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Preparation and characterization of $50SiO_2$–$50Y_2O_3$ sol–gel coatings on glass and SiC(C/SiC) composites

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Abstract

Yttrium silicate (Y_2SiO_5) coatings can complement internal SiC coatings for protecting carbon-fiber-reinforced SiC composites (C/SiC). $50SiO_2$–$50Y_2O_3$ coatings were prepared by dipping samples into sol–gel solutions. The coatings were deposited on soda-lime glass substrates to evaluate their homogeneity and critical thickness. Crack-free coatings were obtained at withdrawal rates below 16 cm/min with a critical thickness of 80 nm. Thicker coatings (2 μm) were prepared on SiC-coated C/SiC composites using a multilayer deposition process. The gelled sol was also studied by transmission electron microscopy (TEM), thermal analysis (TGA–DTA) and X-ray diffraction (XRD).

Keywords: A. Sol–gel processes; B. Composites; E. Structural applications; Coatings; SiO_2–Y_2O_3

1. Introduction

The use of carbon-fiber-reinforced SiC composites (C/SiC) as structural hot-section components for propulsion systems would allow significantly higher operating temperatures than those tolerated by conventional nickel-based superalloy materials. However, the factor that currently precludes the use of C/SiC composites in high-temperature structural applications is the oxidation of carbon fibers above 400 °C. External coatings are the most common method for protecting these composites against oxidation. Conventional coatings consist of multiple layers of various materials, and, in general, most multilayer systems use SiC as an internal coating because of its similarity to the substrate [1].

Different compounds have been proposed in the literature to complement SiC coatings [2,3]. One promising candidate is the yttrium silicate (Y_2SiO_5) obtained by Ogura et al. [4]. The resulting material combines a low Young's modulus, good erosion resistance, and a low thermal expansion coefficient, very similar to that of SiC. These properties ensure a multilayer coating with good chemical stability and very low residual stresses at the SiC/Y_2SiO_5 interface. Moreover, the low evaporation rate and oxygen permeability of this material complement an excellent group of oxidation-resistance characteristics. A previous work described a feasible procedure for producing thick (100 μm) Y_2SiO_5 coatings on SiC-coated C/SiC composites using concentrated aqueous slips. The coatings provided suitable protection against oxidation at 1600 °C as evidenced by isothermal tests. However, a stepwise oxidation test showed a strong weight loss between 400 and 700 °C, caused by surface microcracks [5,6].

The sol–gel process is a suitable procedure to prepare thin coatings for a wide range of compositions on different substrates. Coating composition and deposition parameters can be designed as a function of the final properties and substrates. The advantages of the sol–gel process to prepare coatings in comparison with the use of aqueous slips are better wettability, lower temperatures of thermal treatment and higher homogeneity. The main disadvantage is the low thickness obtained in a single coating. The use of alkylalkoxysilanes as sol–gel precursors allows hybrid organic–inorganic coatings with higher thickness than those prepared only from alkoxides to be obtained [7]. Another alternative for producing thicker sol–gel coatings is the

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multilayer deposition process, i.e. deposition of several layers with intermediate thermal treatment after each layer.

The goal of the present work was to develop homogeneous and crack-resistant $50SiO_2$–$50Y_2O_3$ sol–gel coatings on glass and C/SiC composites already protected with a SiC coating substrate. Another purpose was to analyze the homogeneity of the oxides produced by sol–gel.

2. Experimental

$50SiO_2$–$50Y_2O_3$ sol was obtained by the sol–gel method using methyltriethoxysilane 98% (MTES) [$SiCH_3(OC_2H_5)_3$] and yttrium methoxyethoxide 99% (MEY) [$Y(OCH_2CH_2OCH_3)_3$], 15–18% in methoxyethanol (ABCR, Gelest Inc., Tullytown, PA, USA) as starting materials. Since the hydrolysis rates of the two precursors are very different, MTES being much slower than MEY, they were modified before mixing. MTES was pre-hydrolyzed with bidistilled water (molar ratio of $H_2O/MTES = 0.5$) and HCl 37% for analysis from Panreac (molar ratio $HCl/MTES = 0.072$), diluted with half the volume of 99.8% ethanol (solvent) and stirring at room temperature for 1.5 h. If not properly controlled, the hydrolysis reaction of MEY is much faster than the condensation reaction, and consequently, precipitation of the molecular aggregates of hydrated yttrium oxide species can occur. However, under carefully controlled conditions, it is possible to form soluble polymeric intermediates which undergo further polymerization to form a clear sol. In this work, the hydrolytic reactivity of MEY was controlled by forming a complex compound with acetylacetone, which reduces the reactivity, presumably by steric effects (molar ratio of $AcAc/MEY = 2$). This complex solution was poured into ethanol and stirred at room temperature for 1 h, then further incorporated in the pre-hydrolyzed MTES by stirring for an additional 30 min. The remaining amount of water to complete the molar ratio of water/precursors = 3 was added drop by drop, and the solution was stirred at room temperature for 2 h. The final sol had a concentration of 35 g/l of oxides.

The substrates were soda-lime glass slides and C/SiC composites (42.3 vol.% carbon fibers) coated with a 25 μm layer of SiC deposited by chemical vapor deposition (CVD). The later was supplied by Daimler-Benz Aerospace (Dornier Research, Friedrichshafen, Germany), produced through infiltration and pyrolysis of polycarbosilanes. Coatings were first obtained by dipping soda-lime glass substrates in room conditions in order to determine the critical thickness as a function of withdrawal rate. The withdrawal rate varied between 6 and 20 cm/min, and the coated samples were treated at 500 °C in air for 1 h. The thickness was measured by using a profilometer (Talystep, Taylor-Hobson, UK) after densification on a step made by scratching the coating immediately after deposition. The homogeneity was evaluated by optical microscopy. Thick coatings were obtained on C/SiC composite materials using a multilayer deposition process with a withdrawal rate of 13 cm/min, and intermediate thermal treatments at 500 °C in air for 1 h between each deposition. The coating thickness was measured in this case by scanning electron microscopy (SEM; Model DSM-950, Karl Zeiss, Inc., Thornwood, NY, USA)

The sol was poured into plastic tubes sealed with plastic wrap, and placed at room temperature for gellation. Several holes were punched in the wrap to allow evaporation of the solvent. The gelled samples were extracted from the tubes and dried at 50 °C for 2 weeks. TEM observations of crushed samples were performed with a Hitachi H-7000 operating at 125 kV. The thermal behavior (TGA–DTA) of gel powder was examined using a Netzsch STA 409 with a heating rate of 10 °C/min in air. X-ray diffraction (XRD) was performed using a Siemens Model D5000 on samples heat-treated at temperatures up to 500 °C.

3. Results and discussion

The sol was yellow and transparent, and the gellation process produced yellow, transparent and monolithic samples. Fig. 1 shows the log-log plot of the thickness versus withdrawal rate obtained with coatings on glass substrates. Thickness, t, of coatings applied by sol–gel dip-coating process is a function of several parameters: $t = f(\eta v/\rho g)^{1/2}$, where η is the viscosity of the sol, v is the withdrawal rate, ρ is the density of the sol, and g is the gravitational acceleration [8,9]. The slope of the $\log t - \log v$ plot is 0.54, close to the theoretical value. Crack-free coatings were obtained with withdrawal rates below 16 cm/min, placing the critical thickness, defined as the maximum thickness without cracks, at 80 nm.

Coatings on C/SiC composite substrates were prepared by dipping with a withdrawal rate of 13 cm/min, corresponding to a thickness of 70 nm on glass substrates. Multilayer coatings were produced with 20 layers deposited successively with intermediate thermal treatments between layers. Fig. 2 shows a cross section of an unpolished sample with the C/SiC composite at the bottom, the SiC layer in the middle, and the $50SiO_2$–$50Y_2O_3$ coating at the top. The $50SiO_2$–$50Y_2O_3$ coating has a thickness of about 2 μm. The higher thickness obtained on C/SiC composite materials

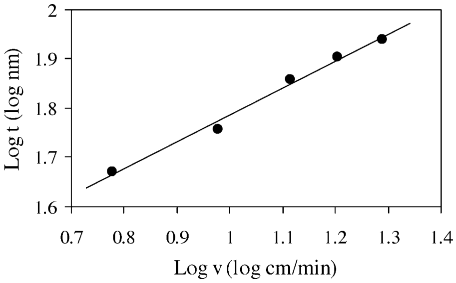

Fig. 1. Thickness of $50SiO_2$–$50Y_2O_3$ coatings as a function of withdrawal rate.

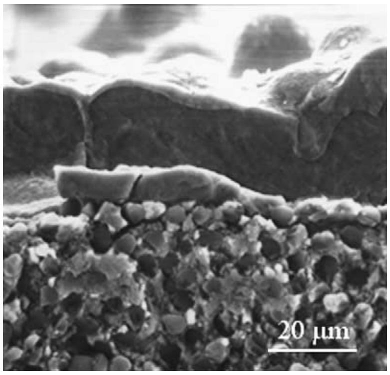

Fig. 2. SEM photograph of $50SiO_2–50Y_2O_3$ coating on SiC-coated sample treated at 500 °C.

compared to the glass slides could be attributed to the roughness and porosity of C/SiC materials. The photograph shows the $50SiO_2–50Y_2O_3$ coating perfectly adhered to the SiC layer, covering all the substrate. The deposited layer acts also to seal the substrate microcracks, an important fact for oxidation protection coatings.

Fig. 3 shows a TEM microphotograph of a crushed $50SiO_2–50Y_2O_3$ gel treated at 500 °C. The sample presents a homogeneous structure, typical of powders obtained by the sol–gel process with a good mixture of precursors. XRD patterns of crushed gels treated at different temperatures up to 500 °C only show the typical amorphous broad peak at about $2\theta = 24°$, characteristic of silicate gels.

The TGA–DTA curves of the $50SiO_2–50Y_2O_3$ gel dried at room temperature is shown in Fig. 4. The TGA curve can be divided into three regions: a first region between room temperature and 170 °C with the maximum rate of weight loss at 110 °C (derivative curve), a second region between 170 and 700 °C with a lower but continuous weight loss, and a third region above 700 °C without changes in weight. The weight loss in region I (12%) is mainly attributed to desorption of physically adsorbed water and residual solvents from the sol preparation. This value is relatively high because the gel was only dried at room temperature.

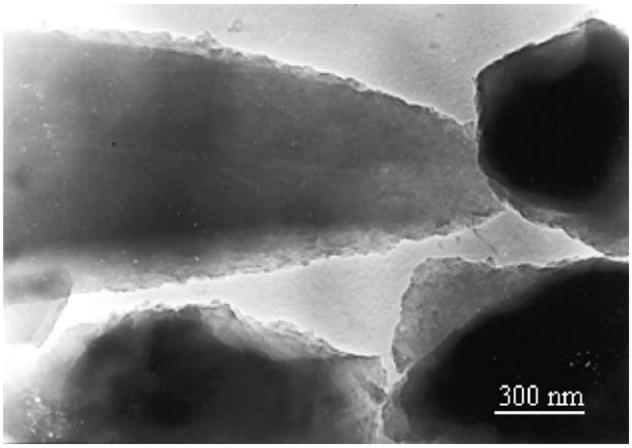

Fig. 3. TEM photograph of crushed $50SiO_2–50Y_2O_3$ gel treated at 500 °C.

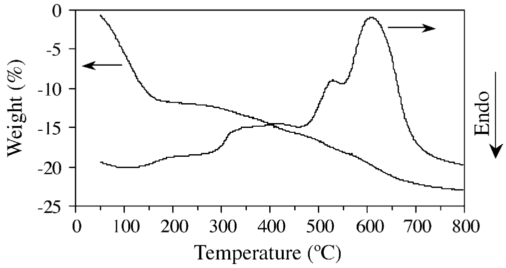

Fig. 4. TGA–DTA curves of $50SiO_2–50Y_2O_3$ gel dried at room temperature.

The continuous weight loss in region II is assigned to several processes [7,10–12]:

(a) Oxidative decomposition of organic residues from unhydrolyzed ligands bound to silicon and yttrium atoms. These groups result from an incomplete hydrolysis reaction.
(b) Combustion of solvents trapped within the solid porous texture.
(c) Loss of water from condensation reactions of some M–OH into M–O–M bonds.
(d) Combustion of acetylacetone.
(e) Oxidation of methyl groups.

The DTA thermograph of the $50SiO_2–50Y_2O_3$ gel dried at room temperature is also displayed in Fig. 4. There is a very small and broad endothermic peak at low temperature centered at about 110 °C due to residual water and solvents desorption. This peak is assigned to the weight loss observed at the same temperature on TGA curve in region I. There are also three exothermic peaks at higher temperatures: one broad peak between 300 and 450 °C, and two peaks centered at 540 and 620 °C. These three peaks agree with the continuous weight loss that appear in the thermogravimetric curve at the same temperature range in region II. The broad peak between 300 and 450 °C is mainly attributed to the oxidation of organic compounds from unhydrolyzed ligands and combustion of residual solvents trapped within internal pores, the exothermic peak centered at 540 °C can be assigned to the combustion of acetylacetone, while the peak at 620 °C can be due to the oxidation of the methyl groups from MTES [7,10–12].

The results presented in this paper show the possibility of using the sol–gel process to prepare $50SiO_2–50Y_2O_3$ coatings on glass and C/SiC substrates. The next step will be the study of the antioxidant properties of the coating, and the influence of the typical glass structure obtained with sol–gel process at low temperature.

4. Conclusion

$50SiO_2–50Y_2O_3$ crack-free sol–gel coatings were obtained on soda-lime glass substrates at withdrawal rates below 16 cm/min with a critical thickness of 80 nm. Homogeneous coatings with thickness of 2 μm were prepared by a multilayer deposition process on SiC-coated C/SiC composites substrates. The TEM microphotographs of the $50SiO_2$–$50Y_2O_3$ gel show an amorphous and homogeneous structure with no different phases. The thermal analysis (TGA–DTA) present the typical behavior of materials produced by sol–gel, with removal of residual water and solvents at low temperature, and organic compounds (unhydrolyzed ligands, acetylacetone and methyl groups) at higher temperatures.

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