

CATALYTIC OXIDATION OF CARBON/CARBON COMPOSITE FRICTION MATERIALS

*T. B. Walker***, *L. A. Booker***, and *R. Donaldson**,
** AlliedSignal Technology Resources, AlliedSignal, Inc.,*
101 Columbia Road, Morristown, NJ 07962-1021

*** Friction Materials Department, Aircraft Landing Systems, AlliedSignal Aerospace, Inc.,*
3520 Westmoor Street, South Bend, IN 46628-1373

Introduction

Effective oxidation protection is an integral component in the design of carbon/carbon composite friction materials for aircraft braking systems, as these load bearing materials routinely experience in-service temperatures which will oxidize unprotected carbon. Operating environments for current commercial aircraft braking systems can be very demanding vis-à-vis oxidation. In addition to high operating temperatures, commercial aircraft are exposed to a variety of materials which catalyze carbon oxidation, from sodium containing salt fogs to a variety of chemicals used in airport environments. In particular, potassium acetate runway deicers are replacing traditional urea based materials due to environmental concerns.

Given the increasing exposure to known catalytic materials, it is advantageous to define their activity ranges both with respect to temperature and concentration. Equally important is to assess the interaction between these catalysts and traditional phosphate based inhibitor systems.

Experimental Overview

Three separate designed experiments were run to evaluate the above-mentioned effects. All experiments used machined, cylindrical oxidation coupons, 49.0 mm dia. X 5.84 mm thickness (1.930 in. x .125 in.), with a typical mass of 19-20 grams, cut directly from full-scale carbon/carbon brake discs with no previous anti-oxidation treatment. CARBENIX® 2110 material (pitch based carbon fiber with a resin and CVD matrix) was used for all samples. All samples were cleaned ultrasonically with acetone and dried to a constant weight. Protected samples were saturation coated with P-13 and then cured using a standard process [1]. Samples exposed to deicer were soaked for 20 minutes in the appropriate deicer solution and then dried. In each experiment, individually numbered coupons were weighed and then randomized into the appropriate groups. Samples were placed into "at

temperature" furnaces and held for the specified time-temperature regimen under constant airflow of ~85 l/hr. (3 scf/hr.)

Experiment I consisted of a three-level by two-level, two-factor experiment. Eighteen coupons were exposed to 100% deicer solution (~ 175,000 ppm K⁺) while an equal number were not exposed. Both groups were oxidized at three different time-temperature regimens.

Experiment II utilized a six-level by two-level, two factor, full-factorial design. Two hundred sixteen samples were split into two groups, one unprotected and the other protected, using a standard anti-oxidant treatment. These groups were then sub-divided into six sub-groups and exposed to six levels of deicer (potassium acetate) solution. Oxidation was performed at 649°C (1200°F) for 24 hours.

Experiment III utilized a three-level by two-level, two factor experiment. The effect of two different anti-oxidant cure temperatures [2] was evaluated at three different deicer (potassium acetate) concentrations..

Experimental Results

Results of Experiment I are shown in Figure 1.

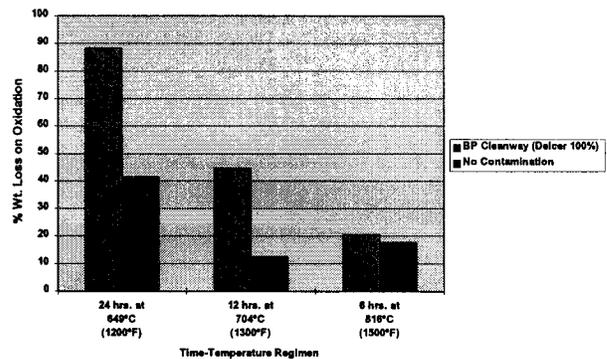


Figure 1. Effect of temperature on catalytic oxidation of CARBENIX® 2110.

Potassium catalysis shows a dramatic effect at both 649°C and 704°C, however the effect drops dramatically at

816°C. This effect was noted previously for sodium catalysis in a similar experiment [1].

Results of Experiment II are shown in Figure 2.

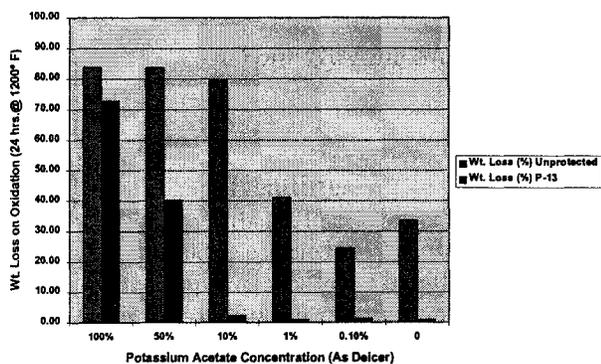


Figure 2. Concentration effect in the catalytic oxidation of CARBENIX® 2110.

The P-13 anti-oxidant is highly effective against catalytic oxidation until higher concentrations of catalyst are present. At the most concentrated level the protective effect is small.

The results of Experiment III are shown in Figure 3.

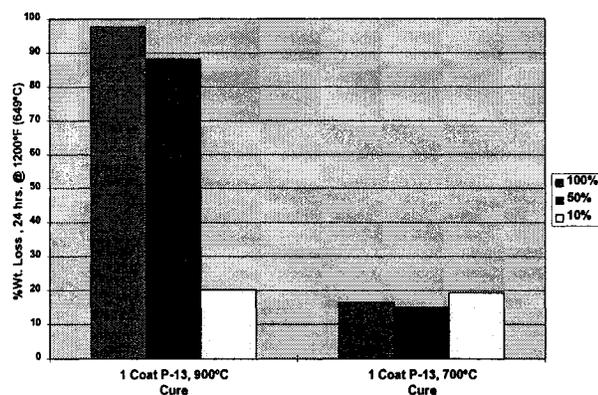


Figure 3. Effect of anti-oxidant cure temperature on catalytic oxidation of CARBENIX® 2110 at various deicer concentrations.

Use of the lower anti-oxidant cure temperature reduces oxidation rates at very high catalyst concentrations by nearly an order of magnitude..

Discussion

The results shown in Figure 1 clearly show that the catalytic effect of potassium acetate is most profound in the 700°C region and diminishes significantly at higher temperatures. This is in agreement with the prevailing theory that Group I metals catalyze by assisting in “active site” formation and that this step is the rate limiting step in this temperature range [3], which also happens to be the

typical operating temperature range for carbon/carbon friction materials. At higher temperatures, oxidation rates are held to be diffusion/convection controlled, hence active site formation by catalysts no longer has a profound influence. The catalyst concentration effects shown in Figure 2 indicate a “threshold” effect in that oxidation rates appear to be unaffected up to a certain level and then accelerate dramatically. (It should be pointed out that these experiments most likely underestimate rates at the higher concentration levels, as the substrate, and hence the reactive surface area, is nearly totally consumed.) As the antioxidant used is primarily a P₂O₅/metal phosphate glass, and such glasses are known to absorb potassium interstitially [4], it is reasonable to assume that the “threshold” represents the maximum absorption capacity above which free potassium rapidly forms active sites. The validity of this assumption is demonstrated in the Experiment III results. Previous work demonstrated that lower system cure temperatures lowered non-catalyzed oxidation rates, due to improved antioxidant retention on the carbon substrate [2]. Use of the lower cure temperature shifts the threshold concentration upwards, consistent with the increased antioxidant concentration. Additional studies have demonstrated that further increases in substrate antioxidant level shift the threshold temperature even higher.

The above experiments demonstrate that potassium catalysis can be a significant factor in oxidation of carbon/carbon friction materials and have established some empirical criteria which can be used to control the problem. Future, carefully controlled kinetic studies in this area may be of significant value in optimizing protection systems for these materials.

References

1. Walker, T. B. and Booker, L. A., in *Carbon '96 (Ext. Abstr. European Carbon Conference)*, Newcastle upon Tyne, England, 1996, pp. 713-714.
2. Walker, T. B. and Booker, L. A. in *Carbon '95 (Ext. Abstr. 22nd Biennial Conf. Carbon)*, San Diego, Ca, 1995, pp148-149.
3. Marsh, H. and Kuo, K. eds. *Introduction to Carbon Science*, Butterworths, London, 1989, pp 107-151.
4. Imaoka, M., *Advances in Glass Technology, Part I*, Plenum Press, New York, 1962, pp. 149-164..