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DEVELOPMENT OF SOL-GEL DERIVED COATINGS FOR NICALON™/SiC COMPOSITES

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ABSTRACT

Mullite and aluminum titanate precursor polymeric sols were developed for applying as coatings on Nicalon™ fabrics and tows. A Nicalon™/SiC composite with a mullite interface was fabricated. The mullite precursor interface coatings were applied by a vacuum infiltration method and the SiC matrix was deposited by a forced flow chemical vapor infiltration process. Thin, uniform mullite interface coatings were obtained. However, the Nicalon™/SiC composite exhibited brittle fracture. Mullite and alumina-titania coatings were applied on Nicalon™ tows and the effect of heat treatment at 1000°C in air is discussed.

INTRODUCTION

Continuous fiber ceramic composites (CFCCs) are being developed for high temperature structural applications, especially for oxidative environments [1]. CFCCs owe their good damage tolerance at room temperature to at least one layer of carbon or boron nitride between the fiber and the matrix. However, after high temperature oxidative exposure in which air is allowed to contact the interface, such composites exhibit brittle fracture due to the oxidation of the interfacial layer. Hence, alternative, oxidation-resistant interface materials need to be identified and developed.

It was observed that a Nicalon™ (Nippon Carbon Company, Yokohuma, Japan) fiber-SiC matrix composite with a mullite interface coating applied by a colloidal route retained fiber pullout even after oxidation [2]. However, non-uniformity of the mullite coatings was a problem and regions with considerable fiber-pullout adjacent to regions of brittle fracture were observed. As a result, a sol-gel route is being pursued to obtain uniform mullite coatings.

A finite element model (FEM) was utilized to understand the influence of different interfacial coating materials [3]. The details of the analysis were reported

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earlier along with material properties [2]. FEM analysis indicates that a low modulus interfacial coating may be effective in reducing the radial residual compressive stresses that result from cooling from the high processing temperatures. FEM results are consistent with the analytical model of Hsueh et al [4]. Analysis of the behavior of composites with a moderate modulus material, mullite, or a low modulus material, aluminum titanate, as an interface coating should aid in understanding such coating effects and were chosen for this study.

Mullite has been observed to be thermochemically stable with respect to the constituents of Nicalon™ and the SiC matrix. Thermodynamic equilibrium calculations performed over a wide range of temperatures (1073 K to 1473 K) and oxygen potentials (from metal to ambient) indicate no interaction between the materials. With regard to aluminum titanate, under some conditions TiC is predicted to form along with mullite.

In this study, the synthesis procedure and interpretations of high temperature X-ray diffraction (XRD) and differential scanning calorimetry (DSC) of the mullite and aluminum titanate precursor gels are presented. Additionally, the fabrication procedure for a Nicalon™/SiC composite with a mullite interface is presented. Finally, the coatings obtained from the polymeric aluminosilicate and aluminum titanate precursor sols are described.

EXPERIMENTAL PROCEDURE

Mullite gels have been prepared and investigated by Yoldas [5] and Huling and Messing [6]. The procedure used in this work for the preparation of the polymeric mullite precursor sol has been slightly modified from that of Yoldas [5]: The mullite sol has a lower molar concentration; the amount of water added for hydrolysis during the stages of sol formation and gelation are different; and no acid catalyst is employed during the formation of the mullite precursor sol.

105 g ethanol was added to 1.5 g water in a flask. To this mixture, 30.8 g aluminum sec-butoxide (ASB) was added and the solution was shaken to form a white slurry. This white slurry converted to a clear, water-like liquid within 12 h when kept at 55°C, and is termed the polymeric alumina precursor sol.

Two mullite sols were obtained as described below. To about 60 cc alumina precursor sol, either 2.23 cc tetramethoxy silane (TMOS) or 3.35 cc tetraethoxy silane (TEOS) was added. Then, 0.27 cc water mixed with 50 cc ethanol was added to produce a clear, water-like liquid and is referred to as the polymeric mullite precursor sol. The mullite precusor sol obtained from the ASB/TMOS formulation and the ASB/TEOS combination are termed as MI and MII, respectively. For gelation studies, 2.71 cc water in 25 cc ethanol was then poured into each of the mullite sols (MI and MII) and gelled at 60°C. This gel was dried at 60°C for 168 h. For coating application, the MI and MII sols were further partially hydrolyzed by a water/ethanol mixture. Additionally, polymeric aluminosilicate precursor sols with final alumina/silica ratios of 0.75 and 3 were synthesized using the ASB/TEOS combination.

For synthesizing the aluminum titanate precursor sol, 10 cc titanium ethoxide was first dissolved in 40 cc of 2 methoxyethanol. 23.62 cc of the above mixture was then poured into 60 cc of alumina precursor sol. Next, 0.27 cc water in 50 cc ethanol was added to produce a polymeric aluminum titanate precursor sol. For gelation studies, 3.25 cc water in 25 cc ethanol was poured into the aluminum titanate sol and gelled at 60°C. This gel was then dried at 60°C for 168 h. For coating application, the aluminum titanate precursor sol was further partially hydrolyzed by a water/ethanol mixture.

High temperature XRD patterns were obtained using a Scintag PAD X θ/θ diffractometer equipped with a Cu X-ray tube, a Buehler high temperature furnace and a mBraum position-sensitive detector. A finely ground powder sample of the precursor gel was prepared as a thick film on a Pt/30%Rh heater strip. The XRD patterns were collected in a dynamic air atmosphere over the scan range of 20° to 70° 2θ at 5°/min at several temperatures up to 1350°C for the mullite precursor gel and 1450°C for the aluminum titanate precursor gel. Differential scanning calorimetry (DSC) (Stanton Redcroft DSC 1500) runs were conducted in a Pt crucible with sapphire as the reference material. The DSC furnace was ramped at 20°C/min between 25°C and 1450°C and the measurements were conducted in both air and argon.

Fibrous preforms for making composite samples were prepared by stacking multiple layers of plain-weave Nicalon™ cloth (46 in total) in a graphite holder, the details of which are described elsewhere [2]. Mullite sol (MI) was then vacuum infiltrated into the fibrous preform three times and then the preforms were sintered at 1100°C in argon for 1 h. The SiC matrix was then infiltrated into the coated preforms using the forced-flow chemical vapor infiltration (FCVI) process, which is described elsewhere [2].

Nicalon™ tows 15 cm long were withdrawn from the 3 wt% mullite and aluminum titatnate precursor sols at the rate of 3.7 cm/min. The coated tows were then heated in air at 1000°C for 1 h or 10 h. In addition, Nicalon™ tows were dip-coated in the synthesized polymeric aluminosilicate sols having different alumina/silica ratios and heat treated at 1000°C for 1 h.

RESULTS AND DISCUSSION

The DSC curve obtained from the mullite precursor gel (MI) shows a sharp exothermic peak around 990°C indicating mullite crystallization (Fig. 1). High temperature XRD results indicate that mullite formation occurs around 1050°C for both the tetramethoxy silane-aluminum sec-butoxide (MI) and the tetraethoxysilane-aluminum sec-butoxide (MII) combinations. Figure 2 shows that the formation of mullite from the MII gel takes place between 1000°C and 1050°C. Hence, a mullite coating can be obtained on Nicalon™ at a temperature of ~ 1050°C.

The DSC curve obtained from an aluminum titanate precursor gel indicates that titania and α-alumina crystallize at 900°C and 1000°C, respectively, and aluminum titanate forms at ~ 1400°C [7]. The high temperature XRD patterns also

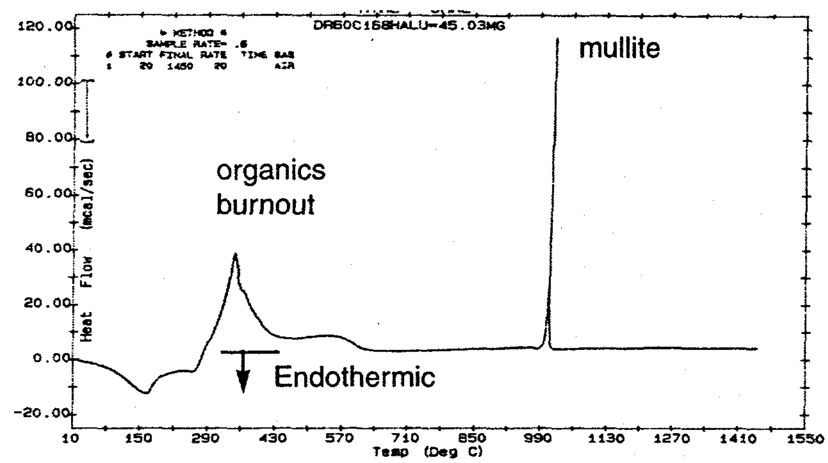

Fig. 1 DSC *curve* obtained from the mullite precursor gel (MI) shows that mullite crystallization occurs around 990° C

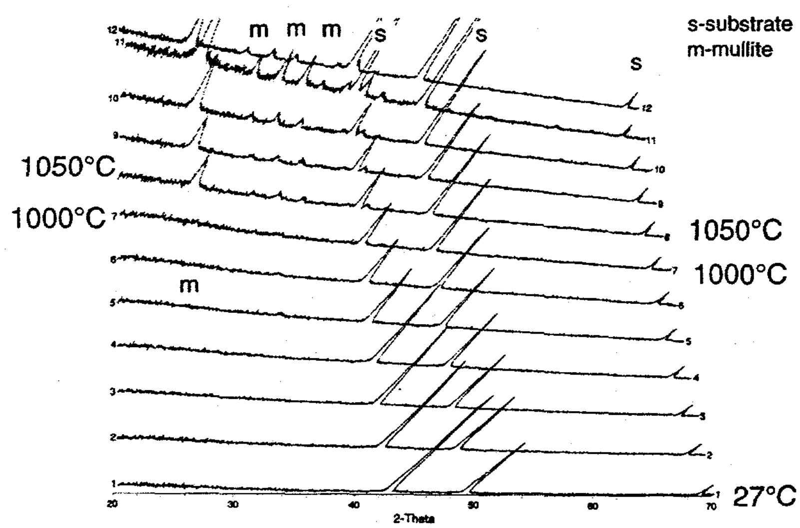

Fig. 2 High temperature x-ray diffraction pattern shows mullite evolution at 1050°C from the mullite precursor gel (MII)

show that titania cystallization occurs at 900°C followed by alumina crystallization at 1000°C (Fig. 3). Alumina and titania then react to form aluminum titanate around 1400°C. However, residual amounts of alumina and titania remain at 1400°C. Hence, aluminum titanate cannot be obtained as coatings on Nicalon™ below 1400°C from the aluminum titanate sol. Coatings obtained from the aluminum titanate sol on Nicalon™ were heat treated at 1000°C in air to yield an alumina-titania coating.

The room temperature XRD pattern of Nicalon™ cloth dip-coated in mullite sol three times and heat treated at 1050°C in air for 30 minutes indicated mullite formation [7]. Figure 4 shows a transmission electron image of an as fabricated Nicalon™/SiC composite with a mullite interface. A thin uniform mullite coating of 50 nm thickness was obtained. In addition, a thin silica layer was present between the mullite interface and the Nicalon™. Flexural bars sectioned from the composite did not exhibit any damage-tolerant behavior and underwent brittle fracture [7].

Coated Nicalon™ tows were used to determine whether Nicalon™ is damaged during sol-gel processing. Nicalon™ tows were dip-coated in mullite sol (MII) at various withdrawal rates and it was found that a slow withdrawal rate (3.7 cm/min) resulted in thin (100 nm or less) and much more uniform coatings than other withdrawal rates (> 3.7 cm/min). Figure 5 shows a secondary electron image of a mullite coating on a Nicalon™ tow heat treated at 1000°C along with an energy dispersive X-ray (EDX) spectrum. The EDX analysis indicated that the relative intensity of aluminum to silicon peaks vary from one region to another in the tow [7].

Nicalon™ tows coated with a mullite (MI) sol (alumina/silica ratio = 1.5) and heat treated at 1000°C for 1 h in air had poor handleability. Thus, suggesting that the coated Nicalon™ tows were embrittled. In contrast, Nicalon™ tows coated with a mullite sol obtained from the ASB/TEOS (MII) formulation and similarly heat treated had better handleability. However, longer heating times (10h) in air resulted in poor handleability.

The tows dip-coated in an aluminosilicate precursor sol with a lower alumina/silica ratio of 0.75 and heat treated at 1000°C in air were less handleable than those dip-coated in a mullite sol (MII). Further, the tows dip-coated in an aluminosilicate precursor sol with a high alumina/silica ratio of 3 had good handleability. At the present time, we have not made any quantitative measurement of the strength of the fibers after coating. Further work has to be done to understand the mechanism and the extent of fiber damage during sol-gel processing.

Figure 6 shows a secondary electron image of Nicalon™ tows coated with the aluminum titanate precursor sol and heat treated at 1000°C for 1 h in air. The coated Nicalon™ tows had good handleability, and this persisted even after longer heating times (10 h) in air.

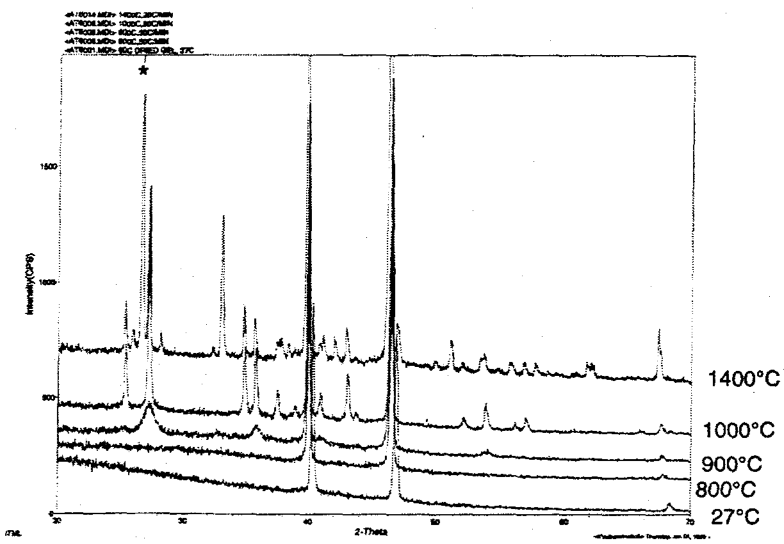

Fig. 3 High temperature XRD study shows that aluminum titanate forms at 1400°C (aluminum titanate major peak is marked by *)

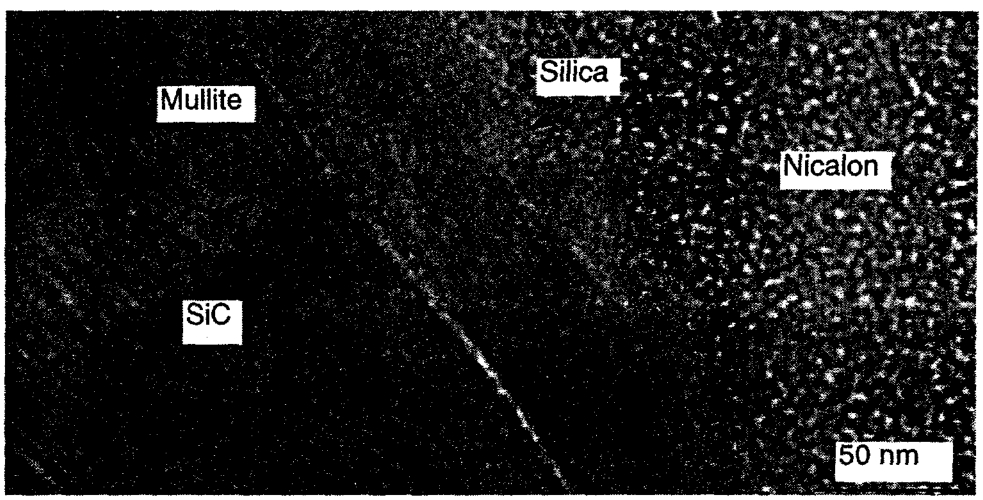

Fig. 4 TEM image of a Nicalon^{TM}/SiC composite with a mullite interface shows a thin, uniform mullite coating

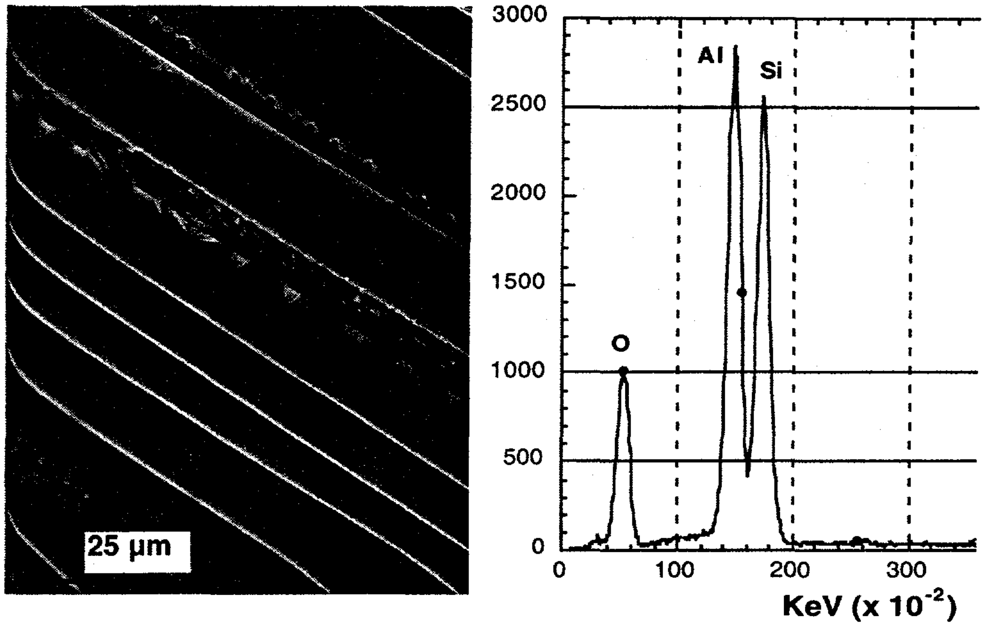

Fig. 5 SEM image of a mullite coating on a Nicalon tow heat treated at 1273 K along with an EDX spectrum

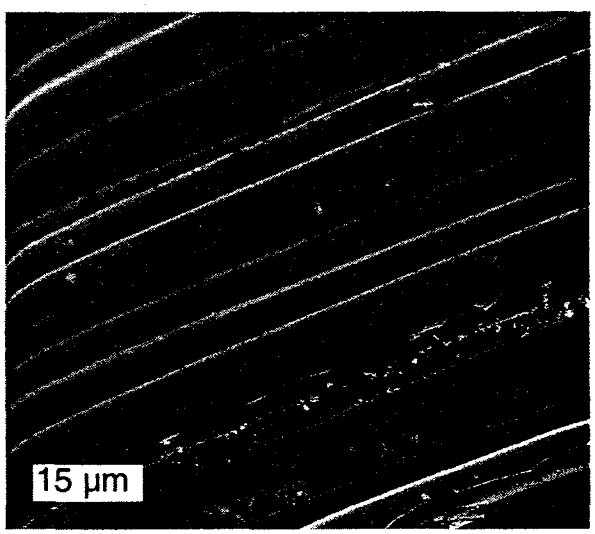

Fig. 6 SEM image of an alumina-titania coating on a Nicalon tow heat treated at 1273 K

CONCLUSIONS

Mullite and aluminum titanate precursor polymeric sols were developed for coating applications. DSC and high temperature XRD studies identified that mullite crystallization and aluminum titanate formation occurs around 1050°C and 1400°C, respectively. Uniform, thin mullite interface coatings were obtained for Nicalon™/SiC composite, but the composite exhibited brittle fracture. Nicalon™ tows dip-coated in mullite sols had poor handleability after heat treatment at 1000°C in air. However, Nicalon™ tows dip-coated in alumina-rich aluminosilicate (alumina/silica ratio =3) and aluminum titanate precursor sols had good handleability after heat treatment at 1000°C in air. Further work is needed to understand the mechanism and the extent of damage during sol-gel processing of the coatings on Nicalon™. Alumina-titania coatings and alumina-rich aluminosilicate coatings should be pursued as interfacial coating materials for Nicalon™/SiC system.

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