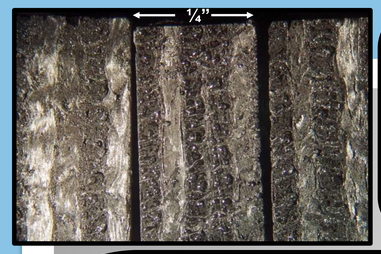

Evolution of Potassium Aluminum Phosphate Anti-oxidant Coatings during Thermal Oxidation of Carbon-Carbon Composites

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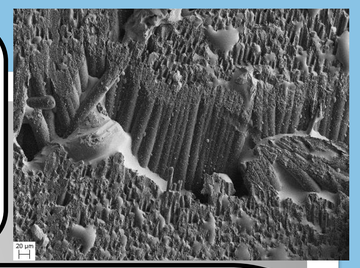


Introduction.

- Carbon/carbon (C/C) composites, used as brake pads in the aviation industry, are susceptible to oxidative corrosion in the presence of potassium acetate (KAc) runway de-icers.[1]
- Patented anti-oxidant (AO) coatings have been developed, some of which also contain potassium as a major component.[2]
- What role does potassium play in both protecting and catalyzing thermal degradation of C/C composites? How does the inorganic AO interact with the graphitic carbon surface?

Thermal oxidation of graphitized CVI carbon / carbon fiber (C/C) composites.

C/C samples were formed by chemical vapor infiltration (CVI) of thermally decomposed carbon on the inner surfaces of PAN carbon fiber preforms, followed by high temperature graphitization in an inert atmosphere. Although 10 ~ 15% porous, as-manufactured samples have surface areas well under 1 m^2/g. In spite of low nanoporosity, thermal oxidation damage of a C/C monolith propagate into the bulk material rather than only attack the outer surface.[3] AO coatings inhibit this structural damage.

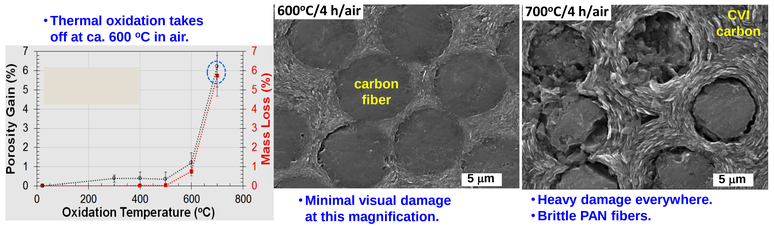


Fig. 1(Left). Porosity increase and mass loss acquired for multiple ¼" x ½" x ¼" C/C samples isothermally heated in stagnant air at the temperatures indicated. (**Right**) Secondary SEM images of the middle interior of cross-sectioned C/C samples after oxidation at 600 and 700 °C. Samples were diamond saw cut and polished with 1500 grit SiC paper to enhance details in the more brittle regions.

Sequestering contaminant potassium salts. Anti-oxidants often include aluminum and phosphate components. Potassium combines with these elements to form metaphosphate glasses at 1100 °C $[(1\text{-}x)KPO_3{\cdot}xAl(PO_3)_3]$.[4] Although their melting points exceed 1000 °C, increasing K^+ content lowers the glass softening temperature to well below 700 °C. This property allows faster rates of ambient K^+ uptake, as well as a degree of AO mobility within the C/C monolith.

➢ *KAc contaminated C/C*

➢ *No anti-oxidant*

➢ *500 °C air oxidized*

- Bulk K-salts are confined to outer surface of C/C monolith.
- Trace K-salts found throughout, especially defining CVI carbon - PAN fiber interfaces.
- Thermal oxidation damage created the inner transport paths for the K-salts?

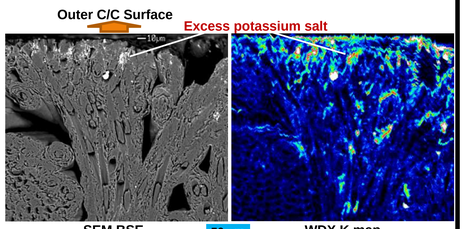


Fig. 2. SEM secondary and backscattered electron images and corresponding WDX potassium element map of a select location within a cross-sectioned C/C sample infiltrated with 17.5 wt% aq. potassium acetate (KAc), dried, and thermally oxidized at 500 °C for 4 h in stagnant air. [Bulk KAc decomposes to K_2CO_3.] The sample was diamond saw dry cut, dry polished with 1500 grit emery paper, sonicated in abs. ethanol, polished with 1 μm diamond paste and sonicated in abs. ethanol to remove debris and the organic carrier.

➢ *C/C with Al-P AO + KAc*

➢ *600 °C air oxidized*

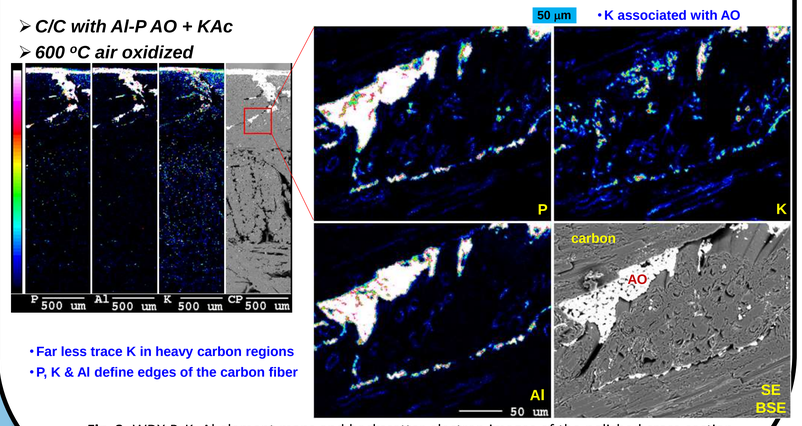


Fig. 3. WDX P, K, Al element maps and backscatter electron images of the polished cross-section of an aluminum metaphosphate-coated C/C sample after infiltration with 17.5 wt% KAc and thermal oxidation at 600°C/4 h/air. See Fig. 2 for sample processing.

Impact on C/C thermal oxidation rate.

Without AO protection, K^+ contamination decreases the onset temperature due to the catalytic influence of potassium.[5] When aluminum metaphosphate is incorporated, carbon loss rates decrease dramatically. Additional K^+ accelerates carbon loss, although the loss rate slows with time. Best results are obtained when the aluminum metaphosphate fully binds K^+ to form a glass.

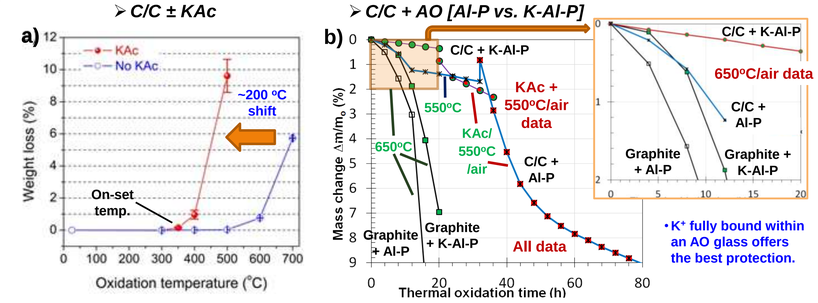


Fig. 4. (**a**) Mass loss vs. oxidation temperature of untreated and 17.5 wt% KAc-infiltrated C/C samples (32 samples, 4 h each in air). (**b**) 4 samples [2 dense graphite pieces and 2 C/C pieces treated with either aluminum metaphosphate (Al-P) or potassium aluminum metaphosphate (K-Al-P)] subjected to multiple thermal cycles at 650 °C. C/C+Al-P was also thermal oxidized at 550 °C. C/C+Al-P and C/C+K-Al-P were then infiltrated with 17.5 wt% KAc and thermal oxidized at 550 °C over multiple 4 h cycles.

What is being protected? Although sequestering free K^+ is important, other factors need to be considered. The pore performance of the dense, commercial graphite in Fig. 4b is likely due its randomly oriented crystallites. In contrast, the C/C material is composed of layered graphitic sheets densely covering a graphitized PAN fiber matrix. The orientation of these sheets on each fiber leads to pore walls covered by a higher percentage of low reactivity basal plane faces. The outer C/C surfaces, however, are mechanically ground such that a high percentage of both CVI graphitic sheet edges and carbon fiber surfaces are exposed. The glassy AO interacts very differently with the different graphitic surfaces and structures.

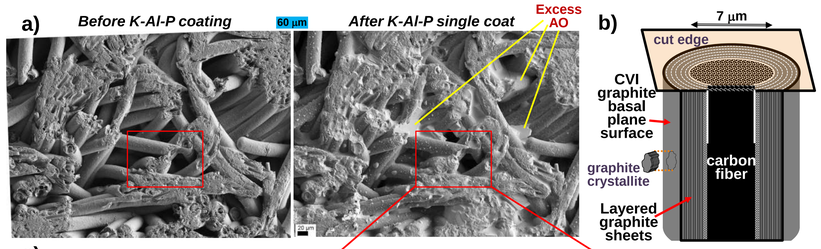


Fig. 5. SEM secondary images of the same outer surface location of a C/C sample before and after coating with potassium aluminum metaphosphate. **(a)** lower magnification, **(b)** schematic structure of a CVI coated carbon fiber, and **(c,d)** higher magnification SEMs.

How does the AO protection change? The 500 to 900 °C composition of $[(1\text{-}x)KPO_3{\cdot}xAl(PO_3)_3]$ is complex; undergoing glass-crystal phase transitions and variation in hydration state. As a consequence, local changes in "x" over time will cause re-distribution of K, P and Al.

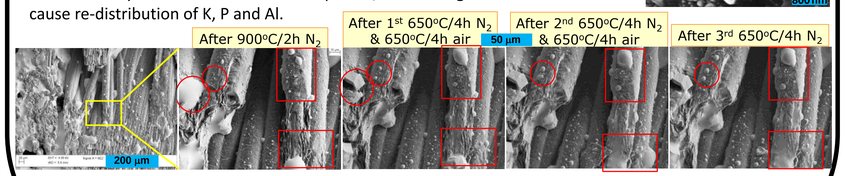


Fig. 6. Series of SEM images of the same K-Al-P coated C/C surface location taken after being sequentially treated (from left to right) under the conditions indicated.

EDX analyses. Spot analysis of various AO locations gave very different results.

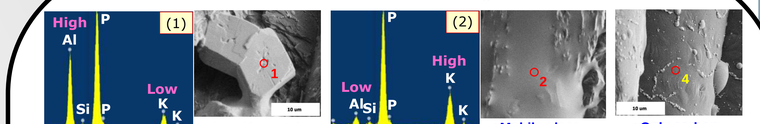


Fig. 6 cont. EDX analyses of select locations found in Fig. 6 (taken after the 3rd 650°C/4h N_2 cycle).

While CVI surfaces poorly wet, fiber and rough CVI surfaces easily wet during air oxidation, allowing them to act as conduits for AO mobility. Bulk AO mobility is also likely driven by consolidation during phase changes.

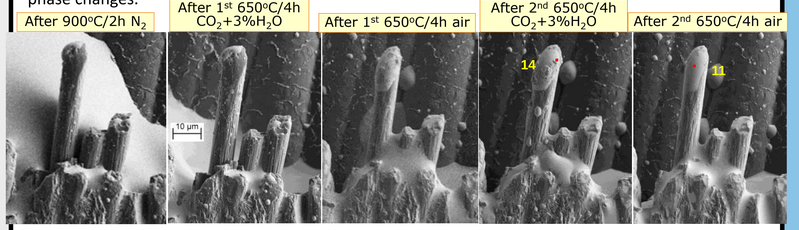
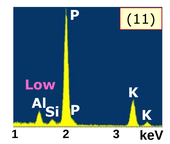


Fig. 7. Series of SEM images of the same K-Al-P coated C/C surface location taken after being sequentially treated (from left to right) under the conditions indicated. Numbered locations indicate where select EDX spot analyses were acquired.

- EDX analyses at #14 and #11 were nearly identical.
- In air at 650°C, AO migrated ca. 40 μm up the fiber in 4 h.
- High relative K^+ content enhanced this glass migration.



How does the carbon surface oxidation state impact AO migration? For graphite, surface oxygen is mainly confined to sheet edges, rather than basal planes. The more disordered the crystallite structure, and the smaller the crystallites, the more sheet edges are present on the outer surface. As a consequence, the most disordered graphites should have the highest surface oxygen content, and is easiest to wet by the polar AO. For the C/C, this means the graphitized PAN fiber. This result is influenced by the highly varied surface roughness of the different graphitic materials.

Conclusions. Highly heterogeneous AO-C/C materials are surprising robust to thermal oxidation, considering the lack of an oxide protection layer and how poorly the AO coats the graphite surface. Key to reducing thermal oxidation of carbon composites is strategic placement of the anti-oxidant.

Factor	Result
• High temperature exposure.	• AO annealing will generate crystals. • K^+ build-up in the glassy AO phase. • Lower glass transition temperature. • Higher glass mobility.
• Thermal oxidation.	• Carbon loss produces increased roughness? • Increased surface oxygen content on carbon. • Carbon surface wetting changes.
• Introduction of potassium acetate.	• Increased carbon loss rate until K^+ is sequestered; increased AO mobility.

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