Siliciding of carbon fabrics with gaseous SiO

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Abstract. Silicon carbide fabrics were synthesized through siliciding of carbon fiber precursors with gaseous SiO using three original batch-type reactors of different design. The prepared samples were analyzed by XRD and SEM/EDX. It was found that the choice of SiO gas source affected the microstructure characteristics of SiC fiber materials obtained by the proposed method.

1. Introduction

Silicon carbide fibers and fabrics made thereof have attracted much attention due to their superior high temperature thermal stability and mechanical properties [1–4]. Two widespread methods now exist for producing SiC fibers on a commercial scale: i) chemical vapor deposition using methylchlorosilanes as a source gas and tungsten or carbon filaments as a substrate [5]; ii) pyrolysis of polycarbosilane polymer filaments [6]. An alternative cost-effective and convenient way to fabricate SiC fiber materials is through siliciding of carbon fiber precursors with gaseous SiO [7–11]. From a chemical standpoint, this method is based on the conversion of carbon into silicon carbide in a SiO gas environment according to the following reaction:

\[ 2C + SiO_{gas} = SiC + CO_{gas} \]  

(1)

The rate of reaction (1) decreases drastically with growing SiC layer inward the carbon filament, therefore a rather long-term heat treatment is required for the complete conversion of the carbon fiber into SiC one. This is obviously a key limiting factor for productivity of the method, but not when using a high-load batch-type reactor which can produce a large amount of material in a single run. In the present work we aim to demonstrate our technical and technological solutions for siliciding of carbon fabrics with gaseous SiO using laboratory-scale batch-type reactors and also to consider issues concerning the choice of SiO gas source.
2. Materials and methods

Carbon fabric with a surface density of 200 g/m² made of Toho Tenax HTS40-E13-3K carbon fiber (Toho Tenax, Japan) consisting of 3000 filaments 7 μm in diameter was used as a carbon fiber precursor. Siliciding heat treatment procedures were carried out using three original batch-type reactors of different design shown in Fig. 1. The reactor was mounted in a vacuum furnace chamber and heated to 1350–1650 °C depending on the choice of SiO gas source. At temperature above 1300°C, the heating rate was maintained at less than 6 °C/min. The whole duration of heat treatment was not less than 2 hours. The gas pressure in the furnace chamber was maintained at less than 0.1 Pa by continuously pumping out the gaseous products over the entire time of heat treatment. In order to generate SiO gas during siliciding treatment, the following three reactive powder mixtures were used: i) an equimolar mixture of Si and SiO₂; ii) a mixture of SiC and SiO₂ taken in 1:2 molar ratio; iii) an equimolar mixture of activated charcoal and SiO₂. The first one was meant to be a base case, and two others were chosen as alternatives. To prevent deposition of SiO gas on cooled parts of vacuum furnace, the activated charcoal was optionally used as a SiO gas absorber.

The prepared samples were analyzed by X-ray diffraction (XRD) using Ni-filtered CuKα radiation, scanning electron microscopy with energy-dispersive X-ray analysis (SEM/EDX), and high-resolution scanning electron microscopy (HR-SEM).

Figure 1. Laboratory-scale batch-type reactors for siliciding of carbon fabrics with gaseous SiO.

3. Results and discussion

3.1. Synthesis of SiC fabrics through siliciding of carbon fiber precursors with gaseous SiO in batch-type reactors

Schematics of the batch-type reactors we used for siliciding of carbon fabrics with gaseous SiO are sketched in Fig. 2. The single-chamber reactor (1CR) has been described in detail elsewhere [11]. A large volume of the reaction chamber and the simplicity of design are major advantages of 1CR. In other hand, when the volume of 1CR is too large, there is a distinct gradient in siliciding environment along the reaction chamber. To overcome this problem, we have designed the reactors provided with a separate semi-closed reaction chamber where the gas environment is assumed to be rather uniform. The two-chamber reactor (2CR) has an additional separate section for SiO gas absorber. The three-
chamber reactor (3CR) is build of three crucibles where the fabrics to be silicided, SiO gas source and SiO gas absorber are placed separately from each other.

Figure 2. Schematics of the reactors: 1CR (a), 3CR (b) and 2CR (c).

Our experiments proved the efficiency and convenience of the above batch-type reactors. In all cases when the technological requirements have been met, the conversion of carbon fabrics into SiC one was fully completed and no carbon residue was present in the products. According to typical XRD pattern given in Fig. 3, siliciding of carbon fiber materials with gaseous SiO resulted in the formation of cubic polytype of silicon carbide (β-SiC). The content of hexagonal and rhombohedral polytypes of silicon carbide (α-SiC) did not commonly exceed 20 vol %.

SEM images of the SiC fibers prepared by siliciding of carbon fiber precursors with gaseous SiO using Si/SiO$_2$ reactive mixture as SiO gas source are shown in Fig. 4. The obtained SiC fibers have a smooth surface with multiple small longitudinal cracks and grooves but no crucial inner damage. The average crystallite size is found to be about 15–20 nm as determined by XRD and HR-SEM.

Figure 3. XRD pattern of the SiC fibers obtained by siliciding of carbon fiber precursors with gaseous SiO.

3.2. Influence of synthesis conditions on the characteristics of SiC fibers

A good way to improve the characteristics of SiC fibers is through providing much milder conditions for siliciding of carbon precursors. In particular, this could be achieved by decreasing SiO gas pressure in the reaction chamber during siliciding treatment. To confirm or deny this supposition, we have experimented with three different reactive powder mixtures to generate SiO gas by the following reactions:

$$\text{SiO}_2 + \text{Si} = 2\text{SiO} \quad (2)$$

$$2\text{SiO}_2 + \text{SiC} = 3\text{SiO} + \text{CO} \quad (3)$$
\[
\text{SiO}_2 + C = \text{SiO} + \text{CO} \tag{4}
\]

As seen from Fig. 5, SiO gas pressure over the systems SiC–SiO\(_2\) and C–SiO\(_2\) is significantly lower compared to that over the system Si–SiO\(_2\). It would seem that this is an excellent reason to use SiC/2SiO\(_2\) and C/SiO\(_2\) reactive mixtures as sources of SiO gas when "mild" siliciding conditions are needed. However, we have actually found that these alternatives cannot be seriously considered to be better choices to serve as SiO gas sources. Their major drawback is that they favor an enhanced crystal growth causing the surface of the obtained SiC fibers to be too rough.

SEM images of the SiC fibers prepared by siliciding of carbon fiber precursors with gaseous SiO using SiC/2SiO\(_2\) and C/SiO\(_2\) reactive mixtures as SiO gas sources are shown in Figs. 6 and 7, respectively.
The observed effect can be explained as follows. The initial stage of the siliciding process is associated with the nucleation of SiC on the surface of the carbon fiber precursors. The nucleation site density depends on the SiO gas pressure in the reaction chamber. When the partial pressure of SiO gas is low, the number of the nucleation sites is small, and therefore the nucleated crystals can grow to large sizes without spatial constraints. Moreover, in the cases of SiC/2SiO$_2$ and C/SiO$_2$ a much higher temperature compared to that for the case of Si/SiO$_2$ is required for the reaction to proceed. This is also an important matter because crystal growth rate tends to increase with increasing temperatures. Thus, such results do not encourage the use of SiC/2SiO$_2$ and C/SiO$_2$ reactive mixtures to SiO gas generating. It is obvious that the strength characteristics of coarse-grained SiC fibers are much worse than those of fine-grained ones obtained using Si/SiO$_2$ reactive mixture as SiO gas source.

4. Conclusion
Being focused on designing and developing techniques for the synthesis of silicon carbide fabrics, we have demonstrated our technical and technological solutions for siliciding of carbon fiber precursors with gaseous SiO using three original batch-type reactors of different design. We have shown that the
choice of reactive powder mixtures to be used to SiO gas generating strongly influences the synthesis conditions that in turn affects the microstructure characteristics of SiC fibers. The better results were achieved when using equimolar mixture of Si and SiO₂ as SiO gas source.

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