Influence of Fiber Surface Structure on Interfacial Structure between Fiber and Matrix in Vapor Grown Carbon Fiber Reinforced Aluminum Matrix Composites

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Vapor grown carbon fiber reinforced pure aluminum matrix composites were fabricated by the hot-pressing method below the melting temperature of pure aluminum. The surface structures of the vapor grown carbon fibers and the interfacial structures between the fibers and the matrix in the composite were observed. The precipitation mechanism of crystalline aluminum carbide was also investigated. An interlayer with an amorphous-like structure formed at the interface between the carbon surface structure and the aluminum matrix. This interlayer between the wave or irregular carbon structure and the matrix grew more rapidly than that formed between the linear carbon surface structure and the matrix. The thickness of the interlayer increased with the increased fabrication temperature of the composite. Crystalline aluminum carbide could not easily be precipitated in the composite fabricated below 933 K owing to the thicker interlayer separating the vapor grown carbon fibers and aluminum. By either extending the heat-treatment time to 18 ks or increasing the fabrication temperature to 933 K, we could promote the precipitation of crystalline aluminum carbide in the composite. After heat-treating the composite produced at 933 K, aluminum carbide crystals precipitated from the stacked carbon lamellae at the interface between the fibers and the matrix.

(Received September 24, 2008; Accepted March 5, 2009; Published April 22, 2009)

Keywords: vapor grown carbon fiber, aluminum, composite, amorphous, interlayer, transmission electron microscopy

1. Introduction

Vapor grown carbon fibers (VGCFs), which have been produced from hydrocarbons in the vapor phase, have two different shape: microcoils, tubular shapes.¹,²,³ A floating reactant method has been developed to prepare tubular VGCFs. In this method, iron particles are used as a catalyst that causes the pyrolysis of a gaseous mixture of benzene and methane.³ Carbon atoms are then deposited on the iron particles to form a stack. Tubular VGCFs have been applied in the electrode of batteries and in probes because VGCFs have high electrical conductivity and resistance to corrosion.⁴ Furthermore, VGCFs have excellent mechanical properties and thermal conductivity, and can also be used to reinforce metal matrix composites.⁵ In recent years, VGCFs have been used to reinforce aluminum (Al) matrix composites (VGCF/Al composite), because of their lower cost and easier dispersion in the Al metal matrix composite (VGCF diameter: 80–200 nm, carbon nanotube diameter: less than 100 nm) compared with carbon nanotubes (CNTs), and similar carbon structures of the CNTs.⁶

In many studies,⁷,⁸ the effect of the interfacial reaction on the mechanical properties of Al matrix composites reinforced with carbon fiber (CF) materials has been pointed out. Aluminum carbide (Al₄C₃) crystals nucleate preferentially on contaminants or structural defects on the carbon material surface during the fabrication of a CF reinforced Al matrix (CF/Al) composite.⁹ Upon heat treatment, the Al₄C₃ crystals grow toward Al matrix and connect with other Al₄C₃ reactants to become a continuous reactive zone or layer at the interface in the CF/Al composite. When a longitudinal load is applied to the CF/Al composite, Al₄C₃ crystals induce the concentration of stress, leading to the degradation of the mechanical properties. However, a few Al₄C₃ crystals that form at the tip of CNTs can stabilize the CNTs in the CNT reinforced Al matrix (CNT/Al) composite. It will be useful to improve the mechanical properties of CNT/Al composites, by a hardening mechanism based on Al₄C₃ precipitation.¹² Therefore, it is important to understand the mechanism of Al₄C₃ formation to produce industrially the Al matrix composites reinforced by carbon fiber materials.

In our previous studies,¹³,¹⁴ we investigated the effect of a polyacrylonitrile (PAN) CF surface structure on the interfacial reaction of PAN CF/Al composites used in liquid infiltration fabrication. From our observation and element analysis results, the formation mechanism of Al₄C₃ crystals was suggested to occur by the precipitation of Al₄C₃ crystals from the irregular precursor structure of Al₄C₃ in CF/Al composites after heat treatment. Another study¹⁵ indicated that the growth mechanism of Al₄C₃ crystals after their formation between the CF and the liquid Al involves (1) the dissolution of carbon atoms from CF, (2) the carbon diffusion in the melt and its transport to the growing carbide surface, and (3) the deposition of carbon atoms in the growth steps of the carbide crystal surface.

Because the high temperature of the liquid Al melt results in a large amount of Al₄C₃ precipitation during the composite fabrication process, in previous studies it has been difficult to distinguish between the various interfacial structures of PAN CF in CF/Al composites. Thus, tubular VGCFs with a highly graphitized carbon structure were chosen to reinforce the Al matrix, and this composite was used to explore the formation mechanism of the interfacial reaction.

In this study, first the surface structures of VGCFs were observed. Then, the variation of the interface structure with increasing fabrication temperature or heat treatment time of VGCF/Al composites was investigated. We describe the influence of the VGCF surface structure on the interfacial structure between the fibers and the pure Al matrix in VGCF/Al composites. Moreover, we discuss the formation mech-
anism of Al<sub>4</sub>C<sub>3</sub> in composites fabricated under the melting temperature of pure Al.

2. Experimental

VGCF (Showa Denko Co., Japan, average diameter: 150 nm, fiber length: 10–20 μm, density: 2 × 10<sup>3</sup> kg/m<sup>3</sup>, electrical resistivity: 10<sup>–6</sup> Ωm) reinforced pure Al (Kojundo Chemical Laboratory Co., Ltd, Al: 99.95 mass%, Si: 0.01%, Fe: 0.04%, Cu: 0.005%, powder average diameter: 3 μm, density: 2.7 × 10<sup>3</sup> kg/m<sup>3</sup>) matrix composites were prepared. The internal carbon structure of the VGCFs was determined by X-ray diffraction (XRD; JEOL JDX-11RA). VGCFs were blended by hand with pure Al powder for more than 1800 s. After stirring the mixed powder for 72 h, a uniform powder was obtained using a V-shaped mixer. The uniform powder was hot-pressed under a pressure of 40 MPa and a vacuum of less than 10<sup>–2</sup> Pa to form a cylindrical specimen that was 10 mm in diameter and 6 mm long. Four different VGCF/Al composite samples (with a volume fraction of VGCF of 20%) were fabricated at temperatures of 673, 773 and 873 K for 1.8 ks and at 933 K. For the 933 K composite, the sample was fabricated at 873 K for 1.8 ks then the temperature was held at 933 K for 0.3 ks. The relative densities of the 673, 773, 873, and 933 K composites all exceeded 94% (673 K: 94.2%, 773 K: 96.8%, 873 K: 98.6%, and 933 K: 98.8%). To promote the variation of the interfacial structure between the VGCFs and the Al matrix, the composites produced at 873 K and 933 K were heat-treated. The samples produced at 873 K were heat-treated at 873 K for 1.8 ks and 18 ks. The sample produced at 933 K was only heat-treated at 873 K for 1.8 ks.

The VGCF surface structure and the interfacial structures between the VGCFs and Al were observed immediately by electron microscopy using a scanning electron microscope (SEM; Topcon, SM-520, 15 kV) with energy-dispersive spectroscopy (SEM-EDS) and a transmission electron microscope (TEM; JEOL JEM-2010, 200 kV) with energy-dispersive spectroscopy (TEM-EDS).

Before the TEM observation, the VGCFs were fixed on the mesh without mounting to protect the surface of the undamaged fibers. After milling the block of the composite, the aggregated VGCFs were observed by SEM, but they would have peeled off the sample upon Ar ion milling. Regions in which the VGCFs were well dispersed in the composite were observed and measured by TEM-EDS. Each cylindrical composite sample was cut into pieces. These pieces were thinned to 100 μm using sand paper without water or the use of a diamond polishing compound. Then, they were ion-milled (ion source: 4 keV, Ar<sup>+</sup>, irradiation angle: 12°). The nanostructures on the VGCF surface were analyzed by a fast fourier transform (FFT) and an inverse fast fourier transform (IFFT) using Digital Micrograph software (Version 3.6.5, Gatan).

3. Results

3.1 Structure of VGCFs

Figure 1 shows X-ray diffraction profiles of the VGCFs and the PAN Cf. The half width of the VGCF carbon (002) plane peak was the lowest (VGCF: 0.539, graphitized PAN: 0.261, carbonized PAN: 0.351). The VGCF axis direction is shown in Figure 2 (a) and (b), and the SAD patterns are shown in Figure 2 (c) (002).
Cf: 2.6, carbonized PAN Cf: 4.7). This result indicates that the VGCFs had the most highly graphitized carbon structure in their interior. Figures 2(a) and 2(b) show the external appearance of the VGCFs with a diameter of about 200 nm and a length of about 5 \( \mu \)m. For the same VGCF, some segments of the fiber appeared to be straight, while other segments showed a curvature. And the VGCF tip was polygonal or hexagonal. The microstructure of a VGCF is shown in the TEM image (Fig. 2(c)). The black lines show the carbon lamellar structure of the VGCF. The inner axle center appeared as a hole. However, the surface structures in the region from the surface of the VGCF to about 10 nm depth were found to be not completely uniform after observing the whole VGCF along the direction of the fiber.

Fig. 3 TEM images and FFT patterns of VGCF carbon surface structures: (a) linear carbon structure, (b) wave carbon structure, and (c) irregular carbon structure.

Fig. 4 Interface between the VGCFs and the Al matrix in VGCF/Al composites fabricated at (a) 673 K for 1.8 ks, (b) 773 K for 1.8 ks, (c) 873 K for 1.8 ks, and (d) 933 K (873 K for 1.8 ks then 933 K for 0.3 ks).
axis. Figure 3 shows three types of surface structure near the VGCF surface. Figure 3(a) shows long linear carbon lamellae and their FFT pattern. The spots of this pattern correspond to carbon (002) and (100) lattice planes. The linear lamellae were regular carbon (002) lattice planes that were stacked in an orderly manner in the direction (c-axis) perpendicular to fiber axis. Thus, the FFT pattern clearly exhibited small spots. Figure 3(b) shows a wave carbon structure which was observed commonly in the curved section (Fig. 2(b)) of the VGCF. Its FFT pattern retained only the spots of carbon (002) lattice planes, which were larger and less clear than those of the linear carbon structure. The carbon lamellar length ($L_a$) was determined to be about 2–5 nm from this FFT pattern. In addition, an irregular carbon structure was observed, whose FFT pattern appeared as a circular spot was shown in Fig. 3(c). This carbon structure was shorter with a $L_a$ about 1.59 nm and less regular than the wave carbon structure.

3.2 Interfacial structure between fibers and matrix in VGCF/Al composites

Figure 4 shows the interfacial structures between the VGCFs and the Al matrix in VGCF/Al composites fabricated at 673, 773, 873, and 933 K. Except for the 933 K sample (Fig. 4(d)), crystalline Al$_4$C$_3$ was not present at the interface between the VGCFs and the Al matrix (VGCF/Al interface) according to the images of the 673, 773, and 873 K composites (Figs. 4(a), 4(b), and 4(c)). Figure 5, however, shows that an interlayer with an amorphous-like structure and about 5–10 nm thickness formed in the 873 K composite. Thus, the effects of the VGCF surface structure and the VGCF/Al composite fabrication temperature on interlayer formation were investigated. The result of which are shown in Figs. 6 and 7 respectively. The VGCF surface structures were distinguished and determined by FFT analysis. Figures 6(a) and 6(b) show the VGCF/Al interface in the 673 K composite. An interlayer with an amorphous-like structure and about 2 nm thicknesses clearly appeared between the irregular carbon structure and the matrix. Figure 6(c) shows the VGCF/Al interface in the 773 K composite. The linear and wave carbon structures were simultaneously produced at the interface. Between this combination of carbon structures and the matrix, an interlayer formed with a thickness of about 2 nm. Figures 6(d) and 6(e) show the interfaces in the composites produced at 873 K. The interlayer between the wave carbon structure and the matrix was thicker (about 10 nm) than that between the linear carbon structure and the matrix (about 4 nm). Using these results, the relationship between interlayer thickness and fabrication temperature is shown in Fig. 7. The interlayer with the amorphous-like structure between the linear carbon structure and the Al matrix was thinner than that between the wave or irregular carbon structure and the matrix at the same fabrication temperature, and the interlayer thickness increased with increasing temperature below the Al melting point.

3.3 Crystalline Al$_4$C$_3$ formation in VGCF/Al composites after heat treatment

VGCF/Al composites produced at 873 K and 933 K were heat-treated at 873 K. Figure 8 shows images of the interfacial structure of the 873 K composites heat-treated
at 873 K for 1.8 ks and 18 ks. Although the amorphous-like interlayer was still observed between the VGCFs and the Al matrix in the high-magnification image, no crystalline $\text{Al}_4\text{C}_3$ formed at the VGCF/Al interface shown in the low-magnification image in Fig. 8(a). Crystalline $\text{Al}_4\text{C}_3$ was observed in addition to the amorphous-like structure at the VGCF/Al interface after heat-treating at 873 K for 18 ks as shown in Fig. 8(b). Figure 9(a) shows crystalline $\text{Al}_4\text{C}_3$ adjacent to the amorphous-like structure in the composite produced at 933 K. Crystalline $\text{Al}_4\text{C}_3$ was not only observed adjacent to the amorphous-like structure (Fig. 9(b)), but was also clearly observed to be precipitated from the stacked carbon planes (Fig. 9(c)) in the composites after heat-treating VGCF/Al composites at 873 K for 1.8 ks.

### 4. Discussion

#### 4.1 Structure of VGCFs

The carbon structures of VGCFs were observed and investigated closely. The VGCFs had a more highly graphitized internal carbon structure than the PAN Cf according to the X-ray analysis result, because they are fabricated by vapor phase growth. Three different structures, the linear carbon structure, wave carbon structure, and irregular carbon structure, existed within 10 nm depth from the fiber surface in the direction of the VGCF axis. In the FFT analysis of the linear carbon surface structure, the spots in the pattern representing (002) plane were sharp and small. This indicated that the carbon lamellar (002) planes were stacked in an orderly manner with the same spacing...
perpendicular to the direction of fiber axis. The (002) plane spacing was 0.3379 nm according to the X-ray diffraction result. For this structure, (100) plane spots appeared in both the selected-area diffraction (SAD) pattern (Fig. 2(c)) and the FFT pattern (Fig. 3(a)). Figure 10(a) shows the (100) plane IFFT image obtained by a transformation of the (100) spots in the FFT image. Because of the tilted (100) planes, it was understood that the (002) carbon lamellae were stacked by glide plane stacking. On the other hand, the carbon lamellae in the wave carbon structure (Fig. 10(b)) were curved and were inserted into other stacked lamellae to form the dislocation defects. The formation of different carbon structures was due to the different fabrication conditions, such as the rate of carbon precipitation from the crystalline planes of the catalyst, process temperature, and gas flux.

4.2 Interfacial structure of VGCF/Al composites

This investigation indicated the effect of the VGCF surface structure on the interfacial structure between the fibers and the matrix in pure Al matrix composites. Upon fabrication at 933 K, no $\text{Al}_4\text{C}_3$ crystals were formed at the interface in VGCF/Al composites, although in other studies, it was reported that the precipitation of crystalline $\text{Al}_4\text{C}_3$ is possible at the interface between Cf and Al at a fabrication temperature of above 773 K. We consider that the more highly graphitized carbon structure of the VGCFs which exhibits greater stability than the irregular carbon structure is connected with the formation of crystalline $\text{Al}_4\text{C}_3$.

From the observation of the VGCF surface structures, a model of the wave surface structure is suggested in Fig. 10(b). It shows that exposed the free carbon atoms at the edge of the intermittent curved carbon lamella were less stable than other carbon atoms inside this carbon lamella. Furthermore, the bonds of carbon atoms inside a curved carbon lamella are also less stable than those inside a linear carbon lamella (Fig. 10(a)). Gu suggested that the structured defects on the Cf surface lead to the formation of crystalline $\text{Al}_4\text{C}_3$ between the Cf and the Al matrix in Cf/Al composite fabricated by the liquid infiltration method. In this study, the surface structure defects were revealed clearly. The defects of the disordered carbon structure may explain why the interlayer with the amorphous-like structure preferentially formed and was thicker from that formed at the wave or irregular carbon surface structure/Al interface.
After milling the block of the VGCF/Al composite, the VGCFs was exposed (Fig. 11(a)). The amorphous-like structure was also observed on those exposed VGCFs surface (Fig. 11(b)). The SEM-EDS analysis, the results of which are shown in Fig. 11(c), revealed that the quantity of Al element in the amorphous-like structure increased with the increasing fabrication temperature. In previous investigation by TEM-EDS analysis, it was generally indicated that the carbon atoms are melted by liquid Al when Cf comes in contact with liquid Al during the Cf/Al composite formation process. In this case, this behavior was precluded because it was more difficult for the carbon atoms to dissolve in the solid Al matrix than in liquid Al. The solubility limit of carbon atoms, which has been shown to be 0.015 mass% in solid Al is lower than that in liquid Al.

The possibility of a chemical reaction between the free carbon atoms and Al atoms was inferred from our results. Xu\textsuperscript{23} showed that the carbon atoms in CNTs can react with Al to form AlC or AlC\textsubscript{2} in CNT/Al composites hot-pressed at 793 K under a pressure of 25 MPa. Thus, the elements of the amorphous-like structure in our VGCF/Al composite before heat treatment were identified more precisely by TEM-EDS analysis. In the 673 K composite (Fig. 6(b)), the average elemental components in the amorphous-like structure were Al: 0.81 at%, O: 0.2 at%, C: 98.99 at%. In the 873 K composite (Fig. 6(e)), the components of the interlayer were Al: 15.01 at%, O: 12.23 at%, C: 72.76 at%. From this result, it is speculated that this interlayer should be aluminum oxide in the 673 K composite, because of its existence on the Al powder surface before the composite formation process. In the Cf/Al composite, the coating of aluminum oxide on the Cf surface prevents undesirable Cf/Al interfacial reactions.\textsuperscript{24}

An increase in the fabrication temperature of composites may cause an interfacial reaction, thus, the increase in the concentration of Al and O and in the thickness of the amorphous-like structure were observed. Suzuki\textsuperscript{25} has also determined that the interlayer compounds are Al\textsubscript{4}O\textsubscript{4}C and Al\textsubscript{2}OC at the Cf/Al interface in a Cf/Al composite. In our composites, the thicker interlayer separated VGCFs from Al, thus, crystalline Al\textsubscript{4}C\textsubscript{3} was precipitated with difficulty.

When the composites were fabricated near the Al melting point or heat-treated for a long time, crystalline Al\textsubscript{4}C\textsubscript{3} was found at the interface. The carbon structure of the VGCFs can be observed in Fig. 9(c). After heat-treating the composite fabricated at 933 K and under a pressure of 40 MPa, the structure which was consisted of a stack of carbon lamellae became irregular near the VGCF/Al interface where the crystalline Al\textsubscript{4}C\textsubscript{3} was precipitated. The edges of the irregular carbon lamellae were exposed to Al matrix according to this observation. This result appeared that the (100) prism planes of the stacked lamellae contacted with Al. The (100) planes of basic structural units in the graphite have higher specific surface energy than the (002) planes.\textsuperscript{26} Thus, the reaction was occurred more easily because a large number of carbon atoms in the prism planes were directly exposed to the Al matrix.

5. Conclusions

(1) The surface structures of VGCFs include a linear carbon structure, a wave carbon structure, and an irregular carbon structure.
(2) Although no aluminum carbide crystals precipitated at the VGCF/Al interface, an interlayer with an amorphous-like structure forms between the VGCF and the
Fig. 10 Analysis and model of carbon surface structures of the VGCFs by FFT and IFFT: (a) linear carbon structure and (b) wave carbon structure.

Fig. 11 Results of SEM, TEM observation, and SEM-EDS analysis for the exposed VGCFs: (a) SEM image, (b) TEM image, and (c) SEM-EDS analysis result for VGCF surface.
Al matrix in VGCF/Al composites fabricated below the Al melting temperature. The wave carbon structure and irregular carbon structure result in the formation of a thicker interlayer at the VGCF/Al interface in the composites than the linear carbon structure.

(3) Aluminum carbide crystals are found in the composites upon increasing the fabrication temperature or heat treatment time. In particular, aluminum carbide crystals precipitate from the stacked carbon lamellae/Al interface of the VGCF/Al composite fabricated at 933 K then heat-treated at 873 K for 1.8 ks.

Acknowledgements

The experiments in this study were performed at Hiroshima University, Japan. The authors thank Dr. Osamu Yanagisawa, Dr. Kenji Shinozaki, Dr. Atusi Sugeta and Dr. Hiroshi Fukushima at the Department of Mechanical Engineering System for help in the investigation and helpful comments.

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