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Oxidation protection of carbon-carbon composites by sol-gel ceramic coatings

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Carbon-carbon composites were coated with Calcium Magnesium Zirconium Phosphate (CMZP) and Mg-doped Al_2TiO_5 sol-gels in order to form an oxygen barrier at temperatures above ~650 °C. The coatings were applied using a dipping technique and controlled drying procedures. It was determined that 10 coats of CMZP sol-gel fired every other coat created crack free coatings and oxidation protection. Mg-doped $AlTi_2O_5$ coatings produced were unsuccessful as oxidation barriers.

1. Introduction

Carbon-carbon (C—C) composites are a lightweight, high strength and modulus class of materials which can be used in high temperature. Introduced in the mid 1950's, these composites were selected for aerospace applications for the following reasons: (1) Strength values were easily reproducible at 1650 °C; (2) modulus and strength values were large enough to resist flight loads and thermal stresses; (3) low thermal expansion coefficient sufficiently reduced thermal stresses and increased structural stability; (4) high mechanical toughness; (5) ability to be manufactured with current technology; (6) oxidation resistance sufficient to limit strength reduction. To date, C—C composites are a frontrunner in similar applications with current technologies facilitating their use in highly oxidative environments [1].

Oxidation protection of carbon has been under investigation since the 1930's when a patent was issued for an antioxidation coating method [2]. Since then, glasses, limited by their relatively low temperatures, and SiC/Si_3N_4, with high CTE mismatch, have been widely studied for oxidation protection coatings [2, 3]. Fundamentally though, and ideal coating has a CTE similar to the substrate to avoid microcracking and delamination, adheres sufficiently to the substrate, and acts as an oxygen barrier. For these reasons, oxide ceramics were chosen as the coating material and applied with the sol-gel method.

A sol-gel process requires the formation of a solution containing stoichiometric amounts of the elements in the desired compound in a solvent. The solution is polymerized to form a gel which is dried and fired to remove the organic components and form the final compound. Ceramic coatings formed via sol-gel are of high purity and can be used to coat very complex shapes. Two ceramics possessing similar coefficients thermal expansion (CTE) to the carbon-carbon composite were selected and a processing method for forming suitable oxidation resistant coating was determined. Specifically, the ceramics chosen were sol-gels of aluminum titanate $[Al_2TiO_5]$ and CMZP $[(Ca_{0.6}, Mg_{0.4})Zr(PO_4)_6]$ with CTE of 2.0×10^{-6}/C and 0.1×10^{-6}/C respectively [4] with the carbon composite having a CTE of approximately 1.1×10^{-6}/C [1].

CMZP is a $NaZr_2(PO_4)_3$ [NZP] type material with an open but rigid crystal structure. The thermal expansion is controlled compositionally by the movement of cations into interstitial positions, resulting in anisotropic thermal expansion of the a and c directions of the structure. In addition to low CTE, CMZP possesses low thermal conductivity, good chemical/thermal stability, and can be produced cost effectively via solid state reaction [5]. Sol-gel derived CMZP coatings have been used as oxygen and alkali barriers on silicon carbides [6, 7] and silicon nitrides [4].

Aluminum titanate is known for its low thermal conductivity, low CTE, and high melting point. Between 800 and 1250 °C, the compound tends to decompose to Al_2O_3 and TiO_2, a problem which can be avoided by small additions of MgO or Fe_2O_3 [8]. Neighboring grains in the ceramic create stress induced microcracks. These microcracks absorb the expansion of neighboring grains upon heating which accounts for the low CTE. However, these microcracks also limit the room temperature strength of the material, a problem which can be avoided by sintering pore-free submicron powders [4]. Sol-gel derived aluminum titanate coatings have been used as thermal insulation in diesel engines [9], oxidation barriers on silicon carbides [6], and as an alkali corrosion barrier [6].

CMZP and Al_2TiO_5 sol-gel derived coatings were applied to C—C composites to form oxidation barriers above the oxidation temperature of carbon (~650 °C). The extent of oxidation was determined by thermogravimetric analysis (TGA) and before/after firing weight ratios.

2. Experimental procedure

2.1. Materials and sol-gel preparations

The substrate material, a layered 90° mesh, was supplied by the National Air and Space Administration, Langley Research Center. Small rectangular coupons approximately 7 by 10 by 2 mm were cut from the material. The coupons were placed in acetone, ultrasonicated, dried, rinsed with acetone, and dried again to thoroughly clean the substrate surfaces.

The CMZP sol-gel was formed with stoichiometric ratios of the precursors calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), zirconium dinitrate oxide ($ZrO(NO_3)_2 \cdot xH_2O$), and triethyl phosphate ($((C_2H_5O)_3P(O))$), which were thinned to 2.5 wt % in a mixture of ethyl alcohol and de-ionized water. The pH was adjusted to pH 2–4 with nitric acid, which formed a milky white sol-gel solution.

The Mg-doped $AlTi_2O_5$ sol-gel was formed with the stoichiometric ratios of the precursors magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), aluminum tri-sec butoxide ($Al[C_2H_5CH(CH_3)O]_3$), and titanium butoxide ($Ti[CH_3(CH_2)_3O]_4$), which were thinned to a viscosity of less than 1.0 cP in a mixture of ethyl alcohol. The pH was adjusted to pH 1–4 with nitric acid, which formed a clear, slightly yellow sol-gel solution.

2.2. Experimental methods

CMZP coatings were produced by immersing and extracting C—C samples from the sol-gel for 10 min, or until no trapped air bubbles were expelled from the porous sample. The samples were stored at 40–80 relative humidity and room temperature for 24 h in order to complete the hydrolysis reaction. Two sets of experimental methods were employed to determine the optimal oxidation coating. First, samples were dipped from 2 to 12 times and the resulting coatings were fired in nitrogen. Second, samples were dipped twice and fired in nitrogen. This second procedure was repeated, dipping twice and firing, until 2–12 coats were obtained. All samples were fired in nitrogen to 1200 °C and soaked at that temperature for 1 h. The heating rate was kept at 1 °C/min in order to reduce the formation of cracks while a furnace cool from 1200 °C (~2 °C/min) was allowed.

Al_2TiO_5 coatings were produced by dipping the carbon—carbon composite samples into the Mg-doped Al_2TiO_5 solution for 15 min to allow any entrapped gases to escape and were then withdrawn at a rate of 4 cm/min. The coated samples were kept at room temperature and at 70–90% relative humidity for 24 h allowing the hydrolysis reaction to occur. The samples were then moved to an oven kept between 65 and 100 °C for an additional 24 h to partially dry them before subsequent coatings were added and before firing. Two dipping procedures were utilized to determine the optimal coating method. First, samples were dipped twice and sintered in nitrogen. This procedure was repeated until twelve coats had been applied to the samples. Second, samples were dipped twelve times and then sintered in nitrogen. All samples were sintered at 1300 °C with a soak at temperature for 6 h. The samples were heated at a rate of 1 °C/min to 200 °C and then at a rate of 10 °C/min to 1300 °C to prevent the crystallization of Al_2O_3 and TiO_2 [4]. The samples were then allowed to furnace cool at a rate of about 2 °C/min.

Oxidation tests were performed by TGA (Model RH 2500, Cahn Instruments, Paramount, CA) up to 800 °C and before/after weight ratios. For TGA, weight measurements were taken every minute. Furnace oxidation experiments were also performed on samples in a muffle furnace heated to 800 °C, soaked for 4 h and quenched in air to ambient temperatures. The samples were weighed using a Sartorius Precision Balance

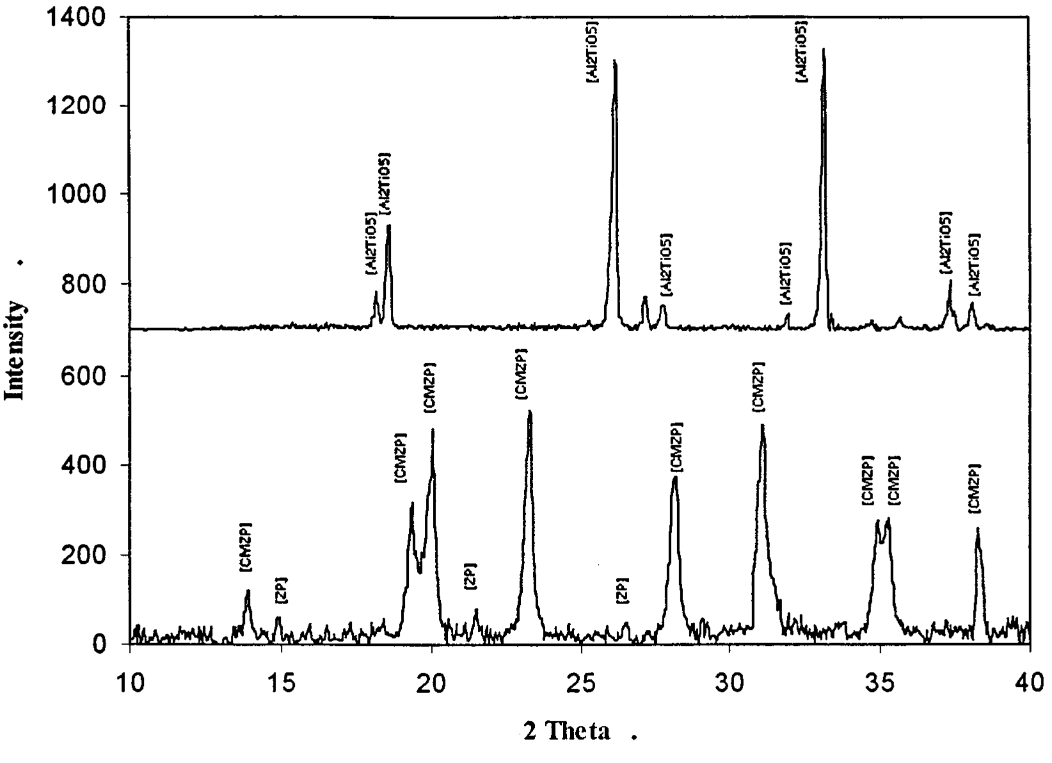


Figure 1 X-ray diffraction patterns for fired CMZP (1200 °C/1 h) and Al_2TiO_5 (1300/6 h).

Model R160P and the % weight loss was calculated. The composite coatings were examined using the Scanning Electron Microscopy (Hitachi, HHS-2R).

3. Results and discussion

3.1. X-ray diffraction

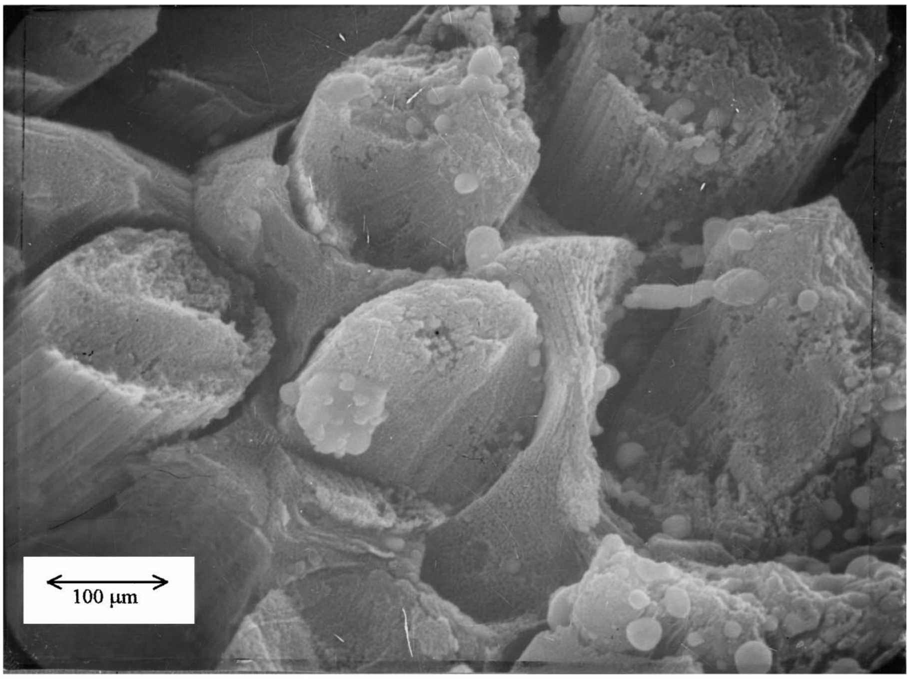
Fig. 1 shows the diffraction patterns for the CMZP and aluminum titanate sol-gels sintered to 1200 °C/1 h and 1300 °C/6 h respectively. There is a trace amount of zirconium phosphate ([ZP] = $(ZrO)_2P_2O_7$) found in the CMZP powder which indicates a small excess of zirconium precursors. There is no evidence of Al_2O_3 or Ti_2O_5 present in the aluminum titanate diffraction pattern suggesting that the addition of Mg^{2+} stabilized the compound [4].

3.2. Oxidation tests

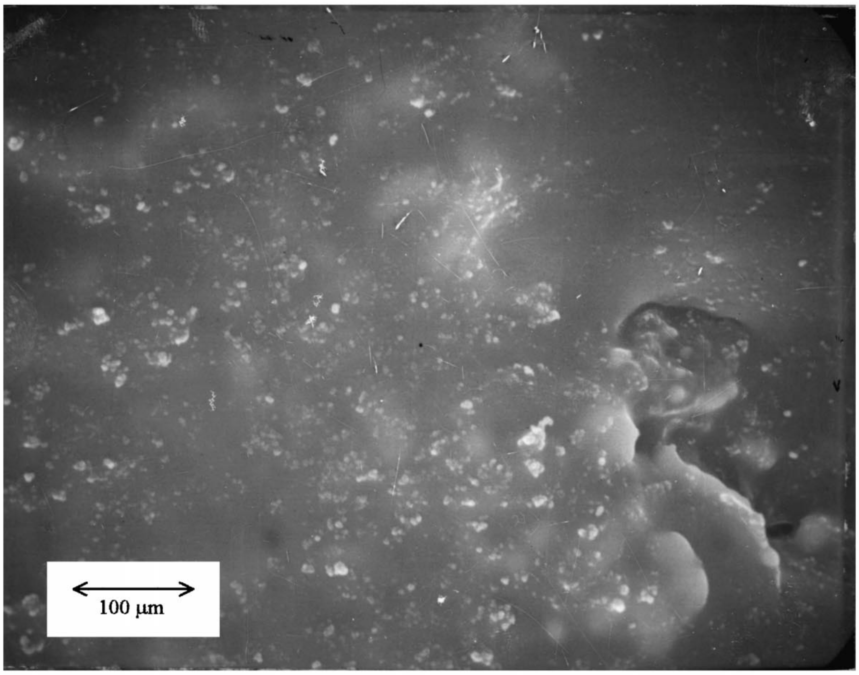
The intent of the experimental procedure is to determine the number of anti-oxidation coatings necessary to sufficiently protect the composite from oxidation. If drying conditions and sol-gel parameters are not investigated sufficiently, small cracks may form in the initial coatings which allow for oxygen penetration and coating ineffectiveness. The addition of subsequent coats is expected to fill cracks in previous layers and provide an effective coating.

3.3. CMZP coatings

Figs 2a and 2b show the composite surface after two and 10 fired coats of CMZP respectively. The relatively



(a)



(b)

Figure 2 SEM micrographs of (a) two coatings and (b) 10 coatings of fired CMZP sol-gel on a C—C composite.

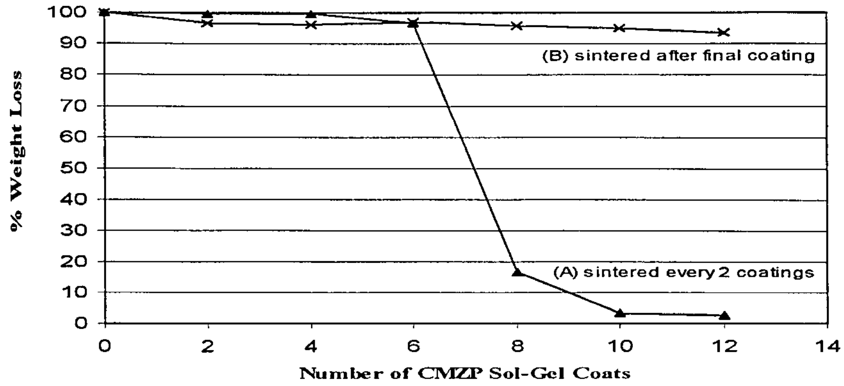


Figure 3 Oxidation test of C—C composite samples, coated with CMZP sol-gel, and fired to 800 °C/4 h in air. The samples fired every other coating (A) exhibited good oxidation protection after 10 coatings (no weight loss) compared to samples with the same number of coatings fired only after the final coat.

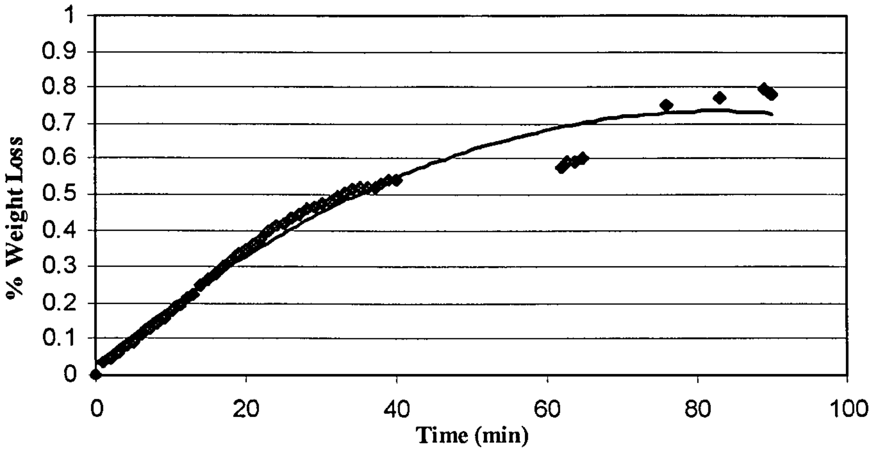


Figure 4 TGA oxidation test of a C—C composite sample, coated with Al_2TiO_5, and fired in air at 800 °C/100 min.

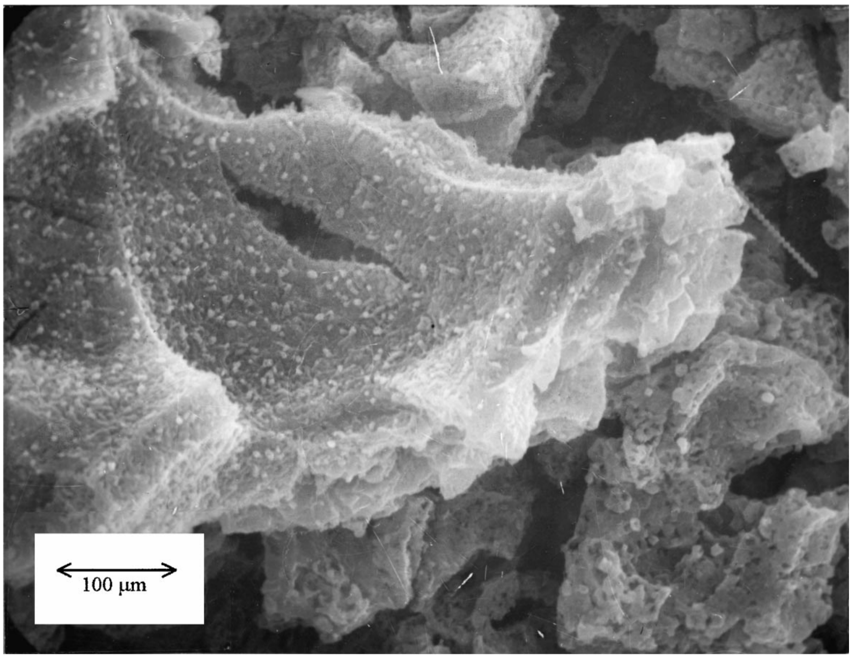


Figure 5 SEM micrograph of a typical $MgTi_2O_5$ sol-gel coating after firing. Microcracks are believed to cause the lack of oxidation protection in all samples.

sparse coating found in Fig. 2a allows a clear view of carbon fibers and matrix while the coating in Fig. 2b has completely covered the composite.

Results of weight loss tests performed in a 800 °C furnace for four hours are shown in Fig. 3. Series (A) consists of samples fired every other coating before oxidation tests were performed. It can be seen that 10 coatings were necessary to effectively protect the sample from oxidation. Series (B) consists of samples coated multiple times and fired after the last coat. It can be seen in Fig. 3 that this method did not produce an adequate coating. The slight drop in weight loss of Series (B) can be attributed to the additional amount of ceramic applied to the sample which does not burn off during the test. This implies that there is an additional amount of coating applied and that subsequent dipping does dissolve unfired coats back into the sol. It is then assumed that the firing stage is responsible for catastrophic cracks to form in the coating and applying additional coats remedies this situation.

3.4. Al_2TiO_5 coatings

The results of the oxidation test at 800 °C can be seen in Fig. 4. This test was performed on the sample with the most uniform coating of the group with twelve coats that were sintered after every two coats. All samples coated with Mg-doped Al_2TiO_5 showed crack formation within a few minutes after withdrawal from the sol-gel solution (Fig. 5). These cracks tended to remain upon sintering and the sintered coatings did not bond to the previously applied coatings or to the surface of the carbon-carbon substrate. Oxygen diffusion though these cracks results in the high weight loss of the sample. Many procedures outlined in previous research [4, 6, 7] were followed in order to reduce the onset of microcracks but all were unsuccessful.

4. Conclusions

Oxidation resistant CMZP and Mg-doped Al_2TiO_5 coatings were applied to a C—C composite via sol-gel dip methods. In order to produce a crack free coating, the process of applying two coats of sol and sintering was repeated until all cracks of previous coats were filled with subsequent coats. Due to poor adherence and excessive cracking, Al_2TiO_5 was not a successful oxidation barrier in this study.

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