Carbon Fiber-Reinforced SiC Composites Produced by Reaction-Bonding

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反応焼結による炭素繊維強化炭化ケイ素複合体の作製

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Carbon fiber-reinforced SiC composites were prepared by reaction-bonding. The formation of SiC (3C type) took place by a reaction between carbon from phenol resin and silicon powder above 1320°C and completed at 1420°C. This reaction did not damage the carbon fiber, and fiber pull-out was observed on the fracture surface. The bulk density and the flexural strength of these composites were 1.7-1.8 g/cm³ and ~130 MPa, respectively. Impregnation with molten silicon at 1600°C increased the bulk density but decreased the flexural strength, due to the reaction of carbon fiber with silicon.

Key-words: Carbon fiber, Silicon carbide, Reaction-bonding, Fiber-reinforcement, Composites

1. Introduction

Continuous carbon or silicon carbide fiber-reinforced SiC composites have been under intensive development for use in advanced gas turbines, heat exchangers and aerospace structures. Fiber-reinforced SiC composites have been processed by chemical vapor infiltration (CVI)¹⁾⁻⁴⁾ and SiC powder impregnation followed by hot-pressing.^{5),6)} The composites fabricated by CVI have advantages of relatively low processing temperatures, the maintenance of high purity levels, and the potential for near net shape manufacturing of complex structural components. However, CVI processes have the same problems of CVD processes; expensive, corrosive, toxic, explosive reactants, and low deposition rates.⁷⁾ The hot-pressing method offers the ability to make dense products. However, it needs a small amount of liquid-phase sintering aids and fabrication is limited to simple shapes.

Reaction-bonding techniques also have advantages of relatively low processing temperatures, the absence of shrinkage during reaction bonding, and the absence of liquid-phase sintering aids. Fitzer et al.¹⁾ prepared carbon fiber-reinforced SiC composites using reaction-bonding by impregnation of carbon fiber-reinforced carbon composites with liquid silicon. However, it could not seem that silicon mass transfer and the reaction occurred homogeneously into the composites.

The purpose of the present study was to prepare

carbon fiber-reinforced SiC composites by using reaction-bonding techniques from a mixture of phenol resin and silicon powders as the matrix phase.

2. Experimental

The carbon fiber used in this study was CARBON-IC-HM60 (Petoca Co., Ltd., Japan). The average diameter of the fiber was about 10 μm. The average tensile strength and elastic modulus of the fiber were 2.9 GPa and 590 GPa, respectively. The carbon fiber-SiC composites were fabricated by passing the carbon yarn through a mixed slurry (molar ratio of Si/C=1/1) of the silicon powder (<74 μm in size; Osaka Titanium Co., Ltd., Japan), phenol resin (Novolac Type; Hitachi Chemical Co., Ltd., Japan), and ethyl alcohol onto a rotating drum, drying the resultant tape at about 70°C for 20 h and then cutting the tapes into the appropriate length. After the tapes were cut to length, sufficient tape was pressed in a steel die under a pressure of about 50 MPa at 130°C for 1 h. The green density of the compact was about 1.7-1.8 g/cm³. The compacts were heated up to 1000°C for 24 h and subsequently heated to the desired temperature and held at the soak temperature for 1 h in Ar. A sample heat-treated at 1430°C for 1 h was heated up to 1600°C for 20 min in Ar and impregnated with molten Si.

Some specimens were cut parallel to the fiber direction, and the products were determined by XRD using Cu Kα radiation. Flexural strength samples (about 1.5-2.5 mm thick by 10 mm wide with 40 mm long) were ground with a 200 grit diamond wheel. Flexural strength measurements were performed at room temperature using a three-point loading device with a span of 30 mm and a crosshead speed of 0.5 mm/min. Some specimens were cut and polished on copper plate using diamond paste to examine microstructure from SEM backscattered electron images.

3. Result and discussion

The formation of SiC (3C type) took place from about 1320°C and completed at about 1420°C. Residual Si was not observed above 1420°C by XRD (Fig. 1). SEM backscattered electron images of a polished transverse section of heat-treated specimens are

Fig. 1. XRD of the heat-treated specimens.

shown in Fig. 2. Large Si particles (larger than $20\ \mu\text{m}$ in size) are observed together with carbon fiber and carbon at 1320°C (Fig. 2(a)). The backscattered electron image (Fig. 2(b)) differentiates the Si and SiC by atomic number contrast, the Si appearing lighter. White small spots show Cu from polishing the specimen. The formation of SiC occurred below the melting point of Si (about 1410°C) and progresses from the surface of Si particles. This may be due to extremely rapid carbon transport within Si.⁸⁾ Many small pores (dark dots) are observed resulting from the volume change of formation of SiC. Fig. 2(c) clearly shows that SiC matrix was formed homogeneously even in the specimen heat-treated at as low as 1430°C .

The specimens heat-treated at 1430°C have a bulk density of $1.7\text{--}1.8\ \text{g/cm}^3$. Significant densification was not observed during the heat treatments. The theoretical density of this composites might be about $2.6\ \text{g/cm}^3$, when the volume fraction of carbon fiber is 60% ($\rho_{\text{SiC}}=3.2\ \text{g/cm}^3$, $\rho_{\text{C-fiber}}=2.17\ \text{g/cm}^3$). The average of the flexural strength of the specimens heat-treated at 1430°C for 1 h was about 130 MPa.

Fig. 3. Fracture surface of a specimen heat-treated at 1430°C (bar= $50\ \mu\text{m}$).

Fig. 4. Transverse section of a specimen heat-treated at 1430°C for 1 h and impregnated with Si at 1600°C for 20 min (bar= $20\ \mu\text{m}$). White areas represent Cu, light areas Si, gray areas SiC and dark areas carbon fiber.

This value of the flexural strength was not high because of the low bulk density. Figure 3 shows fracture surface of a specimen heat-treated at 1430°C . The fiber pull-out is clearly observed, and the surface of carbon fiber seems to be smooth and clean. This means that the bonding between fiber and matrix is weak, and Si did not attack the carbon fiber.

The specimen heat-treated at 1430°C was impregnated with molten Si in Ar at 1600°C in order to in-

Fig. 2. (a) Transverse section of a specimen heat-treated at 1320°C (bar= $20\ \mu\text{m}$). Light particles are silicon. (b) Transverse section of a specimen heat-treated at 1380°C (bar= $20\ \mu\text{m}$). White spots represent Cu, light particles Si, gray areas SiC, and dark areas either carbon fiber or voids. (c) Transverse section of a specimen heat-treated at 1430°C (bar= $20\ \mu\text{m}$). White spots represent Cu, gray areas SiC and dark areas either carbon fiber or voids.

crease the bulk density. The bulk density of this specimen increased from 1.7 g/cm³ to 2.3 g/cm³ after the impregnation. Figure 4 shows SEM photograph of the polished transverse section of a specimen impregnated with molten Si. Si completely penetrated into SiC matrix, and some carbon fiber reacted with Si. The flexural strength of this specimen was about 60 MPa, and fiber pull-out was not observed on the fracture surface.

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