

## OXIDATION MECHANISMS OF CARBON-CARBON COMPOSITES

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### Introduction

The performance of carbon composites as aircraft friction materials is dependent on the oxidation resistance of the composite. In order to improve this oxidation resistance, the mechanisms by which oxidation occurs over the range of temperatures encountered in aircraft braking should be understood. Therefore this investigation was undertaken to determine the rate controlling mechanisms as a function of oxidizing temperature. In particular attempts were made to differentiate between chemisorption, diffusion through pores, and diffusion through a stagnant gas film.

### Experimental Procedure

The composite used in this study was made out of 25% binder A, 15% binder B, 40% carbon fiber and 20% filler. Two forms of composites were studied. One was in bulk form having dimensions of 1.250 x 1.000 x 0.250 in. (henceforth called bulk composite). The other was in ground form with submicron particle sizes (henceforth called ground composite). Three different kinds of test samples were investigated: They were heat-treated at different temperatures ranging between 1000 and 2400°C. The heat treatment was done with an induction furnace under a 99.998% pure argon atmosphere.

The oxidation rates of ground composite were measured by thermogravimetric analysis on a DuPont 950 analyzer, using 5 mg samples. A 100 cc/min flow of air was used as the oxidizing gas. The oxidation rates of bulk composites were measured using a quartz tube furnace. A periodic weight measuring procedure was used. The reaction rates were calculated from plots of weight against reaction time between 5 and 10% sample burn-off.

### Results and Discussion

The oxidation rates of both ground and bulk composite were found to follow the Arrhenius type equation:

$$\text{rate} = A \cdot \exp(-E_a/RT)$$

Table I summarizes the activation energies for ground and bulk composites heat-treated at different temperatures. The range of activation energy for bulk composites is 10.5 to 29.5 kcal/mole while ground composites have a range of activation energies between 35 and 43.3 kcal/mole.

The fact that the activation energy of the ground composite is greater than that of the bulk composite (Table I) from 450 to 650°C indicates that the bulk composite oxidation is occurring by diffusion through pores in this temperature range. The grinding reduces the diffusion path length of the pores such that it is no longer limiting and chemisorption which has a higher activation energy than diffusion through pores becomes the rate controlling oxidation mechanism. If no change in activation energy has occurred with grinding, then it would be concluded that chemisorption was the rate controlling mechanism for bulk composite oxidation. In fact, the bulk composite activation energies are about one half of those of the ground composite as shown in Table I. This is in agreement with Wheeler's discussion (1) which indicates that if the rate controlling step of oxidation is diffusion of oxygen into the pores, the activation energy will be one half of the value one would obtain under a strictly chemically controlled case. Therefore, in the temperature range from 450 to 650°C for bulk composite, the diffusion through pores is the controlling oxidation mechanism. Although the activation energies for ground composites are greater than those for the bulk, its values (35.0 - 43.3 kcal/mole) are still somewhat lower than those for pure carbon or graphite (2) (50-58 kcal/mole). This may be attributable to impurities in the material which are known to lower the activation energy (3).

As the reaction temperature increases, Wicke points out (4) that the rate controlling step becomes the diffusion of oxygen through the stagnant film to the exterior of the carbon sample. Under such a case, Walker (2) shows that the oxidation rate is proportional to the square root of the reactant flow rate, i.e.

$$\frac{\text{Rate (1)}}{\text{Rate (2)}} = \left( \frac{\text{flow (1)}}{\text{flow (2)}} \right)^{1/2}$$

In order to define the temperature at which the diffusion through a stagnant gaseous surface layers becomes the rate controlling step, the oxidation rates of bulk composites were measured at higher temperatures than the preceding experiments at different flow rates. Table II summarizes the results. At 750°C, the relation between rate ratio and flow ratio holds very well, indicating that the predominant oxidation mechanism at this temperature is diffusion of oxygen through the stagnant gas film. However, at 650°C the above equation

does not hold, confirming that the pore diffusion mechanism is dominant at this temperature.

In conclusion the rate controlling mechanisms in carbon composite oxidation is diffusion through pores in the temperature range from 450 to 650°C, while between 650 and 750°C the rate controlling mechanism shifts to diffusion through a stagnant film.

#### References

1. Wheeler, A., Adv. in Catalysis 3 249 (1951).
2. Walker, Jr., P. L., Rusinko, Jr., F., and Auston, L. G., Adv. in Catalysis II 133 (1959).
3. Rakszawski, J. E. and Parker, W. E. Carbon 2 53 (1964).
4. Wicke, E., Proceedings of Fifth Symposium on Combustion p 245 Reinhold, New York 1955.

TABLE I COMPARISON OF ACTIVATION ENERGY (KCAL/MOLE)  
(REACTION TEMPERATURE 450-650°C)

| SAMPLE | GROUND | BULK | RATIO<br>(BULK/GROUND) |
|--------|--------|------|------------------------|
| A      | 35.0   | 10.5 | 0.30                   |
| B      | 39.1   | 19.8 | 0.51                   |
| C      | 43.3   | 29.5 | 0.68                   |

TABLE II RATIOS OF OXIDATION RATES AND FLOW RATES  
(BULK COMPOSITE)

| Flow<br>(cc/min) | $\left(\frac{\text{Flow}}{\text{Flow} = 100}\right)^{\frac{1}{2}}$ | 650°C             |                | 750°C             |                |
|------------------|--------------------------------------------------------------------|-------------------|----------------|-------------------|----------------|
|                  |                                                                    | Rate (% Loss/Min) | Rate (F = 100) | Rate (% Loss/Min) | Rate (F = 100) |
| 100              | 1.00                                                               | 0.11              | 1.0            | 0.29              | 1.0            |
| 500              | 2.24                                                               | 0.13              | 1.2            | 0.71              | 2.4            |
| 1000             | 3.16                                                               | 0.15              | 1.4            | 0.97              | 3.3            |
| 1500             | 3.87                                                               | 0.16              | 1.5            | 1.03              | 3.6            |