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Production of Flexible Metal Matrix Composites Reinforced with Continuous Si-Ti-C-O Fibers by Atmospheric Plasma Spraying

Y. Waku, N. Nakagawa, Y. Ohsora, T. Takahashi, K. Shimizu, T. Yamamura, and A. Ohmori

An investigation of the production of aluminum matrix composite sheet reinforced with continuous Si-Ti-C-O fibers was performed by a plasma spraying method. The unidirectionally reinforced Si-Ti-C-O fiber/Al prepreg sheet (300 by 3000 mm, 0.1 to 0.15 mm thick, with 40 vol.% fiber) was fabricated by plasma spraying under atmospheric conditions. The depth of the oxidation layer formed on the surface of the metal matrix composite (MMC) prepreg sheet was found to be about 200 Å, and this value is almost independent of the atmosphere during plasma spraying. The fibers homogeneously disperse and do not contact each other in the matrix of the MMC prepreg. No damage on the surface of the extracted fibers from the MMC prepreg sheet can be observed. The MMC prepreg sheet was used to produce MMC plate by hot pressing at 640 to 680 °C under 9.8 MPa. The flexural strengths in the longitudinal and transverse directions of the MMC plate pressed at 660 °C were 1.0 and 0.25 GPa, respectively.

1. Introduction

METAL matrix composites (MMC) are expected to find commercial application in fields such as aeronautics and automobiles as a lightweight structural material with a high specific strength, specific modulus, and heat resistance. Aluminum matrix composites reinforced with continuous fibers, *e.g.*, B/W,[1] SiC/C,[2] carbon,[3] Al_2O_3,[4] Nicalon SiC fiber,[5] etc., are currently being investigated as candidate materials for these applications. The methods for producing these aluminum matrix composites can be generally classified into two processes. The first method is the squeeze casting process in which aluminum matrix composites are produced by the high-pressure infiltration of molten aluminum into the fibrous preform composed of carbon[6] or SiC fiber[7] that is fixed in the die cavity. The second method is a diffusion bonding process, also known as hot pressing and hot rolling, whereby aluminum matrix composites are manufactured by using intermediate materials such as prepreg sheet unidirectionally reinforced with B/W[1] or SiC/C fiber,[2] and the preform wires are unidirectionally reinforced with carbon or SiC fiber.[8,9]

The squeeze casting process has attracted attention as a method permitting low-cost mass production, making possible the near-net-shape molding of complicated parts. However, this process is not suitable for producing large-size products because of the difficulty in uniform dispersion of the fiber in the matrix, as well as the degradation of the fiber due to chemical reactions between fibers and molten aluminum during squeeze casting.

The diffusion bonding process is generally considered suitable for producing large products, but the process has several technical problems. For example, the aluminum matrix composites produced by hot pressing using the prepreg sheet reinforced with the B/W and SiC/C fiber have excellent mechanical properties. However, it is difficult to produce parts with complex geometry because the large fibers of 100 to 150 μm in diameter lead to low flexibility of the MMC prepreg.[10] On the other hand, the aluminum matrix prepreg reinforced with carbon fiber of 5 to 10 μm diameter have good flexibility, but the mechanical properties are poor.[1]

In this article, the authors consider the use of Si-Ti-C-O fiber[11-13] that is often referred to by the tradename Tyranno Fiber. This fiber not only has high specific strength and specific modulus, excellent heat resistance, and good compatibility with the aluminum matrix, but also sufficient flexibility to make fabrics such as plain weave, braid, and three-dimensional fabrics.[4] The squeeze cast MMC reinforced with Si-Ti-C-O fiber has superior mechanical properties, particularly with respect to high transverse flexural strength compared with the ordinary MMC.[15-16]

The present work aimed to obtain flexible prepreg sheet by using continuous Si-Ti-C-O fiber and using an air plasma spraying method. The MMC plate was produced by hot pressing the prepreg sheet. The mechanical properties and microstructures of the MMC are reported.

Key Words: aluminum matrix, fiber reinforcement, metal matrix composite (MMC), plasma spraying, prepreg sheet, Si-Ti-C-O fiber

Y. Waku, N. Nakagawa, Y. Ohsora, T. Takahashi, K. Shimizu, and **T. Yamamura,** Inorganic Research Laboratory, Corporate Research & Development, Ube Industries, Ltd., Ube City, Yamaguchi, Japan; and **A. Ohmori,** Welding Research Institute, Osaka University, Osaka, Japan.

2. Experimental Methods

2.1 *Preparation of the Si-Ti-C-O Fiber*

The chemical composition and representative mechanical properties of the Si-Ti-C-O fiber used in this investigation are

Table 1 Chemical Composition of the Si-Ti-C-O Fiber

Element	Composition, wt.%
Si	50
C	30
Ti	2.0
O	18
B	≤0.1

Table 2 Physical Properties of Si-Ti-C-O Fiber

Filament diameter, μm	11.1 ± 1.0
Filament/yarn(a)	400
Density at 25 °C, g/cm^2	2.37
Tensile strength, GPa	3.0 to ~3.6
Tensile modulus, GPa	180 to ~200
Tensile strain to failure, %	1.5 to ~2.0
Coefficient of thermal expansion, °C^{-1} (along fiber axis, 0 to ~500 °C)	3.1×10^{-6}
Specific heat, cal/deg/g	0.19 (330 K) 0.23 (670 K)

(a) Yarn is a bundle of filaments.

Table 3 Conditions of Plasma Spraying

Plasma gas	Ar-H_2
Power of plasma, kW	10-30
Powder feed rate, g/min	10-50
Spray distance, mm	70-200

Table 4 Specifications of Si-Ti-C-O Fiber/Al Prepreg Sheet

Fiber arrangement	Unidirectional
Maximum dimensions (measured along fiber axis)	3000 mm long by 300 mm wide
Thickness	0.1 to ~0.15 mm
Volume fraction of fiber	40 ± 2%
Weight	100 to ~120 g/m^2
Matrix	Pure Al (99.5 wt.%)

shown in Tables 1 and 2. The Si-Ti-C-O fiber was synthesized from an organometallic polymer called polytitanocarbosilane (PTC).[11,12] The tensile strengths and the tensile modulus of the fiber, obtained by pyrolysis of the spun and cured PTC fiber at 1300 to 1400 °C, have maximum values of 3.0 to 3.6 GPa and 180 to 200 GPa, respectively. The Si-Ti-C-O fiber retains the amorphous structure up to 1400 °C and has high heat resistance up to 1200 °C in air.[12]

2.2 *Production of MMC Prepreg Sheet and Fiber-Free Aluminum Prepreg Sheet*

Figure 1(a) shows the process of producing MMC prepreg sheet using Si-Ti-C-O fibers. The pure aluminum (99.5 wt.%) powder with a particle size of 45 to 90 μm (Alloy Metals, Inc.) was used for plasma spraying. The following procedure was used to uniformly disperse the fiber in the aluminum matrix. The yarn of Si-Ti-C-O fiber (400 filaments/yarn) was about 1 mm in diameter after production, and it was spread to a width of 3 to 4 mm and a few filaments in thickness after removal of the sizing agent (polyethylaneoxide). These strips of fiber were then wound on a 1000-mm-diameter drum that was installed so it could be plasma sprayed. The drum was rotated and the fibers were sprayed with aluminum under atmospheric conditions. The conditions of plasma spraying are given in Table 3. Table 4 shows the specification of the prepreg sheet obtained. Plasma spraying was performed with a Plasma Technik PT-M1000 machine.

Two types of fiber-free aluminum prepreg were produced to investigate the effect of plasma spraying on oxidation of MMC prepreg sheet. One type of prepreg was obtained by plasma spraying in air, the same method as that in MMC prepreg, and another type of prepreg was obtained by the plasma spraying in argon gas at 5.2×10^4 Pa using a Metco 7MB machine in a vacuum chamber.

2.3 *Production of MMC Plate and Fiber-Free Aluminum Plate*

The production process of MMC plate is shown in Fig. 1(b). The Si-Ti-C-O fiber/Al prepreg sheet was cut into 60 mm wide by 90 mm long sheets. Then 60 ply of these were unidirectionally piled within a graphite die cavity. After the die was set in the vacuum chamber and heated in a vacuum of 6.65×10^{-2} Pa, the laminated material was hot pressed at 640 to 680 °C under 9.8 MPa for 1 min. The size of the MMC obtained is 60 by 90 by 3 mm. The fiber-free prepreg sheet produced by plasma spraying at the different atmospheres was also hot pressed in a similar manner.

2.4 *Examination of Prepreg Sheet and MMC Plate*

The reduction in the tensile strength of the Si-Ti-C-O fiber in MMC prepreg sheet was examined by extracting the fiber from the prepreg sheet with an aqueous solution of 5% hydrochloric acid. The average tensile strength of 50 filaments of the extracted fiber was measured according to JIS R 7601 (Testing Method for Carbon Fibers).[17] A three-point flexural test was carried out using a plate specimen with dimensions of 40 mm long by 10 mm wide by 2 mm thick, with a span distance of 30 mm, under a crosshead speed of 0.5 mm/min. The test was conducted by using a Shimadzu Autograph DSS-500 testing machine at room temperature in air. The flexural strength was measured in the longitudinal and transverse directions.

The oxidation layer formed on the surface of the aluminum prepreg sheet, which was produced by plasma spraying in air and in argon gas, was analyzed using Auger electron spectroscopy (AES) with a JEOL JACT-30 instrument and electron spectroscopy for chemical analysis (ESCA) using VG-ESCA-LABO-200X equipment. In AES analysis, argon ion sputtering was performed at an acceleration voltage of 10 kV and a beam current of 1.9×10^{-7} A. The beam diameter was about 5 mm.

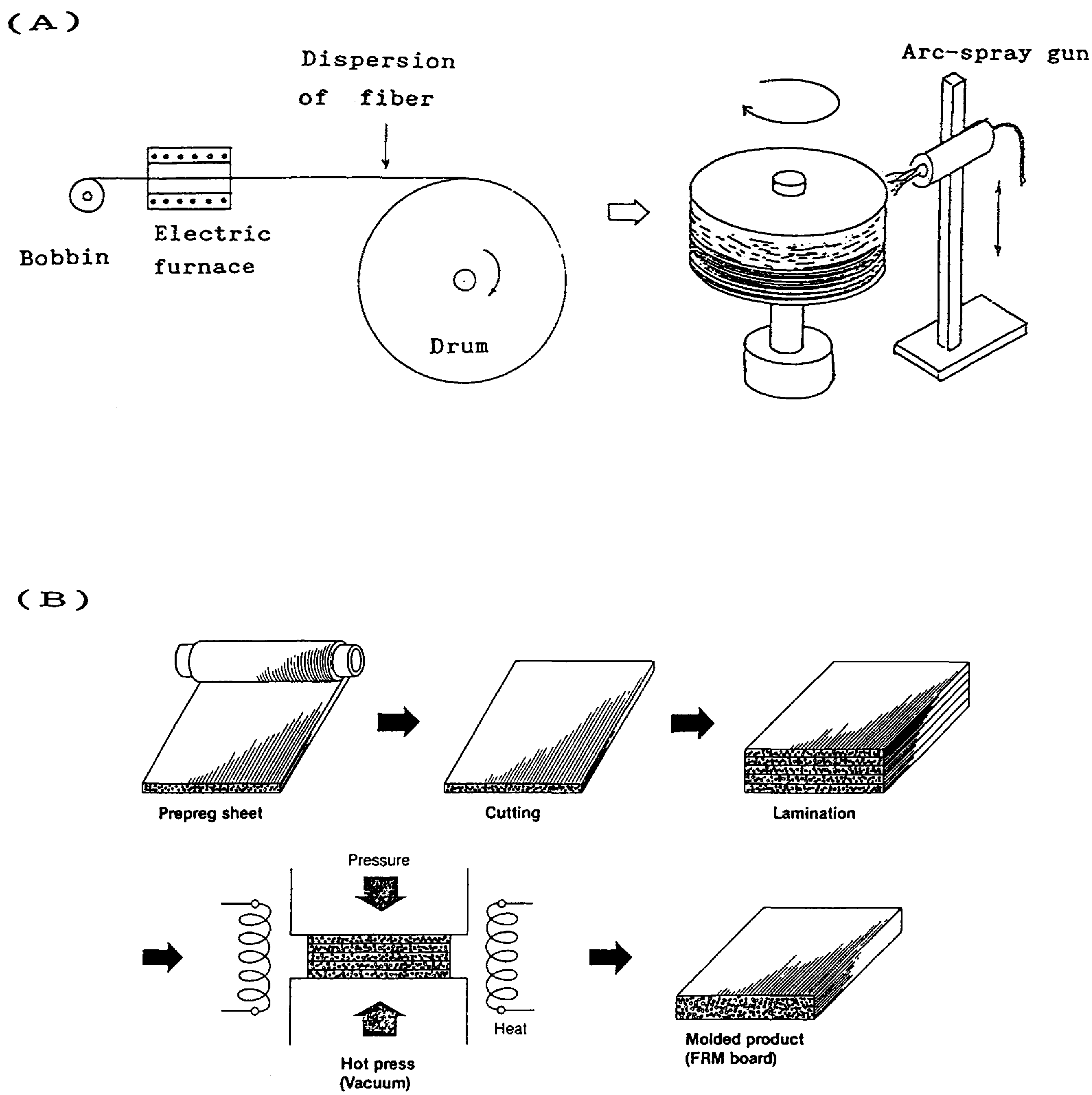

Figure 1 Production of (a) prepreg sheet by plasma spraying and (b) MMC plate by hot pressing.

3. Results and Discussion

3.1 *Oxidation of Prepreg Sheet and Atmospheres for Plasma Spraying*

Figure 2 shows the results of ESCA analysis at the surface of fiber-free prepreg sheet produced by plasma spraying in air (Fig. 2a), and in argon gas (Fig. 2b). As shown in the ESCA profiles, the quantity of aluminum oxide and aluminum hydroxide formed on the surface of aluminum prepreg sheet is almost independent of the atmospheres of the plasma spraying chamber. The results of AES analysis of the same sample are shown in Fig. 3(a) and (b). From oxygen profiles, it is observed that the depth of the oxidation layer of these two prepreg sheets is also almost independent of the atmospheres of plasma spray chamber and is usually about 100 to 400 Å, compared with the 0.15-mm thickness of the prepreg. These data show that it is possible to produce Si-Ti-C-O fiber/Al prepreg sheet by means of plasma spraying

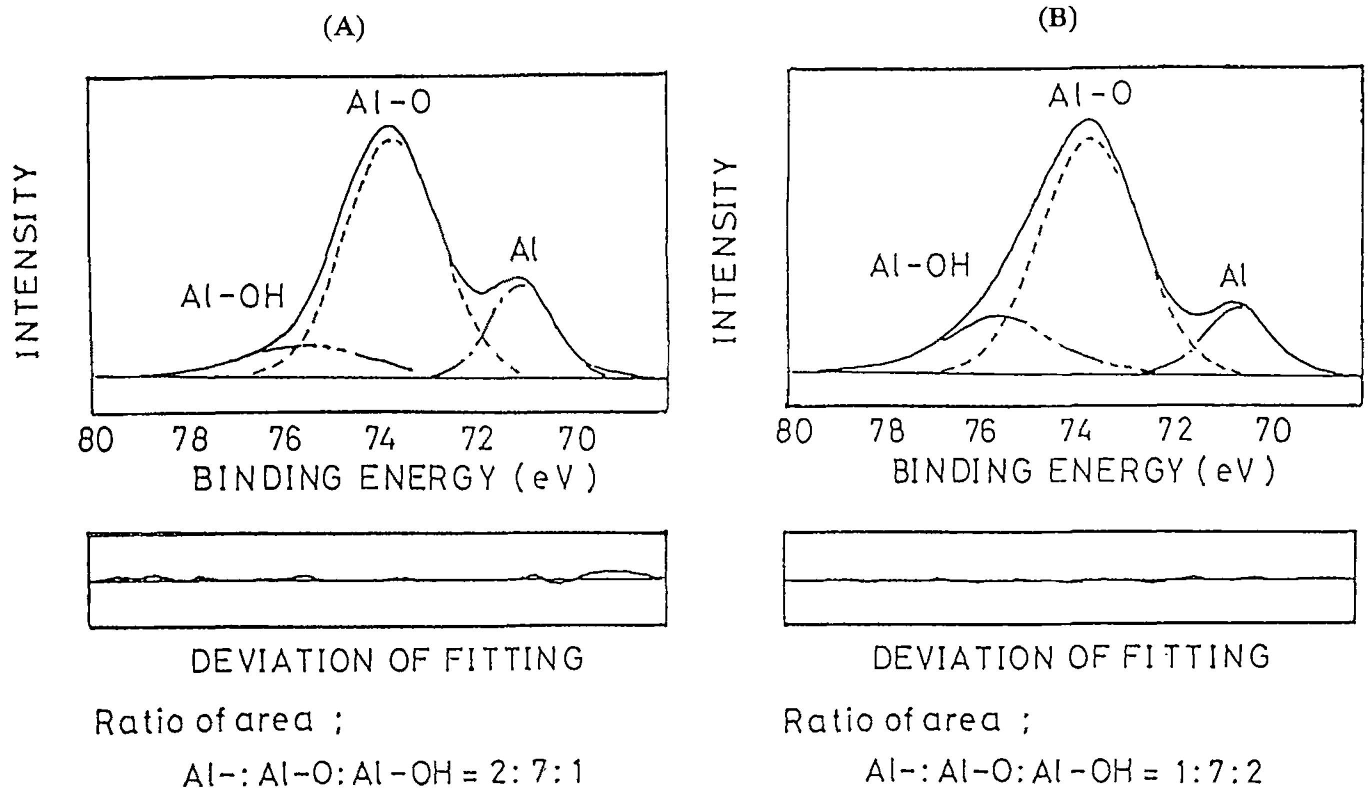

Figure 2 ESCA profiles at the surface of fiber-free aluminum prepreg sheet produced by plasma spraying (a) in air and (b) in Ar gas.

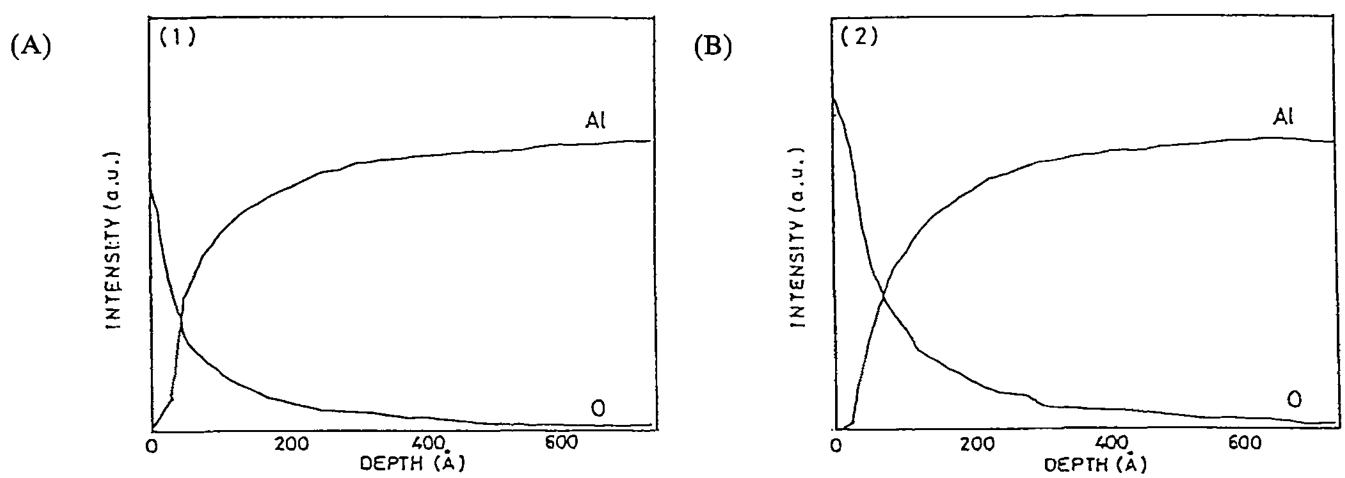

Figure 3 AES analysis of fiber-free aluminum prepreg sheet fabricated by the plasma spraying (a) in air and (b) in Ar gas.

in air. Figure 4 shows AES analysis of the Si-Ti-C-O fiber/Al prepreg. The depth of the oxidation layer is small, about 200 Å, and almost the same as that of the fiber-free prepreg sheet.

3.2 *MMC Prepreg Sheet*

The properties of the MMC prepreg are largely affected by the strength of the fiber in the matrix, which usually decreases because of chemical reactions between the fibers and molten aluminum during plasma spraying, as well as mechanical damage. The mechanical damage is generally demonstrated as a large decrease in the tensile strength of the fibers with a diameter below 10 μm due to mutual contact between fibers when the plasma-sprayed aluminum impacts against the fiber surface.

Figure 5 shows the microstructures of MMC prepreg fabricated by plasma spraying in air. Figure 5(b) illustrates the typical microstructure of MMC prepreg sheet produced under suitable conditions of plasma spraying and dispersion of the fiber. The molten aluminum is well infiltrated among the fibers, and the fibers disperse homogeneously in the matrix with no inter-fiber

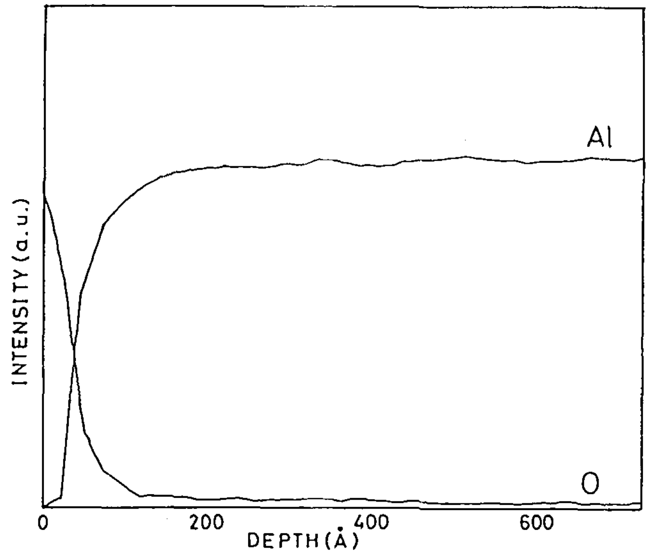

Figure 4 AES analysis of aluminum matrix prepreg sheet reinforced with Si-Ti-C-O fibers.

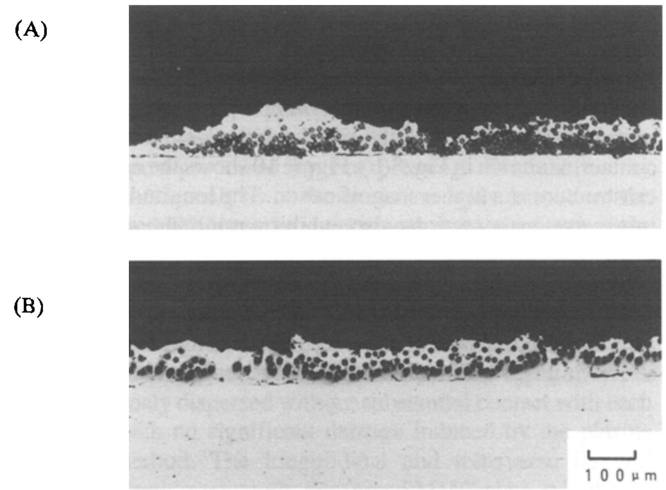

Figure 5 Optical microstructures in the transverse cross section of Si-Ti-C-O fiber-reinforced aluminum matrix composite prepreg sheet produced by plasma spraying in air. (a) Unsatisfactory fiber dispersion. (b) Satisfactory plasma spraying and fiber dispersion.

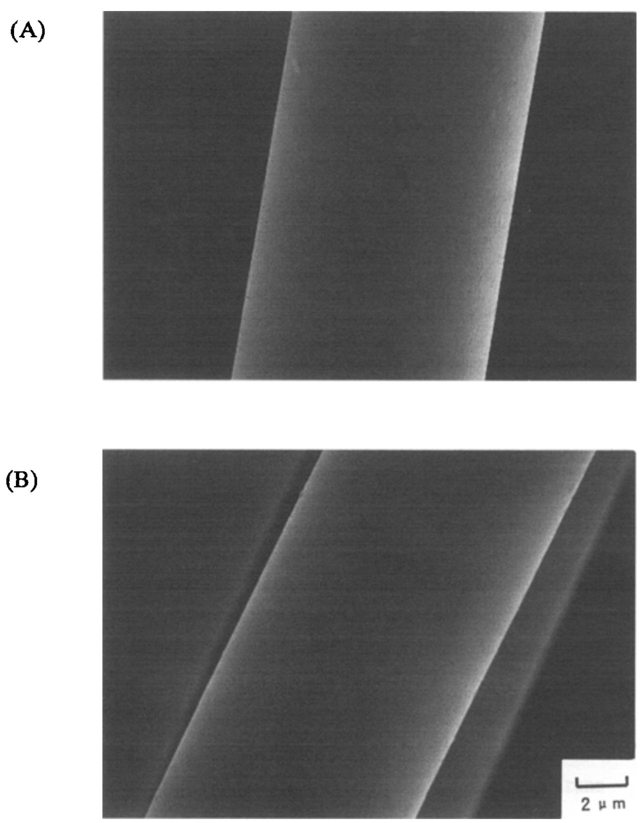

Figure 6 SEM images of Si-Ti-C-O fiber. (a) Original fiber. (b) Fiber extracted from MMC prepreg sheet.

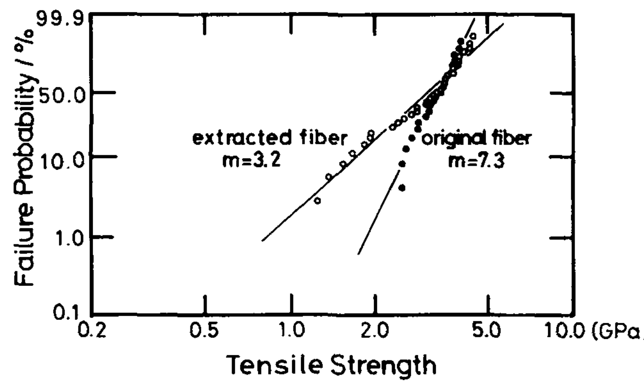

Figure 7 Relation between failure probability and tensile strength of Si-Ti-C-O fiber before and after plasma spraying in air.

contact. Figure 5(a) shows the unsatisfactory microstructure obtained when the molten aluminum was infiltrated into a poor state of fiber dispersion. In this case, the molten aluminum did not fully penetrate the fibers near the surface of the drum. Further improvement of the fiber dispersion and the plasma spraying process enabled the production of more flexible and thinner MMC prepreg.

Scanning electron micrograph (SEM) images of the as-received fibers and fibers that have been extracted from the prepreg sheet are shown in Fig. 6. No damage on the surface of the extracted fiber is observed. Figure 7 shows the tensile strength data distribution analysis performed according to the Weibull method. The decrease in tensile strength of the fiber is small, and the average value of 3.11 GPa is almost the same (3.33 GPa) as the original fiber before plasma spraying. The Weibull modulus has a tendency to decrease after the plasma spraying procedure.

3.3 *MMC Plate*

Typical microstructures of the transverse cross section of the unidirectional Si-Ti-C-O fiber/Al composites produced by hot pressing prepreg sheet that was manufactured by plasma spraying are shown in Fig. 8. Figures 8(a), (b), and (c) correspond to hot pressing temperatures of 640, 660, and 680 °C, respectively. If the temperature of hot pressing is appropriate, then the fiber is uniformly distributed in the matrix with minimum inter-fiber contact, as shown in Fig. 8(b). Figure 10 shows the optimum microstructure at a higher magnification. The longitudinal and the transverse cross sections also exhibit a minimum of structural discontinuities such as shrinkage, pores, and damage, all of which would affect the mechanical properties of the MMC.

The damage on the surface of the extracted fiber from its MMC plate prepared at different hot pressing temperatures is shown in Fig. 9. The optimum pressing temperature of 660 °C indicates a surface with minimum damage, as shown in Fig. 9(b). However, with decreasing temperature, several pores appear in the microstructure, as shown in Fig. 8(a), although no damage of the fiber can be observed, as shown in Fig. 9(a). On increasing the hot pressing temperature, no microstructural discontinuities, as shown in Fig. 8(c) appear, but fiber damage is present, as shown in Fig. 9(c).

The flexural strengths in the longitudinal and transverse directions of the Si-Ti-C-O fiber/Al composites are shown in Table 5. The longitudinal flexural strength changes with the temperature of hot pressing. The flexural strength reaches a maximum of about 1.0 GPa with respect to the hot pressing temperature at 660 °C. Scanning electron micrographs of extracted fibers shown in Fig. 9 revealed that poor flexural strengths

(A)

(B)

(C)

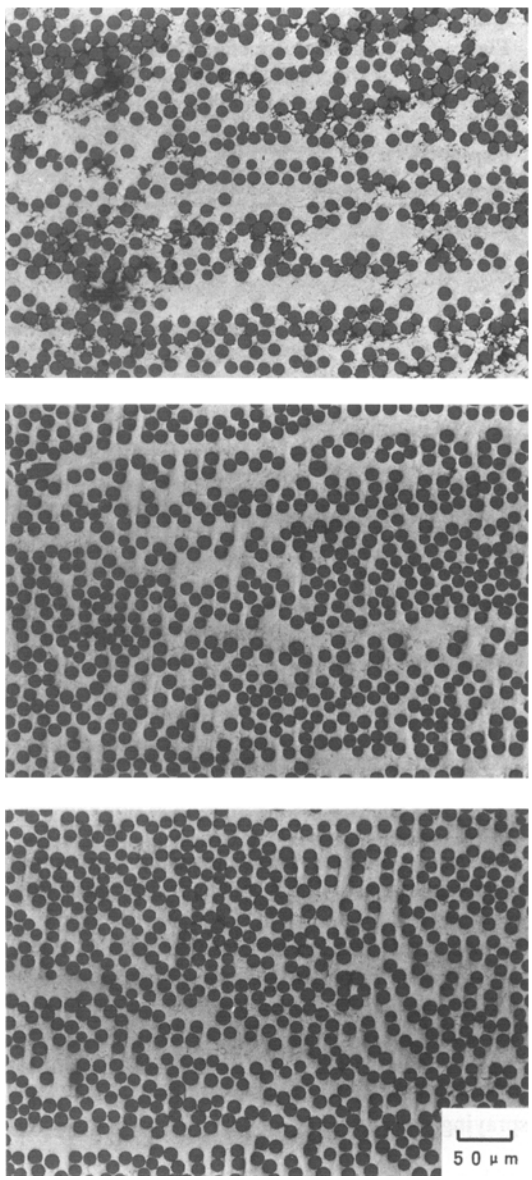

Figure 8 Optical microstructures of the transverse cross section of Si-Ti-C-O fiber-reinforced aluminum composite plate produced by hot pressing at (a) 640 °C, (b) 660 °C, and (c) 680 °C.

(A)

(B)

(C)

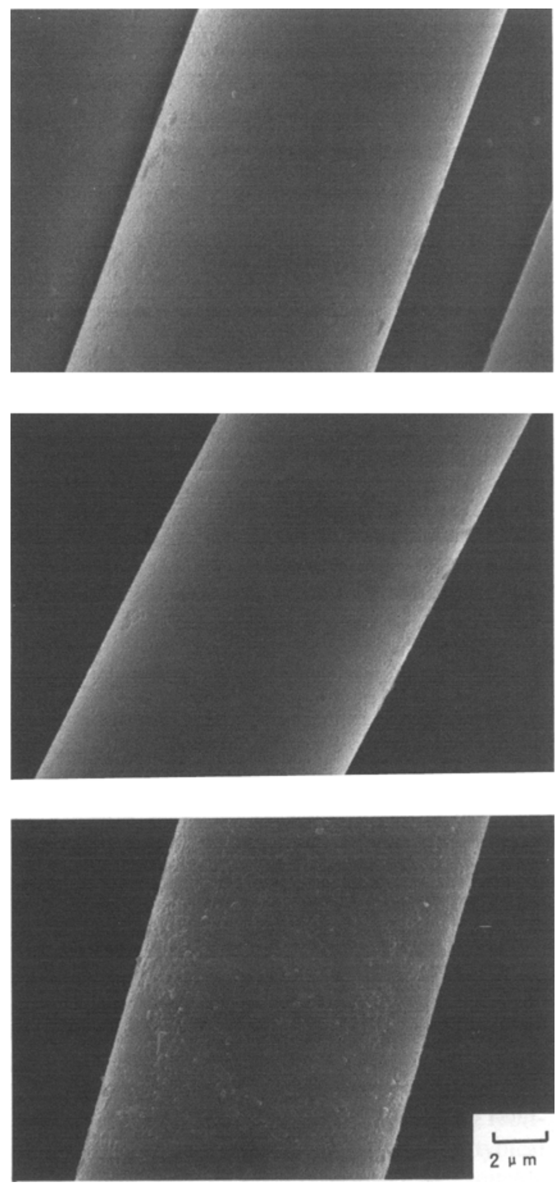

Figure 9 SEM images of fiber extracted from aluminum matrix composite plate; (a), (b), and (c) are micrographs of fibers pressed at 640, 660, and 680 °C hot pressing temperatures, respectively.

above 660 °C were due to fiber damage from a chemical reaction between the fibers and matrix. The insufficient flexural strength below 660 °C arises from the existence of pores, as shown in Fig. 8(a).

The transverse flexural strength changes in a different manner than the longitudinal strength with respect to the hot pressing temperature. The transverse flexural strength increases with hot pressing temperature and reaches a maximum of 0.25 GPa about 660 °C. The transverse flexural strength obtained in this study is considered satisfactory when compared with the maximum flexural strength of 0.04 to 0.05 GPa of composite materials reinforced with high modulus carbon fiber.[18] An SEM photograph of the transverse flexural fracture surface is shown in Fig. 11 and shows a dimpled pattern that is characteristic of ductile fracture. This fracture occurred not at the interface between the matrix and fibers, but within the matrix because of strong bonding between fibers and matrix because these materials have good compatibility. In addition, this fracture behavior confirms that the oxidation layer, formed on the surface of the MMC prepreg during plasma spraying in air, does not significantly affect the mechanical properties.

(A)

(B)

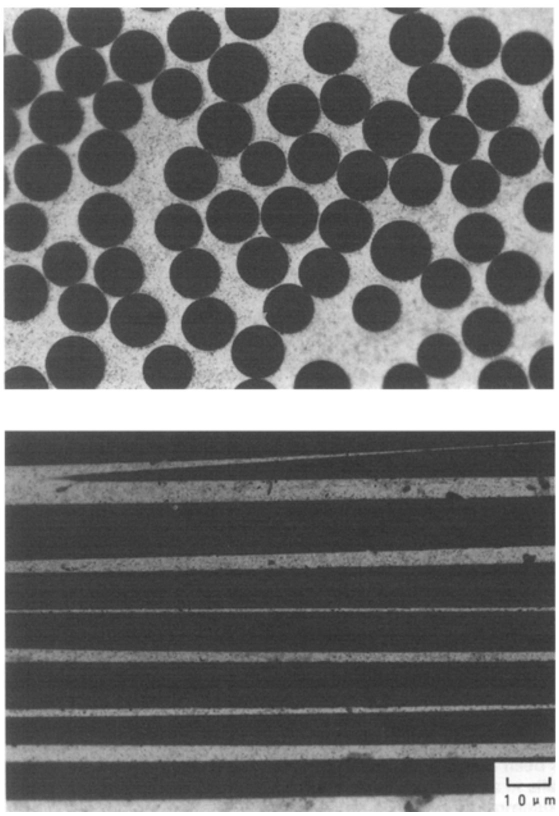

Figure 10 Typical microstructures of advanced MMC. (a) Transverse cross section. (b) Longitudinal cross section.

4. Conclusions

Flexible composite prepreg sheet was manufactured by an air plasma spraying method. The prepreg sheet consisted of an aluminum matrix reinforced with Si-Ti-C-O fibers. The prepreg sheet was post-processed by hot pressing. Examination by ESCA and AES analysis of the oxidation layer formed on the surface of the MMC prepreg sheet revealed that the depth of the oxidation layer is about 200 Å. The oxidation depth is independent of the atmosphere in the plasma spraying chamber, whether it is air or argon. The plasma spraying method enabled manufacture of a more flexible and thinner composite prepreg sheet than other technologies. The fibers in this prepreg sheet are homogeneously dispersed without substantial contact with each other and with no significant damage induced by the plasma spraying method. The longitudinal and transverse flexural strengths of unidirectionally reinforced MMC plate, which was obtained by hot pressing at 660 °C, are 1.0 and 0.25 GPa, respectively.

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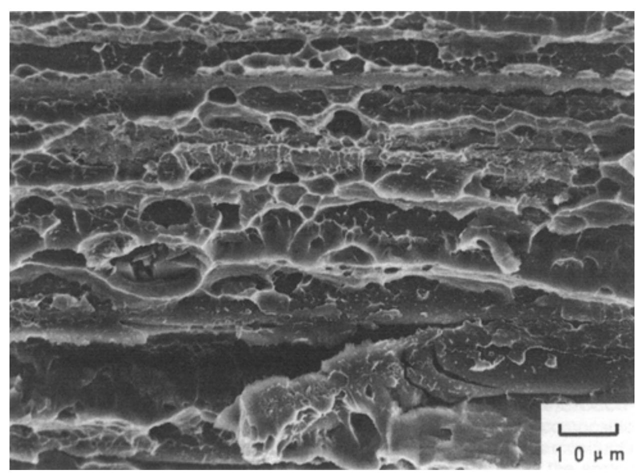

Figure 11 SEM image of the transverse flexural fracture surface.

Table 5 Flexural Strength of MMC Plate

	Strength at hot pressing temperature of:			
	630 °C	640 °C	660 °C	680 °C
Longitudinal flexural strength, GPa	0.56	0.67	1.00	0.64
Transverse flexural strength, GPa	0.14	0.18	0.25	0.23

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