

BORON-INDUCED CHANGES IN THE OXIDATION BEHAVIOR AND STRUCTURE OF CELLULOSE-DERIVED CARBON

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Introduction

Two critical factors (poor oxidation resistance and high-cost, time-consuming preparation process) have been limiting the applications of carbon fiber reinforced carbon (CFRC) composites despite the advantages of these composites compared to alternative metallic materials. Therefore, the key question remains how to overcome these two obstacles, preferably at the same time.

Use of substitutional boron is still considered to be among the most attractive options because it enhances graphitization, forms a protective oxide film and causes a potentially beneficial redistribution of π electrons in the basal plane[1].

The topic of this communication is the effect of substitutional B in carbon at different heat treatment temperatures. The goal is to find the conditions of preparation of CFRC composites that both improve the material's oxidation resistance and maximize the degree of its densification. Cellulose was selected as the model carbon precursor because of its purity and non-graphitizability.

Experimental

Cellulose (Aldrich) was heat-treated in the presence and absence of B at temperatures ranging from 600 to 2600 °C. In doped samples, cellulose was mixed with elemental B (Union Carbide, 99.999%) at 1 wt.% initial B loading.

Carbonization/graphitization experiments were conducted in a ceramic boat that was placed and sealed in a quartz-tube within a Lindberg furnace. Nitrogen (99.999%) was flushed at 250 cc/min for 30 min, and the furnace was then heated to the desired temperature (up to 1000 °C). For higher-temperature heat treatment, the cooled sample was removed from the Lindberg furnace, transferred to a graphitization furnace (Centorr, Inc.) and heated up to 2600°C in Ar (99.999%).

X-ray diffraction (Rigaku Geiger-Flex, 25 mA, 40 kV, Cu- α radiation) and Raman spectroscopy experiments (Labram, He-Ne laser excited at 632.8 nm, scanned between 800 and 1800 cm^{-1}) were performed to evaluate the relative changes in carbon crystallinity and structural order. The oxidation resistance tests were performed in a TGA (Mettler TA 4000) at 0.21 atm O_2 . Some 10-20 mg of sample were placed in a silica crucible and heated in air from 25 to 1000 °C (5 °C/min; 200 cc/min).

Results and Discussion

The non-isothermal reactivity data for B-free carbons are as expected: the oxidation resistance increases monotonically as heat treatment temperature (HTT) increases. Of special interest, however, is the fact that the increase in oxidation resistance in the range 1600-2300 °C is rather small. Only when the temperature is raised above 2500 °C does this carbon become oxidation-resistant (<5% burnoff) above 600 °C. Note also that in all cases carbon is completely consumed at temperatures below 850 °C.

The oxidation behavior of the B-doped samples, shown in Figure 1, is more complicated. First, there is a significant amount of refractory residue, in excess of what can be accounted for by the formation of B_2O_3 , except for the sample heat-treated at the highest temperature. Also, the sample heat-treated at 2600 °C is *less* oxidation-resistant than that exposed to 2300 °C, presumably because of its loss of boron (as evidenced by complete sample burnout).

Table 1 summarizes the structural parameters of all the samples. Based on XRD analysis, all the B-doped samples are indeed seen to have higher crystalline order than their B-free counterparts. As expected also, the degree of crystalline order increases as HTT increases; however, the B-doped sample exposed to 2600 °C is again the exception. Preliminary analysis of the Raman spectroscopy results (courtesy of Dr. J. H. Kwan of Tohoku University, Sendai, Japan) suggests that they are not consistent with the XRD results. The frequency of the G-band and the D-band decreases as HTT increases, confirming the development of a more ordered structure. However, the crystallite width calculated from the empirical equation, $L_a = 43.5/R$ with $R = I_D/I_G$, is seen to decrease as HTT increases. This equation has been used in many prior studies and compared with XRD results [2,3]. The discrepancy reported here needs to be examined further.

References

- [1] Radovic LR, Karra M, Skokova KA, Thrower PA. *Carbon* 1998; 36:1841-54.
- [2] Tuinstra F, Koenig JL. *J. Chem. Phys.* 1970; 53:1126-30.
- [3] Hagio T, Nakamizo M, Kobayashi K. *Carbon* 1989; 27:259-63.

Table 1. Crystallinity characterizations of cellulose carbon from XRD and Raman spectroscopy.

Sample	X-ray diffraction			Raman spectroscopy				
	HTT (°C)	d_{002} (nm)	L_c (nm)	L_a (nm)	ν_G (cm ⁻¹)	ν_D (cm ⁻¹)	R (I_D/I_G)	L_a (nm)
B-free carbon								
600	-	-	-	-	1596	1332	0.97	4.5
1000	-	-	-	-	1596	1333	0.97	4.4
1600	0.350	2.4	3.5	-	1592	1324	0.93	4.7
1900	0.347	2.8	4.3	-	1589	1308	1.02	4.3
2300	0.344	3.5	5.5	-	1586	1305	1.11	3.9
2600	0.341	4.1	6.3	-	1584	1292	1.11	3.9
B-doped carbon								
600	-	-	-	-	1597	1330	0.96	4.5
1000	-	-	-	-	1595	1332	0.97	4.5
1600	0.349	2.7	3.9	-	1592	1324	0.94	4.6
1900	0.345	3.1	4.8	-	1585	1306	1.24	3.5
2300	0.340	4.5	6.6	-	1583	1293	1.21	3.6
2600	0.341	4.2	6.2	-	1587	1309	1.23	3.5

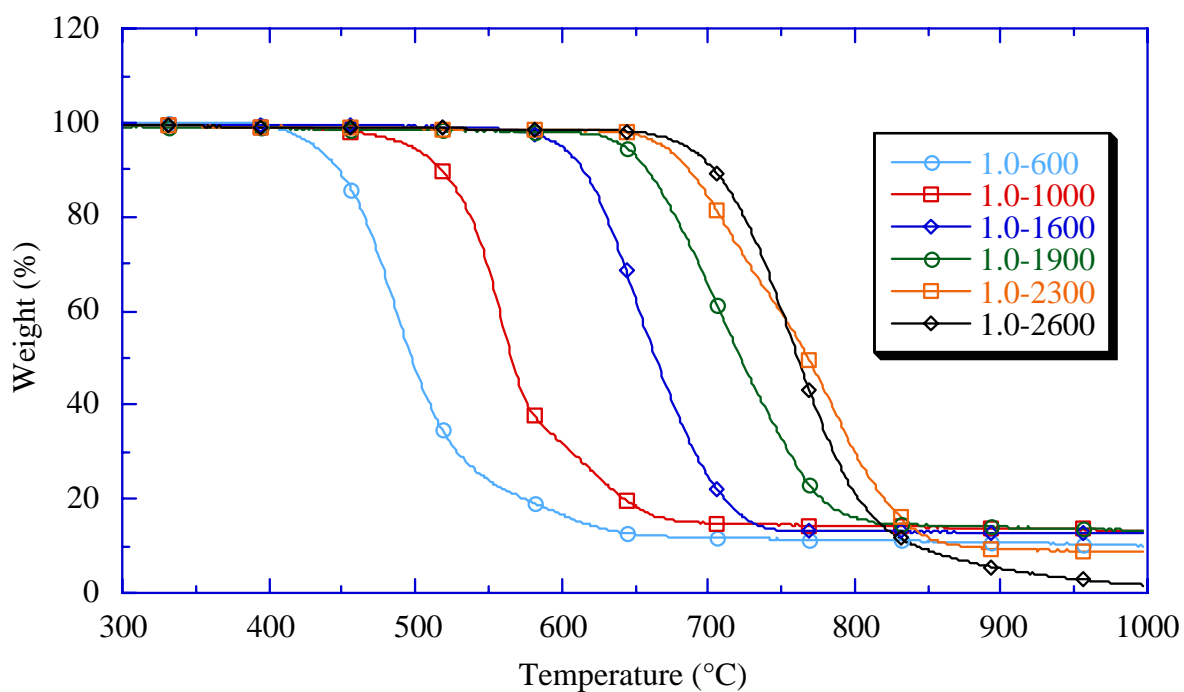


Figure 1. Non-isothermal TGA of B-doped cellulose carbon