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EFFECT OF AIR OXIDATION AT 873 K ON THE MECHANICAL PROPERTIES OF A CARBON–CARBON COMPOSITE

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Abstract—A carbon–carbon composite, composed of semi-random chopped PAN fibers in a resin char and CVD carbon matrix, was oxidized in air at 873 K to burn-offs up to 55%. Composite reactivity increased with increasing burn-off up to about 10% and thereafter remained constant at 1.5%/h. Oxidation had a catastrophic effect on mechanical properties. For example, at 20% burn-off, Young's modulus, flexural strength, work-of-fracture, and fracture toughness were reduced by: 75, 64, 57 and 61%, respectively. Decrease in flexural strength is attributed primarily to a decrease in fracture toughness rather than an increase in flaw size.

1. INTRODUCTION

Carbon–carbon composites are often utilized as high temperature resistant materials as well as wearing resistant materials. In many applications they are used not only at high temperatures but also in oxidation environments. Under these conditions carbon–carbon composites experience oxidation and stress simultaneously.

In general, it is well known that oxidation degrades the properties of carbon materials[1–4]. However, less is known about the effects of oxidation on the properties of carbon–carbon composites, even though much work has been done to determine their properties prior to oxidation[5–8]. It is the purpose of this study to determine the reactivity of carbon-carbon composites in air and the magnitude of the decrease in their flexural strength, Young's elastic modulus, work-of-fracture, and fracture toughness upon oxidation.

2. EXPERIMENTAL

A semi-random chopped fiber carbon–carbon composite was used in this study. The composite was composed of moderate modulus PAN fibers in a matrix of phenol furfural resin char and CVD carbon. The fibers had a diameter of about 8 μm, a length of about 1.3 cm, and a density of 1.76 g/cm^3. Selected properties of the composite are listed in Table 1. Table 2 presents a summary of inorganic elements present in the composite, as determined by emission spectroscopy. A large concentration of phosphorous is present as an oxidation inhibitor.

Oxidation was carried out at 873 K in a horizontally mounted mullite tube furnace in 0.1 MPa of air which was introduced continuously at a flow rate of 900 cm^3/min (NTP). Six samples (15 × 10 × 80 mm), located within the constant temperature hot zone of the furnace, were reacted simultaneously. Reaction was carried out at a sufficiently low temperature such that carbon gasification was essentially uniform throughout the composite.

After oxidation at 873 K for selected periods of time, specimens were cooled down to room temperature in N_2. Specimen weights were measured to determine weight loss as a result of oxidation. Young's elastic moduli were determined on each specimen using the dynamic mechanical resonance technique. Resonance frequencies were measured on a Nametre Model 29 acoustic spectrometer. The oxidized specimens were then cut, using a diamond saw, into bars approximately 5 × 5 × 40 mm for work-of-fracture (γ_f) and flexural strength (σ_f) measurements. The long dimension of the bars was

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Table 1. Properties of the carbon–carbon composite

Density, g/cm^3	1.56
Elastic Modulus, 10^4 MN/m^2	3.1
Flexural Strength, 10^2 MN/m^2	1.2
Fracture Toughness, MN/m$^{3/2}$	10.5
Work-of-Fracture, 10^3 J/m^2	1.75

Table 2. Inorganic elements present in composite

Element	Amount, ppm
B	50
Si	200
P	~10,000
Fe	100
Al	60
Ti	50
Ca	60
Na	~2,000
Ag	< 2
Cu	4
Mg	100
Bi	< 20

Not detected: Zr, Zn, Y, Be, Mo, V, Ni, Co, Cd, Sn, Ge, In, Pb, Sr, Ba, La, Sc

perpendicular to the original direction of molding used to form the composites.

Flexural strengths were measured on an Instron machine in three point flexure at a crosshead speed of 8.5×10^{-5} m/s. Work-of-fracture measurements were also conducted in three point bend over a 30 mm length of span at a crosshead speed of 8.5×10^{-7} m/s. The work of fracture, the energy required for stable fracture of the specimen, is given by

$$\gamma_f = U_R/2A_f \quad (1)$$

where U_R was determined by integrating the load-deflection curve of noncatastrophic, completely stable deflection and A_f is the fracture surface area. Fracture surfaces were examined by scanning electron microscopy. Fracture toughnesses were calculated by:

$$K_{Ic} = (2E\gamma_f)^{\frac{1}{2}} \quad (2)$$

where E is Young's elastic modulus.

3. RESULTS AND DISCUSSION

Reactivity results for the carbon composite are summarized in Fig. 1. At 873 K, gasification is initially show. During gasification for the first 20 h or up to a weight loss of about 10%, the gasification rate increased to essentially 1.5%/h and remained constant thereafter. Some spread in reactivity for the composite samples is seen. An initial increase in reactivity with increasing burn-off is generally attributed to the development of increasing surface area and a concurrent increase in the concentration of carbon active sites where gasification occurs[9, 10].

Table 3 summarizes results for the decrease in density of the composite with carbon burn-off at 873 K. Percentage decrease in composite density ($\Delta\rho$) closely follows percentage burn-off (Δw). This indicates that the decrease in sample volume during gasification was negligible and suggests that gasification through the interior of the samples was uniform. This agreement between $\Delta\rho$ and Δw is in contrast to the results found as a result of air oxidation at 773 K of graphitized carbon artifacts composed of petroleum coke or lampblack as filler and coal tar pitch as binder. Even though gasification rates were considerably lower in the latter case, $\Delta\rho$ was consistently lower than Δw, indicating either that preferential gasification occurred at the exterior surface of the artifact or the artifact contracted as a result of internal oxidation and long time exposure at gasification temperature.

The effects of oxidation and decrease in density of the composite on mechanical properties are summarized in Figs. 2–5. As found previously for fine-grained polycrystalline graphites[11], oxidation has a catastrophic effect on mechanical properties. Oxidation to 20% burn-off results in a 75% reduction in E, which is a similar reduction to that previously found[11]. The reduction in E with decreasing density can be approximated as $E/E_0 = (\rho/\rho_0)^{7.3}$, where E_0 and ρ_0 are initial values. Changes in other mechanical properties with decreases in density could not be approximated by a simple mathematical expression over the broad range of density change present in this

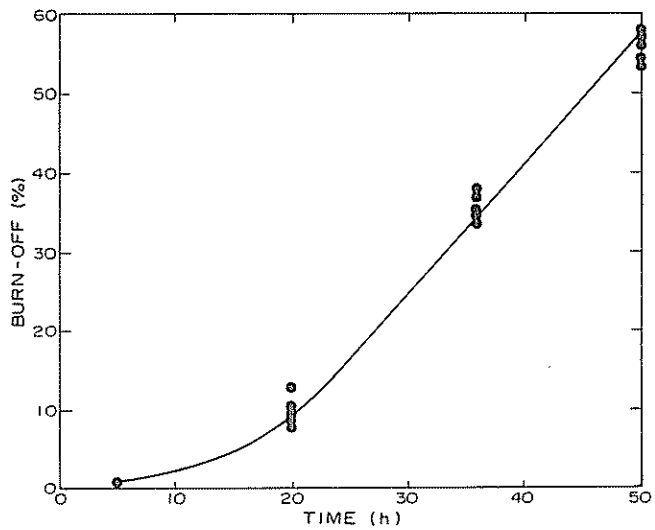

Fig. 1. Reactivity of composite in 0.1 MPa air at 873 K.

Table 3. Change in composite density as a result of oxidation

Δw, %	ρ, g/cm^3	Δρ, %
0	1.56	0
1.0	1.54	1.3
7.4	1.44	6.4
12.9	1.36	11.5
33.9	1.03	32.6
43.3	0.88	43.6
54.8	0.70	55.1

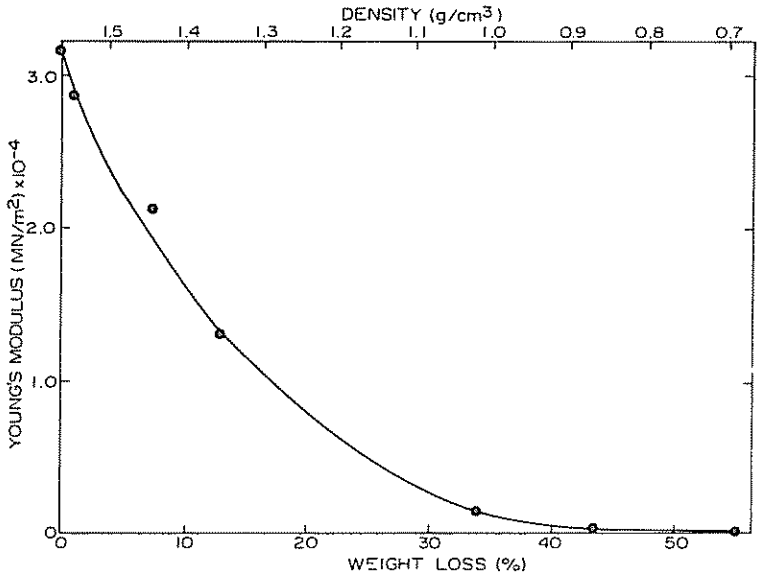

Fig. 2. Effect of oxidation on Young's modulus of composite.

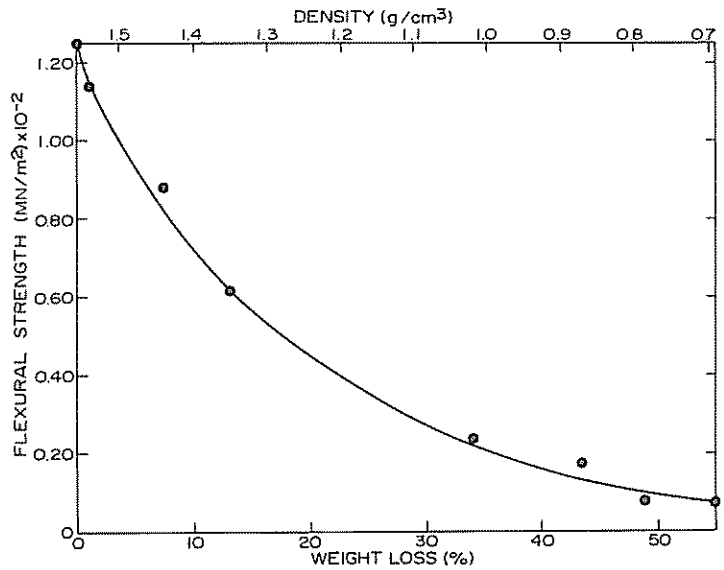

Fig. 3. Effect of oxidation on flexural strength of composite.

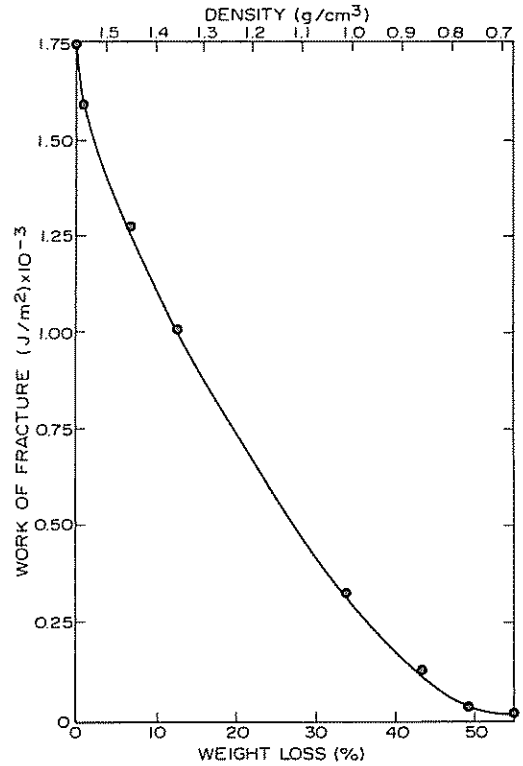

Fig. 4. Effect of oxidation on work-of-fracture of composite.

study. Oxidation had almost as deleterious an effect on σ_f as on E. For example, at 20% burn-off a 64% reduction in σ_f was produced.

Work-of-fracture is defined as energy absorbed during the expansion of a crack over a unit area during the fracture process. The initial value of γ_f for the carbon–carbon composite is one to three orders of magnitude greater than values for graphite single crystals, glassy carbons, and polycrystalline graphites[8]. A 20% burn-off reduced the work-of-fracture by 57%.

In terms of the classical Griffith equation applied to catastrophic failure in brittle materials[12],

$$\sigma_f = K_{Ic} c^{-\frac{1}{2}} Y, \tag{3}$$

where c is the flaw size and Y is a geometric constant ($\approx \pi^{-\frac{1}{2}}$). As is evident from eqn (3), the decrease in σ_f may be from one of two sources—a decrease in the fracture toughness, K_{Ic}, and/or an increase in the flaw size, c. If c is essentially independent of the degree of oxidation of the composite, a plot of σ_f vs K_{Ic} should

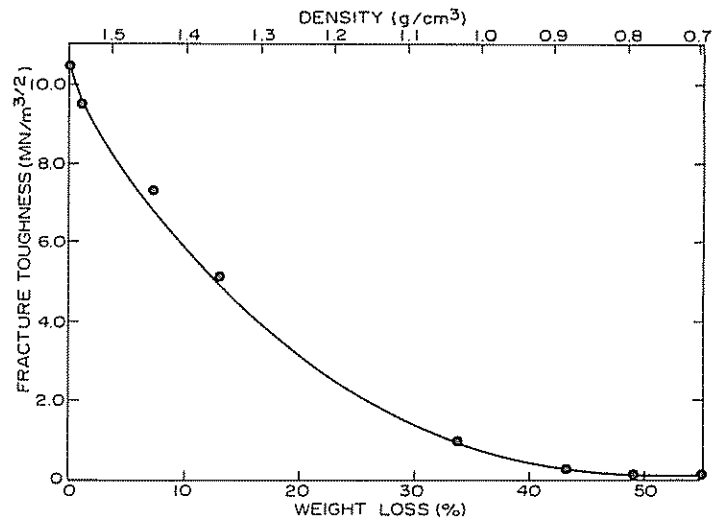

Fig. 5. Effect of oxidation on fracture toughness of composite.

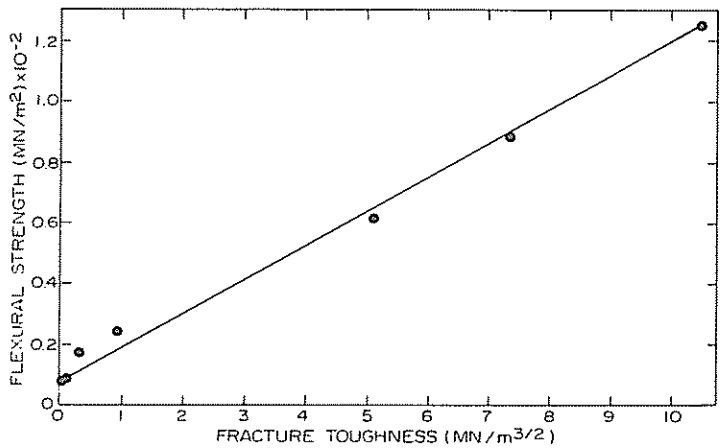

Fig. 6. Flexural strength vs fracture toughness for the as-received and oxidized composites.

yield a straight line of slope $c^{-\frac{1}{2}}Y$. Figure 6 presents such a plot. Linear regression parameters of the plot are slope equals $10.86\,m^{-\frac{1}{2}}$ and intercept equals $9.80\,MN/m^2$, with an R^2 correlation of 99.5%. The linearity of the plot suggests that flaw size does not change appreciably during oxidation and that decreases in strength with oxidation are primarily due to corresponding decreases in the fracture toughness of the composite. From the slope of the plot, the flaw size is estimated to be 0.26 cm.

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REFERENCES

1. R. H. Knibbs and J. B. Morris, 3*rd. Conf. on Industrial Carbon and Graphite*, p. 297. Society Chemical Industry, London, 297 (1971).
2. P. A. Thrower, J. C. Bognet and G. K. Mathew, *Carbon* **20**, 457 (1982).
3. J. L. Wood, J. X. Zhao, R. C. Bradt and P. L. Walker, Jr., *Carbon* **19**, 61 (1981).
4. J. X. Zhao, J. L. Wood, R. C. Bradt and P. L. Walker, Jr., *Abstracts 15th Conf. on Carbon*, 522 (1981).
5. J. L. Perry and D. F. Adams, *Carbon* **14**, 61 (1976).
6. J. S. Evangelides, G. H. Sines and S. B. Batdort, UCLA-ENG-7975 (1979).
7. H. O. Pierson and M. L. Lieberman, *Carbon* **13**, 159 (1975).
8. J. X. Zhao, R. C. Bradt and P. L. Walker, Jr., *Abstracts 15th Conference on Carbon*, 274 (1981).
9. P. L. Walker, Jr., F. Rusinko, Jr. and L. G. Austin, *Advances in Catalysis*, Vol. 11. Academic Press, New York (1959).
10. N. R. Laine, F. J. Vastola and P. L. Walker, Jr., *J. Phys. Chem.* **67**, 2030 (1963).
11. J. L. Wood, R. C. Bradt and P. L. Walker, Jr., *Carbon* **18**, 179 (1980).
12. A. A. Griffith, *Phil. Trans. Roy. Soc.* **A221**, 163 (1920).