

# THE INFLUENCE OF ALUMINUM PHOSPHATES ON GRAPHITE OXIDATION

*C.R. Maier and L.E. Jones  
Ceramic Engineering and Materials Science,  
Alfred University, 2 Pine St., Alfred, NY 14802*

## Introduction

Composites based on graphite benefit a number of applications where low density, high-temperature strength and thermal shock resistant materials are needed. Carbon composites are currently used in applications such as thermal barriers for reentry vehicles and aircraft brakes[1,2]. However, despite the unique high-temperature properties of these composites, their susceptibility to gasification in oxidizing environments limits their usefulness at elevated temperatures. Thus, most composites require some form of protection against oxidation in order to permit their use in demanding applications.

A protective coating must fulfill four fundamental requirements in order to provide high temperature stability to carbon composites. The coating material must: 1) maintain mechanical stability and adhere well to the composite surface throughout all use temperatures, 2) prevent the ingress of oxygen or other oxidizing species towards the substrate, 3) exhibit chemical compatibility with the substrate, and 4) resist corrosion from the outside environment[3,4]. It is well known that refractory ceramic coatings such as SiC inhibit carbon oxidation at high temperature ( $>1000^{\circ}\text{C}$ )[1-5] owing to their low oxygen diffusivity and chemical compatibility with carbon substrates. However, such coatings are inevitably subject to mechanical flaws such as delamination and microcracking from thermal expansion mismatches between the coating and substrate. As a consequence, some portions of the substrate are exposed and unprotected in intermediate temperature regimes ( $400^{\circ}\text{C}$ - $1000^{\circ}\text{C}$ ), where oxidation can still occur.

Binary protective systems comprised of a low  $T_g$  glaze overlay coating in conjunction with an already deposited ceramic coating have been shown to protect carbon composites against oxidation to temperatures as high as  $1700^{\circ}\text{C}$ [1]. Glazes with high silica contents, while having excellent barrier properties, are typically not sufficiently fluid at intermediate temperatures to fill the cracks and voids on the ceramic coating[3]. Therefore there is great

interest in formulating low  $T_g$  glazes that exhibit sufficient fluidity at ambient temperatures to protect carbon materials against oxidation. Various low  $T_g$  coatings based on mixtures of silicate, borate, and/or phosphate compounds have been investigated for this purpose at intermediate use temperatures where refractory coatings alone do not provide complete surface coverage.

Glassy coatings based on phosphate compounds have been shown to completely inhibit carbon oxidation to temperatures as high as  $850^{\circ}\text{C}$ [6]. From work performed by researchers thus far, it is believed that phosphate coatings, similar to boron based coatings, may inhibit the carbon oxygen reaction by three primary mechanisms. When added in sufficient quantities to form a continuous outer glaze coating, phosphates can act as an oxygen diffusion barrier, thereby preventing atmospheric oxygen from reaching the carbon surface. However, it has also been observed carbonaceous materials react with limited amounts of phosphate additives in the form of a liquid or gas and form strongly adsorbed phosphate surface complexes that block active carbon surface sites, where oxygen-containing species would otherwise chemisorb[1,6-8]. Finally, aqueous phosphate-based penetrants can also neutralize impurities in the composite body that otherwise catalyze oxidation.

The most stable oxide of phosphorous is phosphorous pentoxide,  $\text{P}_2\text{O}_5$ . All four crystalline forms of  $\text{P}_2\text{O}_5$  may be melted and cooled to form stable glasses. Pure phosphate glasses consist of various linear, sheet, or cyclic structures comprised of  $\text{PO}_4^{3-}$  tetrahedron that form a continuous polymeric network. The fact that only 3 out of 4 oxygen atoms in each  $\text{PO}_4^{3-}$  unit are bridging affords phosphate glasses a less rigid structure compared to silicate glasses. Thus, it is not surprising that phosphate glasses exhibit lower softening temperatures than most ordinary silicate glasses, and are thus able to spread over carbonaceous surfaces more readily at lower temperatures. Pure  $\text{P}_2\text{O}_5$  glass, however, is of little use at high temperature due to

its inherent susceptibility to moisture attack and volatilization.

Crystalline aluminum orthophosphate,  $\text{AlPO}_4$ , is isostructural with quartz and exhibits remarkable high temperature stability ( $T_M > 1500^\circ\text{C}$ ). However, glasses in the  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  system are also known to exist[9,10], and have been experimentally shown to have a similar vitreous structure to amorphous silica[10]. Binary mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ , prepared from aqueous precursors under controlled conditions, result in viscous, adhesive solutions that polymerize on dehydration to form solid aluminum phosphates[11]. Based upon the chemical similarities between aluminum phosphates and silica, it would be expected that an aluminum phosphate coating would not be subject to the ordinary disadvantages of volatility and moisture attack associated with glasses based primarily on  $\text{P}_2\text{O}_5$  or  $\text{B}_2\text{O}_3$ .

The purpose of this work is to evaluate the effects of different coatings in the  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  system on graphite oxidation at temperatures in the range, 600-1000°C. The thermal stability of aluminum phosphate coated SP1 graphite powders is analyzed in argon, oxygen, and oxygen/steam atmospheres. DRIFT spectroscopy is utilized to study interactions occurring at the aluminum phosphate/graphite interface.

## Materials and Experimental

The graphite powder (SP1) used for this investigation is a spectroscopically purified grade of natural graphite produced by Union Carbide Corp. Concentrated phosphoric acid (Sigma Chemical Co.) and aluminum dihydrogen phosphate (Fluka Chemie AG) solutions were used as coating materials for the SP1 powders.

### *Protective Coating Application*

SP1 graphite powders are thoroughly mixed in dilute aqueous solutions having variable Al:P ratios for a period of 24 hours. Thereafter the excess water is slowly evaporated from the mixture at  $\sim 85^\circ\text{C}$ . The coated SP1 powders, once dry, are collected and stored in closed containers for later subsequent thermal analysis.

### *Thermal Analysis Studies*

Thermogravimetric analysis of all specimens is accomplished with a Setaram TAG-24 Thermoanalyzer (Caluire, France) coupled with a Ametek Dycor mass spectrometer (Pittsburgh, PA) and a Nicolet Magna-IR<sup>®</sup> 560 FTIR spectrometer (Madison, WI) for the characterization of all exhaust species. Decomposition experiments are performed in the temperature range, 600-1000°C, under both isothermal and non-isothermal conditions. For this study, samples are oxidized in flowing

ultrahigh purity  $\text{O}_2$  and ultrahigh purity  $\text{O}_2/\text{steam}$  mixtures at a constant flow rate of  $20 \text{ cm}^3 \cdot \text{min}^{-1}$  and total pressure of 95 kPa. Identical mass loss experiments are also performed in flowing ultrahigh purity Ar to determine the high-temperature stability of each phosphate-based coating.

### *Interface Analysis*

The coated SP1 powders are characterized using DRIFT spectroscopy (Nicolet Magna-IR<sup>®</sup> 560 FTIR spectrometer) after various calcination treatments under ultrahigh purity Argon. Of particular interest are detectable chemical interactions occurring at graphite/coating interface.

## Results and Discussions

Figure 1 shows the mass loss of SP1 powders coated with 2wt% aluminum dihydrogen phosphate,  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , under flowing ultrahigh purity argon up to 1000°C. The SP1 powders were coated, dried, collected and tested with no further treatment. The data show very slight, yet consistent mass loss up to approximately  $\sim 800^\circ\text{C}$ . This result is likely due to minor  $\text{P}_2\text{O}_5(\text{g})$  volatilization, which is expected in this temperature range[9]. Around  $800^\circ\text{C}$ , however, there is a clear shift in the mass loss behavior of the  $\text{Al}(\text{H}_2\text{PO}_4)_3$  coated powder, which most likely is due to evaporation and/or desorption of the aluminum phosphate coating. Therefore, the data suggest that the aluminum phosphate species remain adsorbed on the graphite powder surfaces up to a maximum temperature of roughly  $800^\circ\text{C}$ .

Figure 2 compares the burn-off behavior for SP1 powder coated with 2 wt.%  $\text{Al}(\text{H}_2\text{PO}_4)_3$  with that of untreated SP1 powder. Upon initial inspection of the data, it is immediately apparent that the aluminum phosphate has increased the critical onset temperature of oxidation for the SP1 graphite powder. Figure 3 shows the calculated instantaneous mass loss rate, taken as the instantaneous change in mass with time, as a function of temperature for each sample. The maximum mass loss rate observed for the untreated and aluminum phosphate coated SP1 powders were:  $0.06 \text{ mg/mg} \cdot \text{min}$  and  $0.45 \text{ mg/mg} \cdot \text{min}$  respectively. The corresponding temperatures at which these maximum rates occurred,  $\sim 729^\circ\text{C}$  and  $\sim 825^\circ\text{C}$ , differ by roughly 100 degrees.

## Conclusions

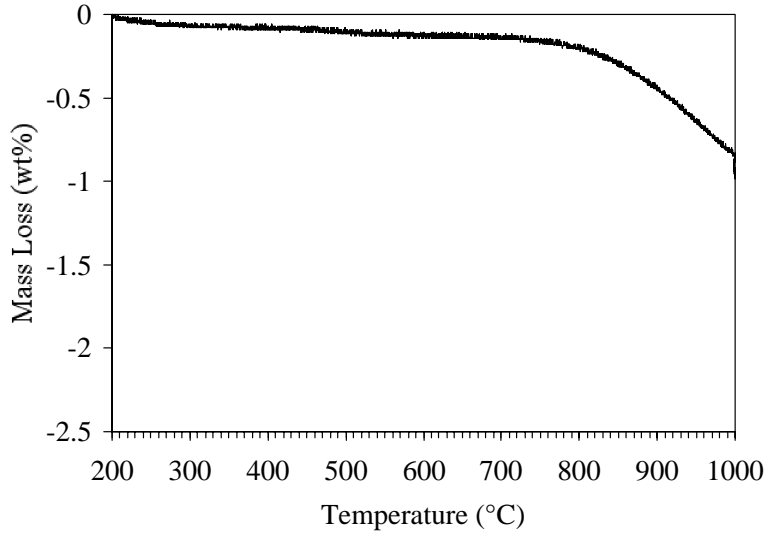
Initial experimental results from this study have shown that:

- Simple treatments of graphite with an aqueous aluminum phosphate solution alone can improve the oxidation resistance of graphite both by increasing the onset temperature for oxidation as well as lowering the overall mass loss rate.

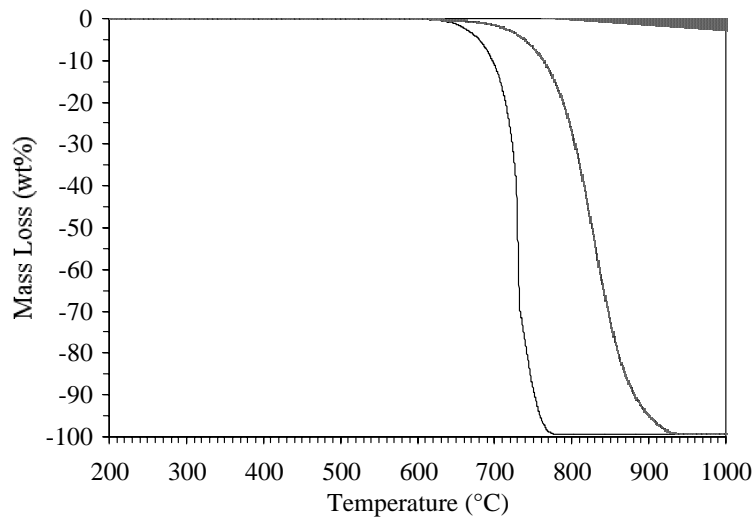
•Under inert conditions, aluminum-phosphate complexes remain adsorbed to graphite surfaces up to 800°C.

## References

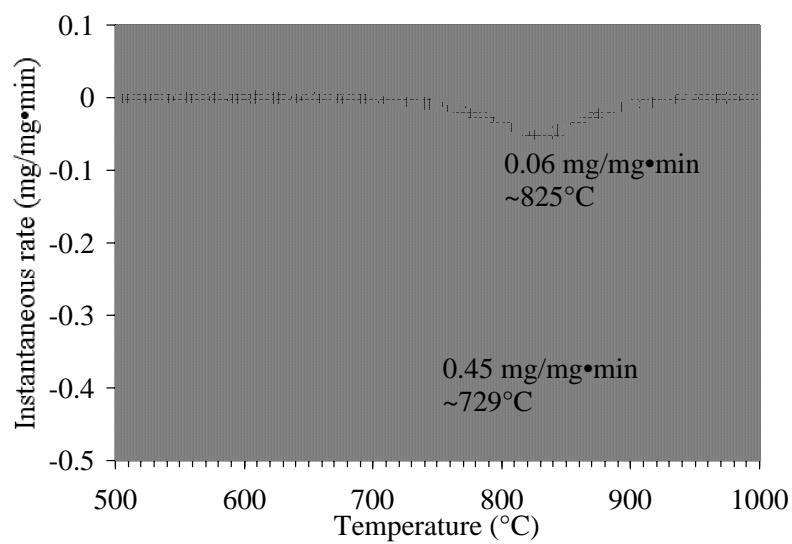
1. Dhami TL, Bahl OP, Awasthy BR. 1995. Oxidation-Resistant Carbon-Carbon Composites Up To 1700°C. *Carbon*;33(4): 479-490.
2. Sheehan, JE. 1989. Oxidation Protection For Carbon Fiber Composites. *Carbon*;27(5): 709-715.
3. Strife JR., Sheehan JE. 1988. Ceramic Coatings for Carbon-Carbon Composites. *Ceramic Bulletin*;67(2): 369-374.
4. Westwood ME, Webster JD, Day RJ, Hayes FH, Taylor R. 1996. Review: Oxidation protection for carbon fibre composites. *Journal of Materials Science*;31: 1389-1397.
5. LoBiondo NE, Jones LE, Clare AG. 1995. Halogenated Glass Systems for the Protection of Structural Carbon-Carbon Composites. *Carbon*;33(4): 499-508.
6. Oh, SG, Rodriguez NM. 1993. *In situ* electron microscopy studies of the inhibition of graphite oxidation by phosphorous. *Journal of Materials Research*;8(11): 2879-2888.
7. Vast, PH. 1995. Oxidation Protection for Carbon Materials by Oxifluoride Phosphate Compounds. *Ceramic Engineering and Science Proceedings*;16(5): 1063-1069.
8. Labruquere S, Pailler R, Naslain R, Desbat B. 1998. Oxidation Inhibition of Carbon Fibre Preforms and C/C Composites by  $H_3PO_4$ . *Journal of the European Ceramic Society*;18: 1953-1960.
9. Stone PE, Egan EP Jr., Lehr J.R. 1956. Phase Relationships in the System  $CaO-Al_2O_3-P_2O_5$ . *Journal of the American Ceramic Society*;39(3): 89-98.
10. Wignall GD, Rothern RN, Longman GW, Woodward GR 1977. The structure of amorphous aluminum phosphate by radial distribution functions derived from X-ray diffraction. *Journal of Materials Science* 12: 1039-1049.
11. Greger, HH. 1943. Preparation of Aluminum Phosphates. US Pat.2,460,344.



**Figure 1.** Mass loss versus temperature curve for SP1 powder coated with 2 wt% aluminum dihydrogen phosphate in ultrahigh purity argon ( $20 \text{ cm}^3 \cdot \text{min}^{-1}$ , 95 kPa,  $10^\circ\text{C} \cdot \text{min}^{-1}$ ).



**Figure 2.** Comparison of decomposition behaviors for (—) untreated SP1 powder and (---) SP1 powder coated with aluminum dihydrogen phosphate in ultrahigh purity oxygen. ( $20 \text{ cm}^3 \cdot \text{min}^{-1}$ , 95 kPa,  $5^\circ\text{C} \cdot \text{min}^{-1}$ ).



**Figure 3.** Instantaneous decomposition rates for (—) untreated SP1 powder and (---) SP1 powder coated with aluminum dihydrogen phosphate in ultrahigh purity oxygen. ( $20 \text{ cm}^3 \cdot \text{min}^{-1}$ , 95 kPa,  $5^\circ\text{C} \cdot \text{min}^{-1}$ ).