although extensive microstructural and mechanical studies have been conducted for fibers that have been exposed in environments such as argon, air, oxygen, hydrogen-water vapor, and CO at different temperatures and pressures [2-9], little effort was focused on the variation of SSA. So, in this paper, effect of heat treatment in argon on the SSA of Si-C-O fibers was investigated and morphologies of the treated fibers were studied using scanning electron microscopy (SEM).

Experimental Procedure

Polycarbosilane-derived Si-C-O fibers, marked as KD-I, were produced with oxygen content of 18 wt% [10]. Their average diameter and average tensile strength were 13.5μm and 2.60GPa, respectively. The fibers were heat treated at 873K in air for 1 h to remove protective glues, and were cooled to room temperature and weighed, marked as w_1. Subsequently, they were put into a quartz tube and heated to 1573K in an argon gas flow at a heating rate of 10K/min. The fibers were treated at 1573K for a period of time and cooled to room temperature. The cooled fibers were weighed and marked as w_2. Weight loss was calculated according to Eq.1.

$$\text{Weight loss (wt\%)}=(w_1-w_2)/w_1\times 100 \quad (1)$$

Filament strength (25mm gauge length) was tested using a universal testing machine, at a constant displacement rate of 2mm/min until fracture occurred. Peak load and measured cross-sectional area values were used to calculate fiber strength. A minimum of 30 filaments was tested per condition to provide statistical significance to the results.

SSA of the treated and untreated fibers was determined from N_2 adsorption/desorption isotherms. All of the samples were degassed at 573K for 1 h prior to the experiments. SSA was calculated from the adsorption data in the relative pressure interval 0.05-0.30 using the conventional BET method.

Fracture and surface morphologies of the treated and untreated fibers were observed with SEM. Fracture samples were prepared by tensile breaking fibers in oil, dissolving them in ethanol and mounting them on the edge of an aluminum stub using double stick tape with fracture surface facing up. Samples were sputter coated with a layer of Au to enhance their conductivity before observation.

Table 1 Effect of heat treatment on weight loss and SSA of Si-C-O fibers

Sample	Treatment time [h]	Weight loss [wt%]	SSA [m^2/g]	Flow rate of argon [ml/min]	Tensile strength [GPa]
#0	0	0	0.07	-	2.60
#1	5	1.5	0.25	10	2.25
#2	10	2.1	0.28	10	1.92
#3	16	5.0	2.44	10	1.63
#4	10	4.0	5.56	140	1.56
#5	16	6.4	6.38	140	1.24
#6	32	9.1	23.76	140	0.95

Results and Discussion

Variations of weight loss and SSA. Effect of heat treatment on the weight loss and SSA of Si-C-O fibers are listed in Table 1, in which sample #0 is the as-received Si-C-O fiber with tensile strength of 2.60GPa. The relationship between weight loss and treatment time, and those between tensile strength, SSA and weight loss are shown more clearly in Figs. 1 and 2, respectively.

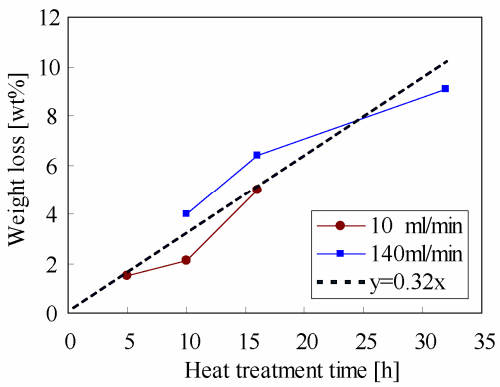

Fig.1 Relationship between weight loss and heat treatment time.

Two flow rates of argon, 140ml/min and 10ml/min, were applied in the study. It seems that the flow rate of argon has some positive effect on the rate of weight loss, e.g., 4.0wt% vs 2.1wt% at 10h, 6.4wt% vs 5.0wt% at 16h. But if the effect was neglected considering the deviation of measurement, as shown in Fig.1, a linear relationship might be found between the weight loss and the treatment time. Its slop is about 0.32wt%/h. This can be understood that the decomposition of $Si_xC_yO_z$ phase (Eq.2) at 1573K is mainly restricted by thermodynamics other than kinetics [4], so the flow rate of inert gas has neglectable effect on the rate of weight loss.

$$Si_xC_yO_z\ (s) = (x-z)\ SiC\ (s) + z\ SiO\ (g) + (y-x+z)\ C\ (s) \quad (2)$$

As shown in Fig.2 (a), the tensile strength decreases slowly as the weight loss increases, being similar to the literature [2-4]. But there is a difference that the decreasing rate is slower in this study. When the weight loss reaches above 9wt%, the tensile strength decreased below 1.0GPa. No further weight loss was studied so as to maintain the fiber shape.

The SSA of the as-received Si-C-O fiber is only ~0.07m^2/g, indicating a very dense surface structure. As shown in Fig.2 (b), the SSA remains no obvious change below the weight loss of 4wt%, and increases sharply when the weight loss reaches above 6wt%. When the weight loss reaches 9.1wt%,

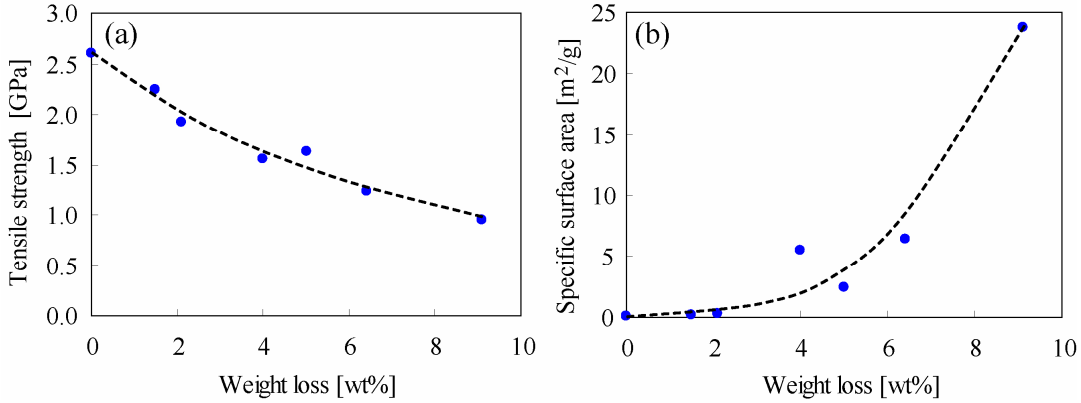

Fig.2 Relationships between (a) tensile strength, (b) specific surface area and weight loss.

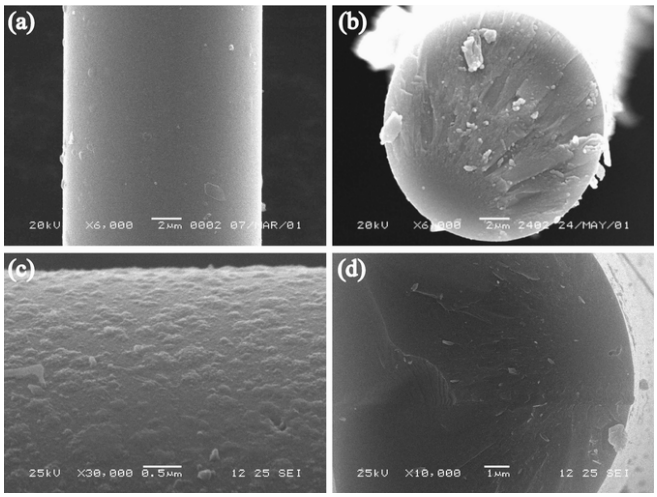

Fig. 3 Surface and fracture morphologies of (a, b) as-received and (c, d) 32h-treated Si-C-O fibers.

SSA of 23.76m^2/g can be achieved.

The exponential-like relationship in Fig.2 (b) is much different from the linear-like relationship in activation of carbon fibers [11], because the activation process forms micro-pores inward from outside while this process is a self-decomposition process forming micropores outward from inside. The sharp increase in Fig. 2 (b) might be the stage that core-to-surface nanochannels come into being.

Morphologies of treated and untreated Si-C-O fibers. SEM morphologies of the as-received and 32h-treated fibers Si-C-O fibers are shown in Fig.3.

As shown in Fig.3 (a, b), the as-received Si-C-O fiber has a smooth surface and a dense body, showing a typical mirror morphology on the fracture surface. This contributes it a high tensile strength, and is in good accordance with its little SSA.

When heat treated at 1573K for 32 hours, as shown in Fig.3 (c, d), the Si-C-O fiber was deposited with many strumaes on the surface and becomes very rough, which is the main reason why tensile strength was much decreased. However, pores can not be seen directly on the fracture surface. It might be inferred that macropores have not yet been formed at this stage and the pore diameters might still in the nanometer scale. This is just the requirement of materials in the field of adsorption, gas separation, gas storage, and so on.

Summary

Rough and porous SiC fibers with much increased SSA can be obtained from Si-C-O fibers by proper heat treatment. The weight loss is proportional to the treatment time and the SSA has an exponential-like relationship with the weight loss. As an example, SSA of 23.76m^2/g can be achieved when the Si-C-O fibers with SSA of 0.07m^2/g are heated at 1573K for 32 hours. No macropores were observed on the fracture surface of the sample fiber.

Acknowledgement

We gratefully acknowledge the financial support of National Natural Science Foundation of China (NSFC, grant number 50403010).

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