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Aluminum Oxide and Chromium Oxide Coatings on Ceramic Fibers via MOCVD

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The overall strength and toughness of ceramic matrix composites is very much affected by the interfacial properties that govern the bonding between the reinforcing fibers and the matrix. The ability to control this interaction is very important. One method involves coating the ceramic fibers with an appropriate material. There is a definite advantage in using lower-temperature processes to produce the coatings: fibers subjected to high-temperature coating processes are more prone to degradation due to microstructure and crystallization changes. Matrix and fiber materials could also react at high temperatures to form a strong bond at the interface making the composite brittle. Metal−organic precursors were used to produce aluminum oxide and chromium oxide coatings on SiC and $Al_2O_3-SiO_2$ based ceramic fibers. These metal oxides were deposited on the reinforcing fibers by the pyrolysis in air of their respective metal acetylacetonates at temperatures of 500 °C or less. The coated ceramic fibers showed some reduction in tensile strength but still had considerable strength for use in composites.

Introduction

Chemical vapor deposition (CVD) has rapidly developed as a method of producing thin films or coatings of materials on substrates for a variety of applications ranging from electronic components to corrosion resistant coatings.[1] The advantage of CVD compared to other coating techniques is that it is not a line-of-sight method. CVD can also provide a uniform coating on complicated shapes. This method is used to produce protective metal oxide coatings for high-temperature applications.[2,3] Protective coatings and interfaces are widely employed for many structural materials such as in ceramic matrix composites (CMC),[4−7] and on metal and alloy surfaces.[8] Commonly used reinforcing materials include SiC, carbon, Al_2O_3, and $Al_2O_3-SiO_2$ based fibers for CMCs.[9,10] Tows of these fibers are made up of hundreds of individual fibers bundled together and used as reinforcing materials for composites in high-temperature applications. These fibers are of particular interest for use in ceramic matrix composites due to their high strengths at high temperature. However, a major issue encountered during high-temperature usage is the degradation of fiber strength. The decrease in fiber strength can be caused by several factors. At high temperatures, the fiber and the matrix materials can react, forming a strong bond between the two. This bonding can contribute to the brittleness of the composite and limit the lifetime of the component.[5,11,12] Another reason is corrosion from the environment resulting in the loss of the reinforcing material.[13,14] Thus, a protective interphase coating is critical for using CMCs in high-temperature applications. In addition, the coating−matrix interaction must be strong enough to transfer the load but weak enough to allow fiber pullout in order to produce a tough composite.[15−17]

Initial studies employed CVD carbon fiber coatings on tows and later boron nitride by CVD and dip coating processes with promising results, but both coatings are susceptible to oxidation.[18−20] The carbon interphase in

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SiC/SiC composites is known to exhibit poor oxidation resistance above 400 °C.[14,21,22] Boron nitride interphase coatings have been used in CMCs as well, but they are also susceptible to oxidation.[14,22]

Several alternate coatings have been developed to overcome the deficiencies of carbon and boron nitride. Such coatings include mullite,[7,23−25] monazites and xenotimes,[4,5,11,26−28] ZrO_2,[6,24] and various aluminosilicates.[13,29] These coatings do not suffer the same oxidative limitations of carbon and boron nitride. Most of these metal oxides are applied to fibers using simple techniques such as sol−gel. However, these methods require an additional high-temperature heat treatment process to convert the oxides into useful protective coatings, which can result in fiber degradation and porosity.[30−35]

Al_2O_3 and Cr_2O_3 are widely used as oxidation-resistant coatings for metal and alloy components.[8,36] But there are limited studies regarding their use as interphase materials in CMCs. Unlike carbon and boron nitride, these metal oxides are thermally stable at high temperatures (e.g., >1000 °C) and are not susceptible to oxidation. Both oxides are also chemically inert. These properties make Al_2O_3 and Cr_2O_3 potential candidates for interphase coatings of high-temperature composites if these metal oxides could be applied to reinforcing fibers without severe degradation of the fibers.

Conventional CVD processes to produce the metal oxide coatings involve the reaction of the metal halide precursor and an oxygen source. The temperature of this reaction ranges from 900 °C and above, which can eventually lead to strength degradation of the reinforcing ceramic fibers.[30−35,37] Low-temperature CVD has the advantage of avoiding the microstructural and phase changes of the substrate material which are encountered at high temperatures.[17,38,39] Lower deposition temperatures also minimize the reaction between the coating and the fiber, which at high temperatures can bond the two materials strongly producing a strong interfacial bond diminishing fracture toughness.[5,12]

Metal−organic CVD (MOCVD) can often be done at temperatures below 600 °C. Metal alkoxides and metal alkyl precursors are commonly used in producing MOCVD films and coatings. Metal alkyls are air- and moisture-sensitive making the handling of these compounds very difficult. Metal alkoxides used in MOCVD are also moisture-sensitive. Some of these compounds can form a number of isomeric forms, hence complicating the control of vapor pressure. Alternatively, metal acetylacetonates have been employed to produce metal oxide thin films with varying optical and electronic properties.[40−42] Most metal acetylacetonates decompose at temperatures from 200 to 600 °C, and have sufficient volatility to be used for the deposition of metal oxides. In addition, the acetylacetonate precursors are stable at ambient conditions so no special atmosphere is needed in handling these reagents.

In the presented work, aluminum acetylacetonate and chromium acetylacetonate were used as precursors for MOCVD to deposit aluminum oxide and chromium oxide coatings, respectively, on ceramic fibers at temperatures of 500 °C and below. The use of MOCVD circumvents the high-temperature processes utilized in conventional CVD and sol−gel methods to produce useful metal oxide coatings. Characterization studies were done using X-ray diffraction and scanning electron microscopy. Tensile strengths were measured using an Instron tensile testing instrument to evaluate the effect of the metal oxides on the strength of the ceramic fibers.

Experimental Section

A. Synthesis. *Aluminum Oxide.* The equipment for the CVD of aluminum oxide onto the ceramic tows is shown schematically in Figure 1. The ceramic fibers used are listed in Table 1. Four 2.5-in. lengths of ceramic fiber tows were rinsed with acetone, dried, and then placed into a 5-mm (o.d.) × 6-cm silicate glass tube, 2−4 in. from the entrance end of the reactor furnace. Argon (UHP, Airgas) was purged into the reactor tube until the appropriate temperatures were reached. The sublimation furnace was set at 170 °C and the reactor furnace was set to 500 °C. The sizing on the ceramic fibers was also removed in this heating step. After the setup reached the desired temperatures, an alumina boat containing approximately 0.120 g of aluminum acetylacetonate (Strem Chemicals) was placed into the center of the sublimation furnace. Air was introduced at a rate of 5 mL/min together with argon as the carrier gas at 105 mL/min. After 1 h, the temperature of the sublimation furnace was increased to 180 °C and the reaction was continued for 1 more h. The reactor tube was rotated 180° every 15 min during the entire coating process. The treated tows were cooled to room temperature in flowing argon before taking them out of the reactor tube.

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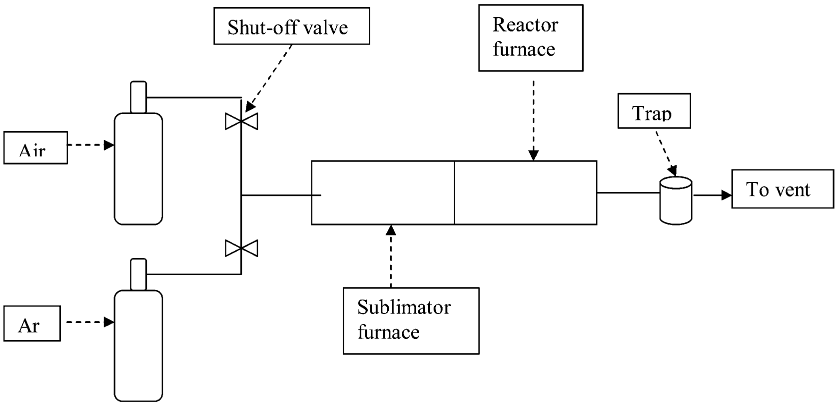

Figure 1. Schematic diagram of chemical vapor deposition apparatus.

Table 1. Different Reinforcing Ceramic Fibers

properties	SiC (Nicalon)	$Al_2O_3-SiO_2$ (S)	$Al_2O_3-SiO_2-B_2O_3$ (Nextel 312)
composition	SiC	Al_2O_3 (85%), SiO_2 (15%)	Al_2O_3 (62%), SiO_2 (24%), B_2O_3 (14%)
diameter (μm)	14	17	11
density (g/cm^3)	2.5	3.3	2.7
fibers/tow	500	500	500
manufacturer	Nippon Carbon	Sumitomo	3M

Chromium Oxide. The procedure is very similar to the aluminum oxide coating procedure except the temperatures were set at 190 °C for the sublimation furnace and 435 °C in the reactor furnace. Only the SiC fibers were tested for coatings of chromium oxide. Several of these fiber tows were placed into a 5 mm × 6 cm silicate glass tube, 2 in. behind the entrance of the reactor furnace. An alumina boat containing 0.130 g of chromium acetylacetonate (Strem Chemicals) was placed inside the center of the sublimation furnace. Argon carrier gas (105 mL/min) and air (5 mL/min) were introduced into the reactor. After 1 h, the temperature was increased to 200 °C. The precursor was completely consumed after another hour. The reactor tube was also rotated 180° every 15 min.

B. Characterization. *XRD.* The X-ray diffraction patterns of the coatings were obtained with a Scintag X-ray diffractometer model XDS-2000 equipped with a Cu Kα radiation source. Several coated yarns were placed side-by-side and flat onto a glass slide. The scan angle was from 5 to 90° with a 4°/min rate of analysis.

SEM. Micrographs of the yarns were obtained using an AMRAY model 1810 scanning electron microscope. The yarn samples were cut by using a razor blade to avoid damaging the coatings.

C. Tensile Strength. The ends of the coated ceramic tows were attached by epoxy onto a 5 × 2 cm rectangular cardboard strip with a 2.5 × 1 cm rectangular hole in the middle. The tows were coated with an acrylic binder to keep the individual fibers together and allow load transfer to all the fibers in the tow. The epoxy adhesive was cured for a week prior to testing to ensure a maximum grip; otherwise the fiber tows could slip from the cardboard attachment. Afterward the cured sample tows were placed in an Instron tester and the edges of the cardboard were cut prior to pulling the tows. This type of yarn testing gives slightly lower values than single fiber tests but a comparison of the average breaking force before and after the coating process can be made. The cross sectional area of the tow was determined by assuming that each tow had 500 fibers, which had average cross sections of 11−17 μm depending on the type of ceramic fiber.

Results

Synthesis. Nicalon SiC fibers are black before the coating process. After the aluminum oxide deposition process, the fibers appeared to be shiny, with an evident multicolor coating. This multicolored coating is the aluminum oxide deposited on the surface of the fibers. The glass tube sample holder was covered with a translucent golden brown film. The part of the reactor tube that was inserted inside the reactor furnace showed traces of coatings as well, especially darker in the deposition zone, which is located 2−4 in. after the entrance end of the reactor furnace. The other side, exposed inside the sublimation furnace, is clear and free of any coatings indicating that no decomposition of the precursor occurred between 170 °C and 180 °C. However, the color of the coating is much more clearly seen for the Sumitomo $Al_2O_3-SiO_2$ fibers. These fibers were initially white. After the aluminum oxide coating process, the Sumitomo $Al_2O_3-SiO_2$ fibers appeared to be slightly brown in color, which is similar to the color of the coated reactor tube for the SiC fibers.

The chromium-oxide-coated SiC fibers are similar in appearance to the aluminum-oxide-coated SiC fibers; they have a shiny, multicolored coating. The glass tube sample holder for the chromium oxide coating was covered completely with a green material. The green color is attributed to the trivalent chromium oxide.

XRD. The XRD patterns for the aluminum-oxide-coated SiC fibers showed no crystalline material, suggesting an amorphous nature. Scraping the inside surface of the sample holder shows that the powder obtained is light brown. This powder on heating to 950 °C/36 h/air turned white. The diffraction pattern gave crystalline phases as shown in Figure 2. This pattern corresponds to γ-Al_2O_3. The amorphous hump is attributed to the SiC substrate. Other phases detected were that of an aluminosilicate which could have come from the reaction between aluminum oxide and silicon oxide scrapings from the quartz reactor tube. It is also possible that the aluminosilicate could be from the reaction of the aluminum oxide coating with SiO gas released off the bulk fiber material. The aluminum oxides coated onto the Sumitomo ($Al_2O_3-SiO_2$) and the Nextel 312 ($Al_2O_3-SiO_2-B_2O_3$) fibers were also amorphous in structure. The amorphous Al_2O_3 phase is

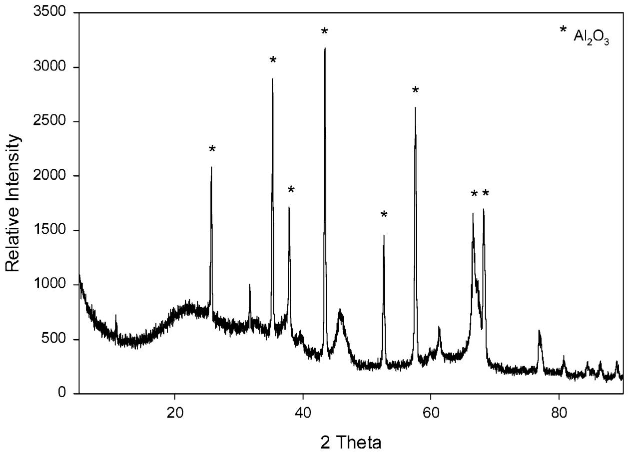

Figure 2. X-ray diffraction pattern of recrystallized aluminum oxide powder.

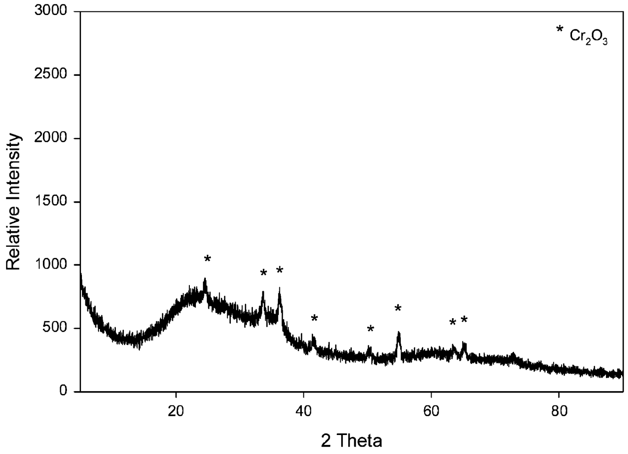

Figure 3. X-ray diffraction pattern of chromium-oxide-coated SiC fibers.

expected with low deposition temperatures (e.g., <700 °C). Crystalline phases of Al_2O_3 are produced at temperatures >700 °C.[43]

X-ray diffraction patterns for chromium-oxide-coated SiC fibers did show crystalline Cr_2O_3 peaks at reaction temperatures as low as 435 °C. The X-ray diffraction pattern is shown in Figure 3. There were no traces of other chromium oxide phases in the diffraction pattern except for the corundum trivalent oxide. In addition, elemental analysis of the coating did not reveal any other oxidation states of chromium. The trivalent phase is sought because hexavalent chromium is environmentally toxic, whereas the 3+ ion is not.

SEM. Scanning electron micrographs of the aluminum-oxide-coated SiC fibers were obtained as shown in Figure 4. The aluminum oxide coating was smooth and had a uniform morphology, except for occasional flake formation near the fiber ends. The thickness of the coatings appeared to be approximately 1 μm. Some occasional fiber bridging by the coating is observed as shown in Figure 4c. Fiber bridging is a common problem encountered when depositing a coating. This problem can be due to rapid deposition resulting in a thick coating onto the fibers not allowing the metal oxide to infiltrate the spaces between filaments. Additional work is being conducted to reduce this effect. Aluminum oxide coated onto the Sumitomo fibers is shown in Figure 5. The coating is not as smooth as those for the coated SiC fibers; the surface seemed to be rough with small bumps.

The surface morphology of the chromium-oxide-coated SiC fibers is also smooth and uniform as shown in Figure 6. The coating is approximately 1 μm thick as well. The fiber ends are exposed from the coating due to the preparation of the fiber prior to microscopic analysis.

Areas of the fiber revealed after removal of the oxide coating are still clean and uniform. From observations of the micrographs, the metal oxides did not seem to attack the fiber surface or to have infiltrated the bulk of fiber material. No remnants were left attached on the revealed surface, suggesting a relatively weak metal oxide interphase and no SiC fiber surface interactions.

Tensile Strength. Preliminary tensile strength testing on the coated SiC fibers showed that both metal oxide coatings degrade the strength. The aluminum oxide coating decreased fiber strength by 20% compared to the chromium-oxide-coated fibers which were 40% degraded. Fibers coated with aluminum oxide yielded an average strength of 2.12 GPa and chromium-oxide-coated SiC fibers gave an average strength of 1.61 GPa compared to untreated fibers, which exhibit an average strength of 2.63 GPa. One notable observation was the breaking point. When the untreated fibers failed, the whole tow cracked horizontally at the center, which is typical for catastrophic failure. However, the treated fibers did not immediately break in half — when the tows failed there were fiber pullouts from the bundle. Heating may have also caused the degradation of strength.[12,15,30−35] The process atmosphere and the precursor used are known to affect the properties of the ceramic fibers as well.[13,44,45] The fiber tows heated under similar conditions without the coating became too separated and difficult to handle so no comparative studies were made for the heat-treated materials.

Because aluminum oxide did not degrade the SiC fibers as much as chromium oxide did, Al_2O_3 was applied onto Sumitomo ceramic fibers. The aluminum oxide coating did not seem to degrade these fibers in terms of strength. The average strength tested for the aluminum-oxide-coated Sumitomo fibers was 0.717 GPa, which was well within 93% of the strength of the untreated ceramic fibers of 0.765 GPa. The color of the coating was slightly brown. The thickness of the coating is comparable to the thickness of the aluminum oxide coated on the SiC fibers. Another type of fiber tested was Nextel 312, which has lower aluminum oxide content, more silicon oxide, and has some boron oxide compared to Sumitomo fibers. The coating severely degraded the strength of these fibers. The average strength of the untreated Nextel 312 fibers was 1.05 GPa, whereas the aluminum-oxide-coated fibers yielded only 0.217 GPa, which is an 80% decrease in fiber strength. The average tensile strengths of all the fibers are summarized in Table 2.

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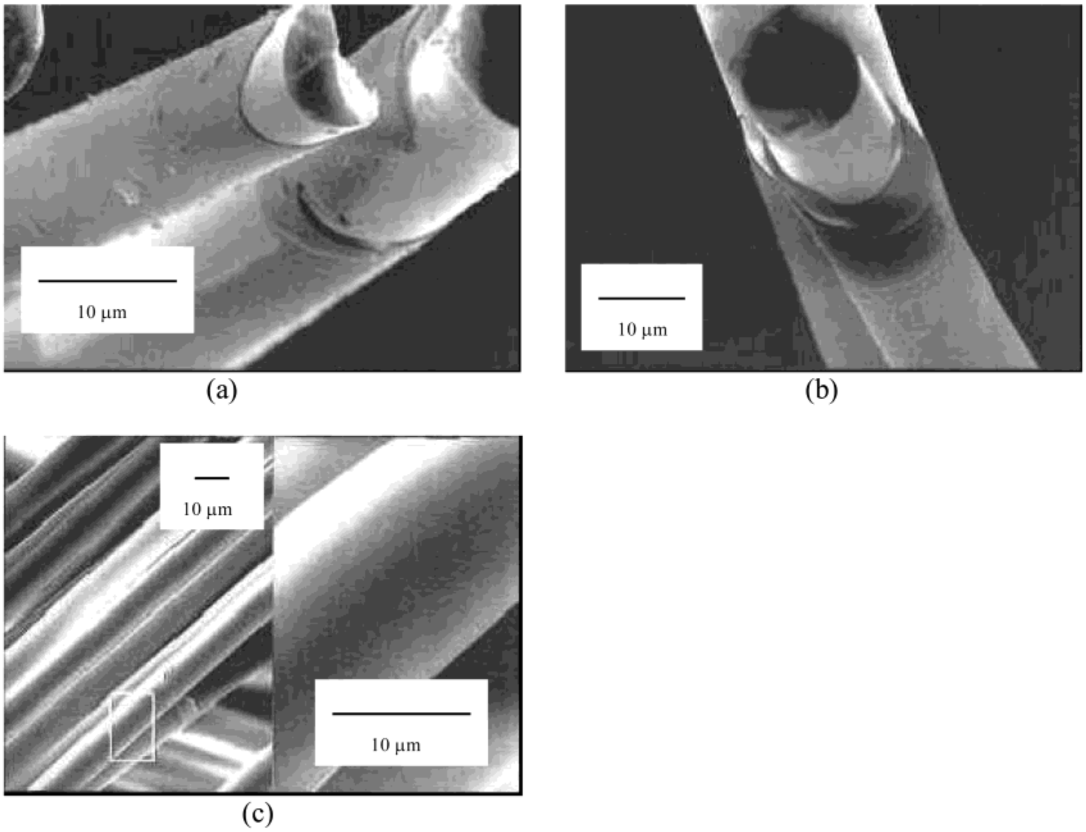

Figure 4. Scanning electron micrograph of aluminum-oxide-coated SiC fibers.

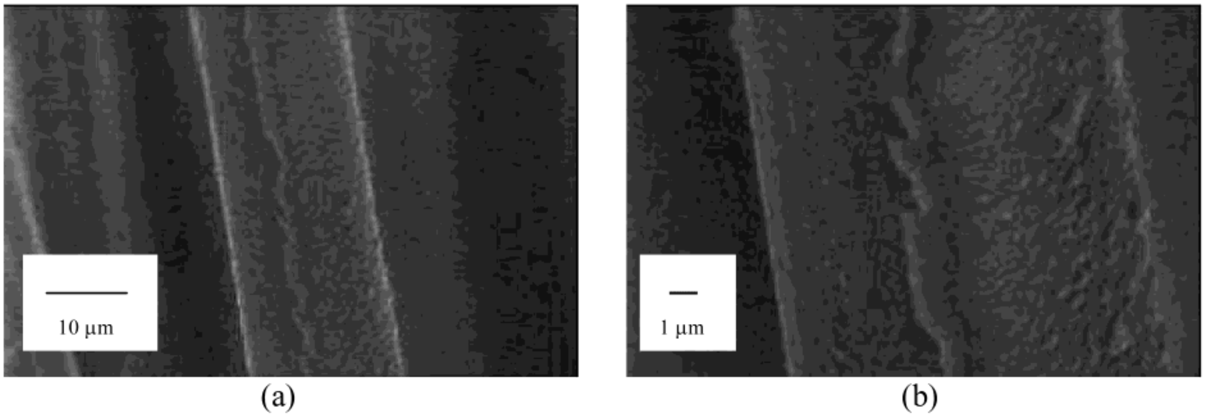

Figure 5. Scanning electron micrograph of aluminum-oxide-coated $Al_2O_3-SiO_2$ fibers.

Discussion

Some of the useful high-temperature reinforcing fibers in CMCs are based on SiC and $Al_2O_3-SiO_2$. At high temperatures, however, material diffusion becomes a problem. Oxygen gas from the atmosphere or from process gases can come into contact with the composite and diffuse into the bulk of the SiC reinforcing fiber. The diffused oxygen eventually oxidizes the SiC fiber material, which could have detrimental effects in terms of high-temperature stability and strength. Another concern is the interaction between fiber and matrix materials at high temperatures. A strong bond between the fiber and the matrix will result in diminished fracture toughness of the composite.

Aluminum oxide and chromium oxide are stable materials at high temperatures; their inertness and stability in oxidizing atmospheres made them potential choices as interphases between the reinforcing fibers and the ceramic matrix. These materials were successfully deposited onto different types of ceramic fibers by MOCVD. The interphase coating of metal oxide could serve as oxygen and material diffusion barrier at high temperatures, slowing down the rate of oxidation of the fiber material.

Aluminum oxide was deposited onto SiC and $Al_2O_3-SiO_2$ based fibers at 500 °C, a relatively low temperature compared to conventional methods of Al_2O_3 CVD, which is around 1000 °C. The coating obtained was amorphous, and heating the collected powder to 950 °C overnight did not produce any crystalline phase. The amorphous phase could be beneficial as a diffusion barrier because this phase has a lower density of pores and exhibits no grain boundaries. Oxygen also diffuses slower in aluminum oxide.[46] When the collected powder

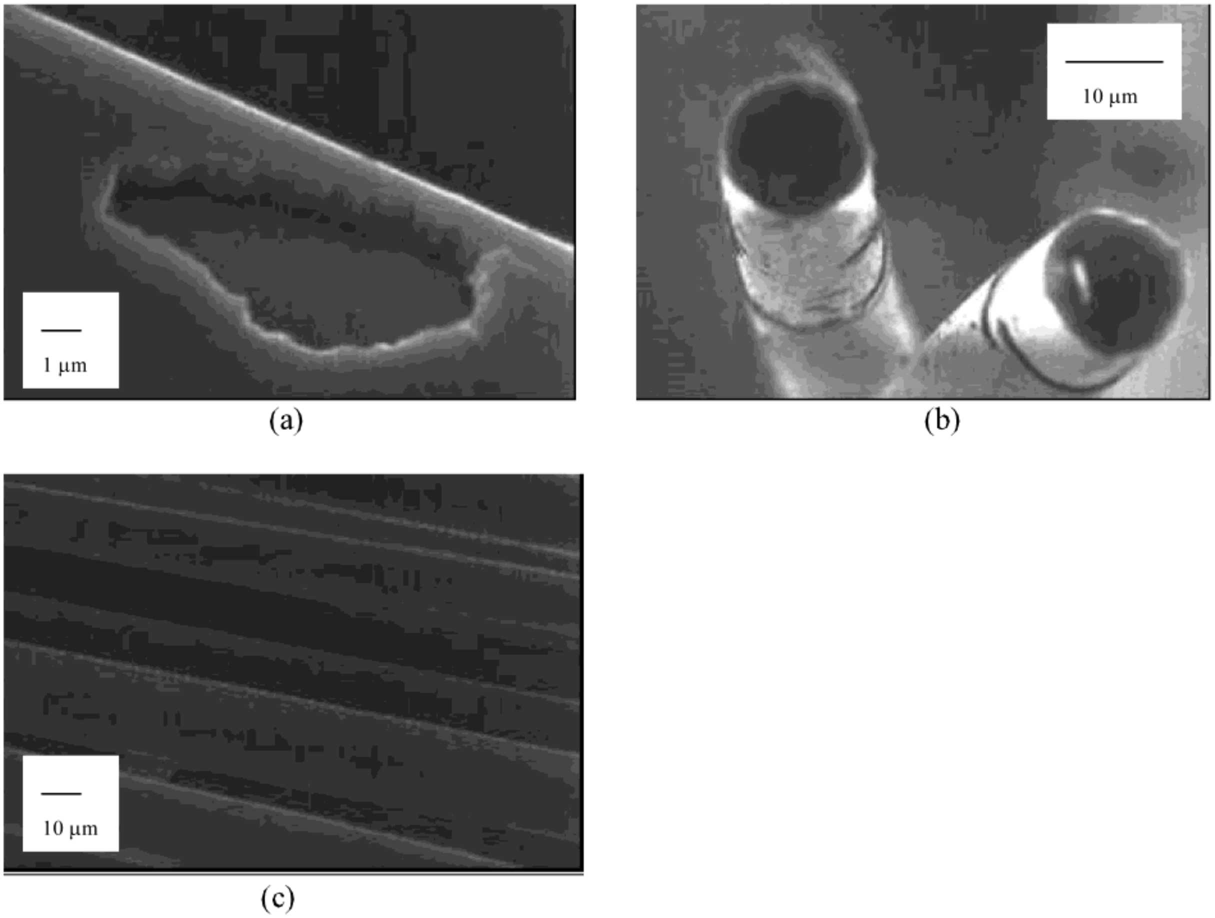

Figure 6. Scanning electron micrograph of chromium-oxide-coated SiC fibers.

Table 2. Average Tensile Strength of the Ceramic Fibers

sample	tensile strength (ksi)[a]	tensile strength (GPa)
SiC (Nicalon)	382.0	2.63
SiC (Nicalon)/Al_2O_3	308.4	2.12
SiC (Nicalon)/Cr_2O_3	232.9	1.61
$Al_2O_3-SiO_2$ (Sumitomo)	111.4	0.765
$Al_2O_3-SiO_2$ (Sumitomo)/Al_2O_3	104.0	0.717
$Al_2O_3-SiO_2-B_2O_3$ (Nextel)	152.9	1.05
$Al_2O_3-SiO_2-B_2O_3$ (Nextel)/Al_2O_3	31.50	0.217

[a] Average of 6 trials.

was heated for more than 36 h, the powder was converted into a crystalline material. The diffraction pattern is γ-Al_2O_3 as shown in Figure 2. The adhesion of the aluminum oxide interphase coating on the ceramic fibers was not very strong. Some flaking and removal of the coating were seen, especially near the ends of the fibers after cutting the fiber tows as shown in Figure 4. The weak interaction between the interphase and the reinforcing fibers can allow the ceramic matrix to crack while the fibers slide out of the matrix without immediately damaging the reinforcing fibers, thus there is fiber pullout from the composite produced using them. Fiber pullout contributes to the toughness of the whole composite.

Tensile strength testing results are summarized in Table 2. The tests showed a 20% decrease in fiber strength for coated SiC fibers, and less degradation of only 7% for the coated Sumitomo fibers. Aluminum oxide coating was also tried onto another type of $Al_2O_3-SiO_2$ fiber, Nextel 312, which has more SiO_2 and less Al_2O_3 than Sumitomo fibers, but the coating totally degraded the strength of this fiber. The degradation of these fibers however, cannot be attributed to the metal oxide only because heat treatment can also be a factor in the reduction of fiber strength.[15,30−35]

The failure behavior of the coated fibers is different from the failure of the untreated fibers. When the untreated fibers failed, the whole tow broke completely in half. The coated fibers did not completely break at once but instead there was gradual pullout of fibers from the bundle before the tow totally failed. This gradual pullout exemplifies the ability of the metal oxide to act as an interphase providing a weak interaction between the fiber and the matrix material.

The aluminum oxide coating process appears to have significantly reduced the strength of the SiC and Nextel fibers but not of the Sumitomo fibers. However, the strength of the Al_2O_3-coated fibers is still adequate for use in composites of ceramic materials containing SiC monofilaments and other $Al_2O_3-SiO_2$ ceramic fibers. The strengths are still greater than many of the metal fibers listed in Table 1.1 of ref 15. In addition, the weak bonding should contribute to fiber pullout and the overall toughness of ceramic composites.

Chromium oxide is also one of the stable oxides at high temperatures. Cr_2O_3 coatings on metals and alloys are effective against hot corrosion.[47] This metal oxide

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was coated on SiC fibers. Despite the low deposition temperature, the chromium oxide obtained at 435 °C was the crystalline corundum trivalent species as shown by the diffraction pattern in Figure 3. The amorphous hump corresponds to the SiC substrate. The morphology of the coating is shown in Figure 6, which is also uniform and smooth, and the thickness of the coating is approximately 1 μm. The Cr_2O_3 coating did have a degradative effect on the fiber strength. Tensile strength of the coated fibers decreased by 40% after deposition of Cr_2O_3.

Conclusions

Deposition of oxidative-resistant metal oxides such as aluminum oxide and chromium oxide onto reinforcing ceramic fibers has been successfully carried out by chemical vapor deposition. The technique employed metal acetylacetonate precursors, which can be converted to the oxide at temperatures from 200 to 600 °C compared to CVD processing of inorganic salt precursors such as halides, which are done at 900 °C and above. Deposition temperatures done below 600 °C in MOCVD can avoid or reduce the degradation of the ceramic fibers caused by conventional Al_2O_3 CVD from halide processes. The aluminum oxide coating produced is the amorphous form and can be converted to crystalline forms, such as γ-Al_2O_3 or α-Al_2O_3 by proper heat treatment. The chromium oxide coating obtained is the corundum trivalent oxide. The coatings and the fiber surface interactions are relatively weak as observed by some flaking of the coatings, which is desirable for fiber pullout. Upon removal of the coating, the fiber surface is still smooth showing no visible surface damage due to the metal oxides.

Further studies are being conducted to lessen the strength reduction of coated fibers. These studies show that Al_2O_3 and Cr_2O_3 can be produced at deposition temperatures <600 °C, which are useful for coating various fibers and other materials.

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