Fabrication of Al_2O_3-Coated Carbon Fiber-Reinforced Al-Matrix Composites

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Received 12 January 1998; accepted 6 February 1998

ABSTRACT: Fine Al_2O_3 coating could be obtained from alumina sols modified by chelator acetylaceton, under exact control of the parameters. Al_2O_3 coating by the sol–gel method on the carbon-fiber (CF) surface was investigated in detail to improve the oxidation resistance of CFs. Further study focused on making the Al_2O_3-coated fiber-reinforced aluminum composite prefabrication. XRD, IR, TG–DTA, and SEM methods were used to analyze the alumina gels, the coated CFs, and the prefabrication. After the coating treatment, the oxidation resistance of the carbon fibers is enhanced, the wetting between the fibers and melting aluminum is greatly improved, and the tensile strength of CF/Al prefabrication is heightened. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 177–183, 1998

Key words: sol–gel; Al_2O_3; carbon fibers; coating; CF/Al prefabrication

INTRODUCTION

Carbon fiber's (CF's) low oxidation resistance in an oxidative environment and chemical reactivity prohibit them from being widely used either in metal–matrix and ceramic–matrix composites or in high-temperature polymer–matrix composites. Moreover, a major obstacle in the realization of CF reinforcement of metal is that to fully exploit the composite properties. The metal matrix must wet the carbon reinforcement yet at the same time not undergo an adverse reaction, impairing mechanical properties. Unfortunately, no pure metal satisfies this criterion. For the particular case of aluminum, it appears to be inert and nonwetting toward CFs at low temperatures but extremely reactive at higher temperatures, forming aluminum carbide,[1] Al_4C_3, by the reaction

$$4Al + 3C \rightarrow Al_4C_3$$

The formation of the friable carbide and its subsequent oxidation during processing, or service at elevated temperature, ultimately leads to disbondment of the fibers and severs the reduction of shear load transfer between the matrix and the reinforcement.

To widen the application of CFs in a metal composite, it becomes clear, therefore, that some form of coating is needed to improve the CF's oxidation resistance and to alleviate the fiber/matrix interfacial reaction. In fact, a number of techniques such as chemical vapor deposition (CVD), physical vapor deposition (PVD), plating, plasma sputtering, and other modern techniques have been used to provide coating for CFs with oxidation-resistant and good combination materials. In recent years, increasing interest has been generated in the development of high-performance ceramic coatings through a solution route. The sol–gel method is one of the most important techniques for the synthesis of various functional films because it posseses a number of advantages over conventional film-formation techniques, such as low-temperature processing, easy coating of a large surface, and possible formation of homogeneous multicomponent oxide films. To have effective protection of the CFs, the coating should be thin, uniform, and well adhered to the fibers. There are many general conditions to be fulfilled to prepare homogeneous coatings having special

Journal of Applied Polymer Science, Vol. 70, 177–183 (1998)
 CCC 0021-8995/98/010177-07

physical and chemical characteristics.[2] These include the molecular structure, rate of hydrolysis, and polycondensation reactions in relation to the chemistry of the sol and the thickness and uniformity of the coating in relation to the viscosity and coating techniques.

This article reports mainly the results of a study of oxidation resistance of CFs, coated with Al_2O_3 thin layers by sol–gel techniques. Studies were made on the effects of some of the parameters on the uniformity of the coating structures and the coating's contribution to the oxidation protection of CFs. Further investigation focused on the fabrication of the CF-reinforced aluminum matrix preformed wire rope. An Al_2O_3 coating has been applied to prevent a harmful reaction at the fiber/matrix interface.

EXPERIMENTAL

Preparation of Sols

The Al_2O_3 sol solution used for the coatings was made from commercial isopropoxy aluminum $Al(OPr)_3$ (98% purity) and i-propanol (H_2O % : 0.1 max). $Al(OPr)_3$ was chemically modified with acetylacetone and subsequently hydrolyzed. To a solution of 1 mol of $Al(OPr)_3$ in 1 L of i-propanol, acetylacetone in i-propanol (1 mol/0.5 L) was added in a 1 : 1 molar ratio. Hydrolysis was then performed by adding 2 mol of water dissolved in 1 L of i-propanol per 1 mol of aluminum. The addition of water resulted in precipitation. The precipitation was dissolved by changing the pH with concentrated nitric acid to below 4.5.

Coating Procedure on Fibers

The CF Torayca T300, which is produced by Toray (Japan), was investigated. It is made of polyacrylonitrile (PAN)-based continuous fibers, with a density of 1.8 g/cm^3. Each fiber bundle consists of 3000 single filaments. The average tensile strength of a single filament is 3520 $\pm$ 260 MPa, and the average diameter of single filament is 6.5 $\pm$ 0.4 μm.

The fibers were passed sequentially through a supply wheel, a furnace to remove the sizing agent at 923 K in argon gas, a glass vessel containing the sols kept at 298 K in an ultrasonic generator, a chamber to gelate the sol coating at 373 K in argon, a furnace to pyrolyze gels in an argon atmosphere at 1173 K to obtain oxide coatings, and, finally, a take-up wheel. The take-up speed was 5 cm/min.

Fabrication of CF-Reinforced Aluminum Matrix Composite Preformed Wire Rope

A continuous CF bundle was passed through a melting aluminum container. Ultrasonic waves were employed to generate high-pressure areas by a bubble effect. Under high pressure, the CFs were forced to scattered in and then combine with the melting aluminum. After a cooling treatment, the CF/Al prefabrication was formed.

Characterization

The sol viscosity was measured using a Wuls viscometer.[3] The crystalline phase of the gels after heat treatment was evaluated using a Siemens D500 X-ray diffractometer. The diffractograms were analyzed for interlunar distance d values, which were then compared with standard ASTM data to ascertain the nature of the coated materials. The coating morphology quality was assessed by observing the surface for cracks or pinholes using an X-165 scanning electron microscope; the experimental voltage was 20 kV.

The tensile strength of the CFs prepared were tested on the individual filament 25 times with a Tension YG-001 (Shanghai, China) tensile tester at room temperature under a crosshead speed of 2 mm/min and gauge length of 20 mm.

The tensile strength of the CF/Al preformed wires were tested on a single wire 25 times with a CSS-1101 electronic universal testing machine at room temperature at a crosshead speed of 5 mm/min and gauge length of 50 mm. The numerical evaluation of the tensile strength tests used a t-distribution statistic process. The cross-section areas of the CF/Al preformed wire were measured by an IBAS image instrument.

RESULTS AND DISCUSSION

Sol–Gel Formation

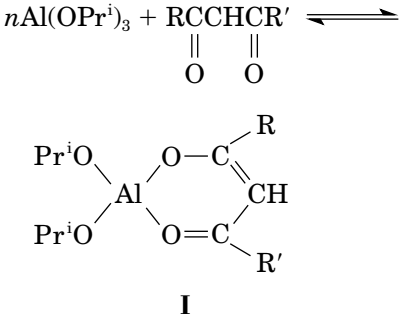
During the hydrolytic condensation, an inorganic network is formed by a chain of hydrolysis and polymerization reactions. Hydrolysis conditions such as the water/alkoxide ratio, catalyst, chelator, molecular separation by dilution, hydrolysis medium, reaction temperature, and alkyl groups in alkoxide determine the kinetics of the reactions that form the molecular structure.

Aluminum alkoxides react with a chelator, such as acetylacetone or ethyl acetate, and give rise to new molecular precursors different from them as demonstrated by Yoldas.[4] Following the

procedure described in the Experimental part, the new precursor sol was prepared. Figure 1 shows the IR spectrum of the obtained sol. The broad band at 3400 cm^{-1} is attributed to the stretching and bonding vibrations of the absorbed and inner macromolecule water. The bands at 1100, 800, 550, and 940 cm^{-1} correspond to the $[Al(OH)_n]^{3-n}$ ion, and the absorption at 1100, 800, and 550 cm^{-1} is due to the bonding and vibration of the Al—OH group, and at 940 cm^{-1}, to the bridging —OH radical vibration. The —C═O stretching vibration exhibits a sharp band at 1670 cm^{-1}.

The effect of the chelator is a twofold one: It modifies the alkoxide by occupying a site for condensation, leading to a different molecular structure of the oligomers. The oligomers become more soluble than the uncomplexing "pure inorganic" hydroxides and higher solid contents can be obtained from the complexing alkoxides. On the other hand, they act as a surfactant, which prevents agglomeration. The chelation and hydrolysis reactions can be written as follows:

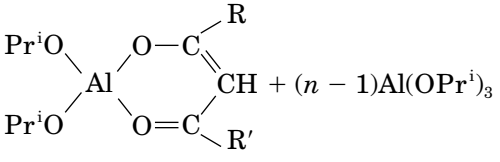
For chelation:



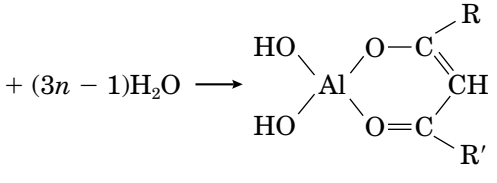
I

$$+ (n-1)Al(OPr^i)_3 + Pr^iOH$$

For hydrolisis:



$$+ (n-1)Al(OPr^i)_3$$



II

$$+ (n-1)Al(OH)_3 + (3n-1)Pr^iOH$$

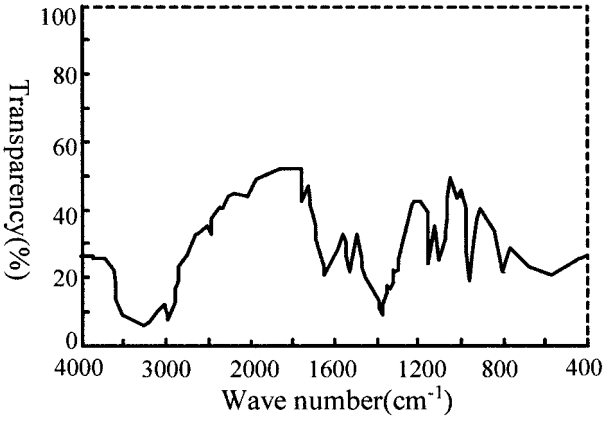


Figure 1 IR spectrum of Al_2O_3 sol.

Acidification of the sols lead to a partial neutralization of the hydroxyl group or acetylacetonate anions, causing charged particles. The influence of the bulky chelating agent is reduced by this process and leads to improved adhesion.

The Al_2O_3 sols show interesting properties for the preparation of dense and crack-free transparent alumina coatings. A low temperature for α-alumina formation, a very small particle size, a solid higher content which is high compared with conventionally used sols, and an adjustable viscosity range (by dilution) of about 2–10 mPa s due to the organic modification are observed. Compared with the alumina coating obtained from pure aluminum alkoxides, the sol modified by acetylacetone gives a better microstructure and shows a high stability.

Changes and Crystallization with the Heat Treatment of the Al_2O_3 Sol–Gel

Figure 2 shows the DTA and TG data for the aluminum sol precursor (condensed) produced by the chemical-modification sol–gel method. The TG curve shows a 20% weight loss below 100°C due to the volatilization of the absorbed water and remaining solvent. At 120°C, the weight loss abruptly increases to 60%, accompanied by two obvious exothermic peaks in the DTA, suggesting the beginning of the dehydration and removal of residual organic radicals in the precursor macromolecule.[5] Above 150°C, with a broad exothermic peak, the organic radical is released gradually and the polycondensation reaction between the macromolecules continues.

The crystallization behavior of the dried gel powder was measured between 400 and 1000°C by XRD diffraction, as show in Figures 3 and 4. The dried gel powder is X-ray amorphous and did not crystallize up to 700°C after sintering for 20

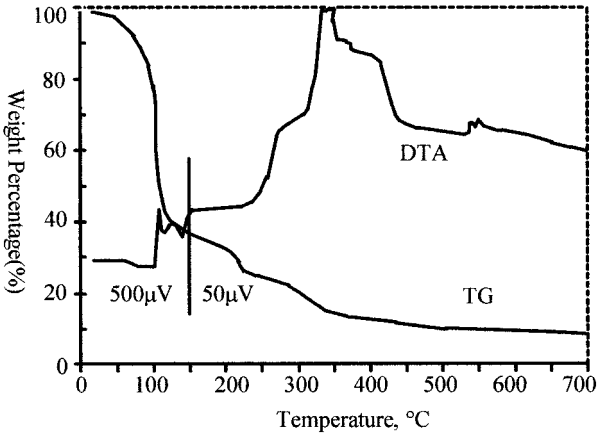


Figure 2 TG–DTA curve of alumina sol.

min. Above this temperature, two broad peaks of low intensity were detected which can be attributed to the metastable alumina phase (δ, θ). The first peaks of α-alumina appeared at 800°C and complete transformation to α-alumina was achieved at 1000°C. The coating from these sols was made by following procedures described in the Experimental part. According to the results of the X-ray studies, calcining up to 900°C gave a transparent alumina coating on the CF surface within 20 min, which is pure α-alumina. Compared with other sol–gel syntheses of α-alumina, for example, α-alumina crystallization from boehmite gels requires 1150°C for 2 h,[6] the crystallization temperature of α-alumina from chelated aluminum hydroxide is rather low.

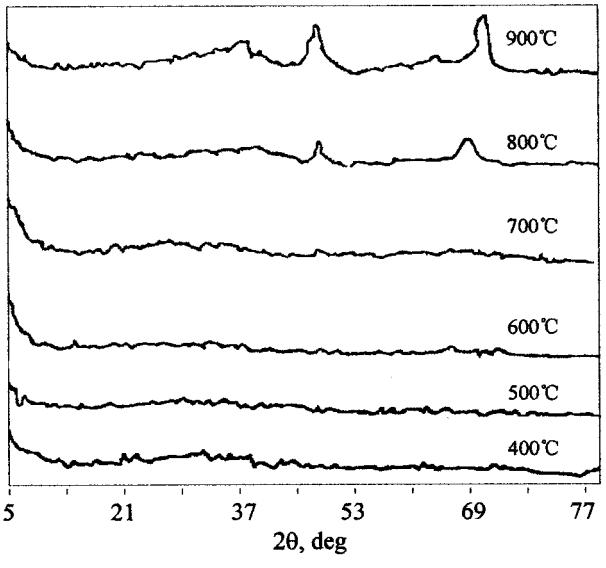


Figure 3 XRD analysis of alumina gel (sintering at various temperatures for 20 min).

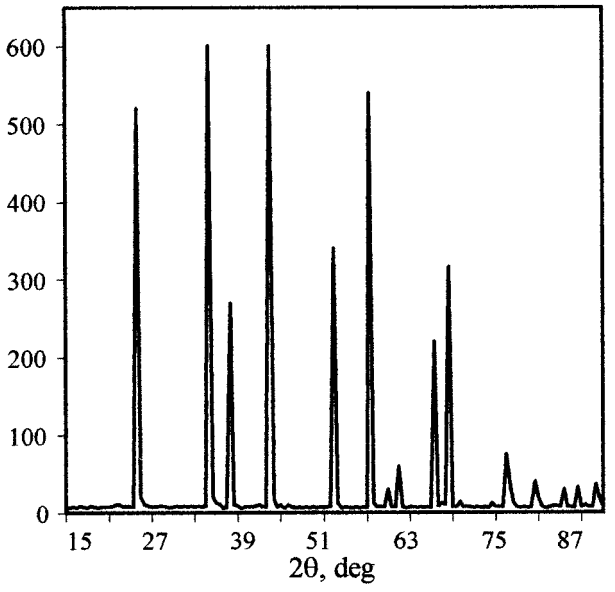


Figure 4 XRD analysis of alumina gel (sintering at 1000°C for 20 min).

Structure of the Coating

Morphology of the Coating

The surface of raw CFs is rough and obviously exhibits cracks and defects, as shown in Figure 5. CFs have higher surface areas because of their small diameter; surface coating is a method of protecting them from oxidation. Al_2O_3 is used for the oxidation protection of CFs in most cases because it is very stable in air below 1273 K. After optimizing the parameters of the sol–gel process, a uniform and transparent Al_2O_3 coating was obtained on the fiber surface. Some particles on the coating were observed by SEM (Fig. 6). Two types of pores present in the Al_2O_3 coating were obtained from the sol. The smaller pores having a radius below 500 nm are barely visible. The larger riverlike pores have a 1000–1500-nm radius and are separated by a distance of about 1 μm. These larger pores appear to contribute somewhat less than one-tenth to the total porosity. These pores are possible channels accessible to transport oxygen atoms, causing the oxidation of CFs. To improve the Al_2O_3 coating, it is suggested that a suitable silicon oxide sol be added to the alumina sol to obtain a mixing sol for coating; the resultant coating containing Al_2O_3 and some amount of SiO_2 (3–50 wt %, preferably) is dense and has a higher oxidation resistance. This needs further research in the future. On the other hand, the porosity in the coating was closely related to the coating process parameters. Hence, the process must be optimized and exactly controlled at every step.

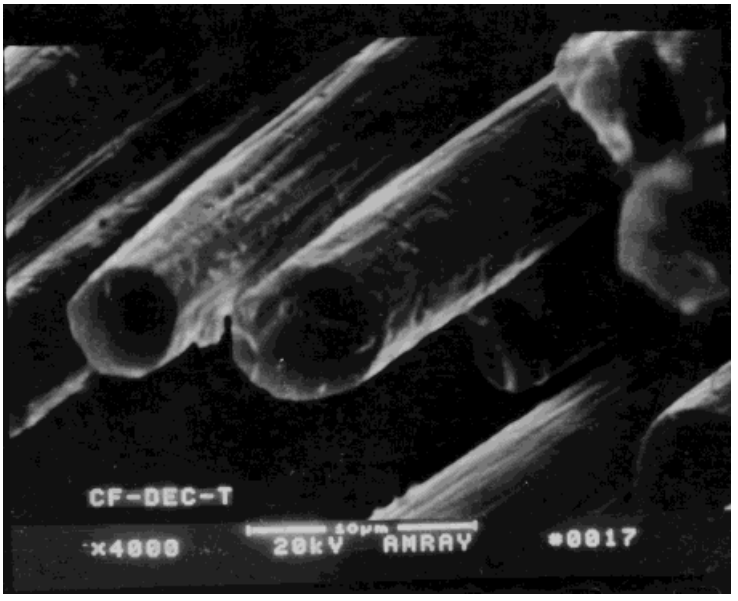


Figure 5 SEM photograph of raw CF (desizing at 650°C).

Heat and Oxidation Resistance of Al_2O_3-coated CFs

The heat and oxidation resistance of CFs are improved by the Al_2O_3 coating, as shown in Figure 7. When heating at 300°C in air for 60 min, the as-received CFs' tensile strength decreases 10%; at 400°C, 40%; and at 500°C, 60%. The Al_2O_3 coating prevents intrusion of oxidation up to 400°C and retards it at temperatures above 400°C.

Study on Al_2O_3-coated CF/Al Prefabrication

The aluminum matrix was reinforced with CF to improve its mechanical properties. In many cases, the average property of the composite may be improved, but most of the components made from that material will be unsuitable for the intended applications because there are three main problems associated with the use of CFs to reinforce the aluminum matrix. (1) The liquid aluminum does not wet the strengthening CF and hence does not penetrate between every filament, as shown in the SEM analysis photograph on the midsection of the raw CF/Al sample (Fig. 8). The average cross-section area of the raw CF/Al prefabrication is 0.2060 mm^2; the CF average volume fraction is 46.8%. (2) The difference in the ther-

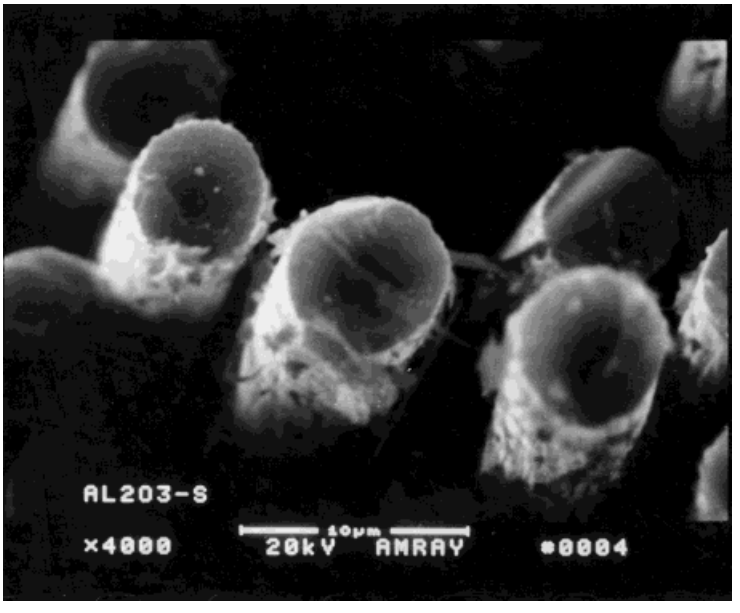


Figure 6 SEM photograph of Al_2O_3-coated CF (sintering at 900°C).

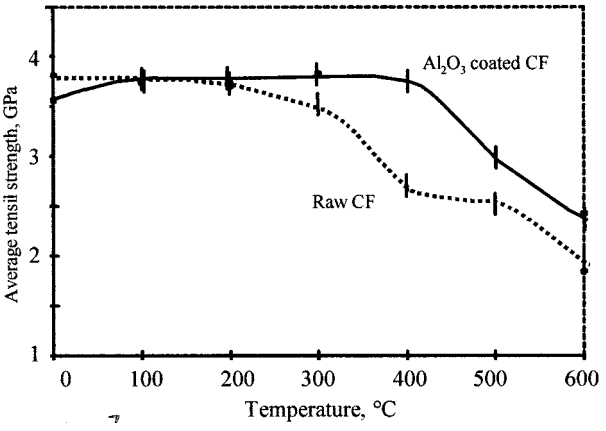


Figure 7 Heat and oxidation resistance of CF.

mal expansion coefficients between the aluminum matrix and the CFs causes open pores to be formed at the fiber/matrix interface and initiates residual thermal stress. (3) The unstable carbide, brittle Al_4C_3, was found after heat treatment of the aluminum graphite system at 500°C, accompanied by a sharp strength reduction.[1] The grave interfacial reaction made the preformed wire exhibit brittle failure features, little matrix deformation took place, and the associated energy absorbed was also small. The average tensile strength of raw CF-reinforced aluminum preformed wire is 808.1 MPa.

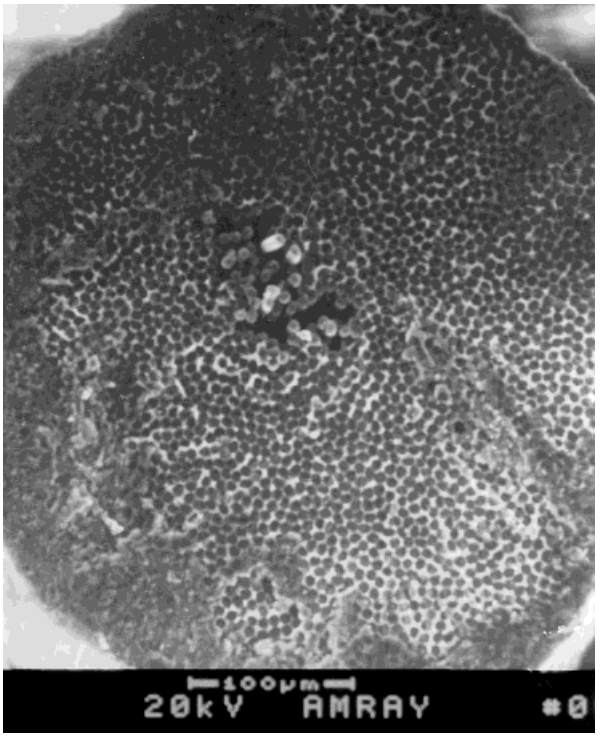


Figure 8 SEM photograph of cross section of uncoated CF/Al prefabrication.

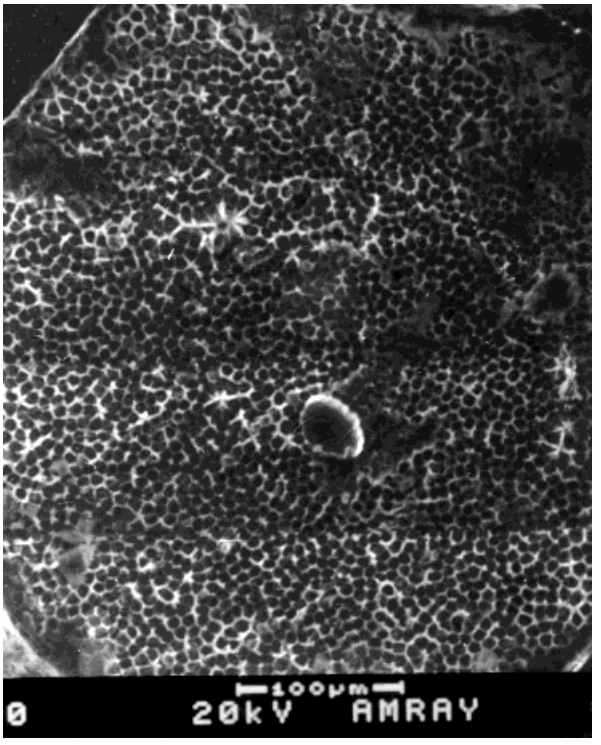


Figure 9 SEM photograph of cross section of Al_2O_3-coated CF/Al prefabrication.

The reliability of these materials was improved considerably when the CF surface was coated with Al_2O_3. Al_2O_3 coating promotes wetting and bonding between graphite and aluminum effectively (Fig. 9). The average cross-section area of Al_2O_3-coated CF/Al prefabrication is 0.1813 mm^2; the CF average volume fraction is 53.2%. The thermal expansion coefficient of Al_2O_3 interposes between that of CF and aluminum; thus, Al_2O_3 coating might help to relieve any thermal stress or strain concentration between the fiber and the matrix. The coating on the fibers can act as diffusion barriers and thereby improve the long-time resistance of composites to property degradation by slowing or preventing a harmful interfacial reaction. At the cross section of Al_2O_3-coated CF/Al preformed wire, matrix deformation occurs. Thus, the stress concentration in the matrix produced by the fiber breaks is reduced by matrix yielding, preventing a matrix crack that may join the fiber fracture at different points. The average tensile strength of single-layer Al_2O_3-coated CF-reinforced aluminum preformed wire reaches 900.3 MPa. It can be expected that a multilayer and composite coating would heighten the CF/Al prefabrication's tensile strength even more.[7]

CONCLUSIONS

Chelation of aluminum isoproxide leads to improved processing properties of the alkoxide during hydrolysis and condensation. Agglomeration is prevented by the chelating agent and gives rise to new synthesis methods of nanosized materials. An alumina coating from these sols on the CF surface shows an ultrafine microstructure. The coatings on fibers act not only as diffusion barriers, enhance the oxidation resistance of carbon fiber, and prevent harmful CF/Al interfacial reactions, but also promote wettability and relieve thermal stress concentration between the CF and the aluminum matrix.

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