

SUBSTITUTIONAL BORON IN CARBON OXIDATION: INHIBITOR OR CATALYST?

M. Karra, R. J. Zaldivar,* G. S. Rellick,* P. A. Thrower and L. R. Radovic
Department of Materials Science and Engineering, Fuel Science Program,
Penn State University, University Park, PA 16802
*The Aerospace Corporation, El Segundo, CA 90245

INTRODUCTION

Boron incorporation into carbon materials is of interest both for oxidative protection of carbon/carbon composites [1-3] and for other purposes [4,5]. Several methods of boron addition have been utilized to increase oxidation resistance. They can be classified as either active site poisoning or formation of an oxygen-impermeable coating [1]. The former method is of interest here. The general consensus has been that substitutional boron acts as an inhibitor of carbon oxidation [1] even though the mechanism of this inhibition is not clear. The following explanations have been offered: (1) Substitutional boron redistributes the π electrons, lowers the Fermi level of graphite, and hence presumably inhibits the desorption of CO and CO₂ [1,2,6]. (2) Substitutional boron enhances the graphitization of carbon [6,7]. (3) As the carbon is consumed, boron oxide forms on the surface and acts both as a diffusional barrier and an active site blocker [1,2,6,8,9]. These explanations are examined in the light of some of our recent results.

EXPERIMENTAL

Boron-doped carbon black (Graphon) and glassy carbon (a phenolic-resin-derived carbon supplied by Alfa-Aesar) were prepared by heating the carbons with elemental boron powder to 2450 °C in inert atmosphere. The carbons were physically mixed with boron powder (99.999%, Alfa-Aesar) at different concentration levels (1, 2 and 5 wt% B). They were then placed in graphite crucibles and heated in Ar to 1500 °C at 25 °C/min. The temperature was raised to 2450 °C at 15 °C/min and the samples were allowed to 'soak' for 45 min to allow boron substitution to occur [8].

Isothermal experiments (~10 mg samples; 0.1 MPa O₂, 99.994%; 250 cc/min) were performed in a Cahn TGA. The reaction temperature was achieved by heating at 25 °C/min. Negligible gasification occurred during this period.

RESULTS AND DISCUSSION

Figure 1 shows the rate (normalized to instantaneous mass) vs. conversion for Graphon

doped at different B levels. Surprisingly, boron was found to act as a catalyst at low levels and as an inhibitor at higher levels. This is in contrast to the reports of previous workers [6,8] that substitutional boron acts as an inhibitor at all concentration levels. In Figure 2 boron is also seen to act as a catalyst of oxidation of glassy carbon. Similar results were obtained with a boron-doped polyarylacetylene resin char that was characterized in detail elsewhere [7].

These results are consistent with the notion that substitutional boron is in fact a catalyst for carbon gasification, whereas boron oxide formed on the carbon surface during oxidation acts as an inhibitor. Thus, depending on the experimental conditions (e.g., boron concentration, surface area of the carbon, temperature, conversion level), one or the other effect can be dominant. This report on the predominance of a catalytic effect is not without precedent. Thomas and Roscoe [10] reported such an effect in moist oxygen.

The confirmation of this proposal requires further research. At this stage, however, two possible explanations for the catalytic effect can be advanced: (a) Simple Hückel molecular orbital theory suggests that the presence of boron in the basal plane weakens carbon-carbon bonds and strengthens carbon-oxygen bonds. The consequence is an *enhancement* of CO and CO₂ desorption. (b) Boron carbide, whose formation has been postulated (admittedly, at high temperature and low pressure), is reported to be a very active catalyst [11]. Recent surface spectroscopy work at Penn State [12] indicates indeed that a much more reduced species than B₂O₃ (e.g., an oxycarbide such as C₂BO) is formed on the surface upon oxidation.

Figure 3 shows no consistent effect of boron on the observed activation energy, especially at low temperatures. Substitutional boron is known to reduce the activation energy of carbon oxidation [6,8]; we too observed such a decrease when higher temperatures are used for Graphon with 2% B. We suggest that the decrease is due to a shift from chemical reaction control to that of diffusion of oxygen through a boron oxide film. Indeed, at the

highest B levels used, Woodley [5] and Jones and Thrower [6] reported activation energies which approach that of oxygen diffusion through molten boron oxide [13].

CONCLUSIONS

In some cases, boron doping of carbons was found to have a catalytic effect in carbon oxidation, despite the fact that boron decreases the Fermi level and thus presumably decreases carbon's affinity for oxygen. The behavior of boron-doped carbons observed here and elsewhere is thought to be a balance between the catalytic effect of substitutional boron and the inhibiting effect of a boron oxide film formed during carbon oxidation.

ACKNOWLEDGMENTS

This work is supported by AFOSR URI (F49620-93-1-0311, Major Thomas Erstfeld, Project Manager).

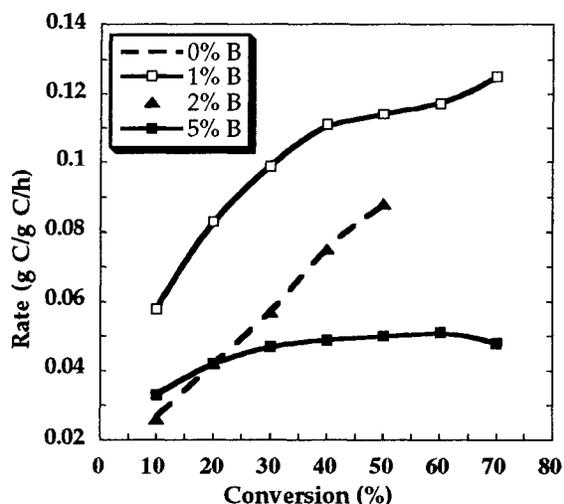


Figure 1. Rate vs. conversion plots for boron-doped and boron-free Graphon (525 °C, 0.1 MPa O₂).

REFERENCES

1. D. McKee, in *Chem. Phys. Carbon* (P.A. Thrower, Ed.), Vol. 23, 173 (1991).
2. W. Kowbel, Y. Huang and H. Tsou, *Carbon* **31**, 355 (1993).
3. J.E. Sheehan, K.W. Buesking and B.J. Sullivan, *Annu. Rev. Mater. Sci.* **24**, 19 (1994).
4. R. Wolf, *J. Nucl. Mater.* **212-215**, 1174 (1994).
5. R.E. Woodley, *Carbon* **6**, 617 (1968); *ibid.* **7**, 609 (1969).
6. L.E. Jones and P.A. Thrower, *J. Chim. Phys.* **84**, 1431 (1987).
7. R.J. Zaldivar, R.W. Kobayashi and G.S. Rellick, *Carbon* **29**, 1145 (1991).
8. D.J. Allardice and P.L. Walker, Jr., *Carbon* **8**, 375 (1970); *ibid.* **8**, 773 (1970).
9. P. Ehrburger, P. Baranne and J. Lahaye, *Carbon* **24**, 495 (1986).
10. J.M. Thomas and C. Roscoe, in 2nd Conf. Ind. Carbon Graphite, London, 1965, p. 249.
11. N.M. Rodriguez and R.T.K. Baker, *J. Mater. Res.* **8**, 1886 (1993).
12. W. Cermignani, T.E. Paulson, C. Onneby and C.G. Pantano, *Carbon* **33**, 367 (1995).
13. K. L. Luthra, *Carbon* **26**, 217 (1988).

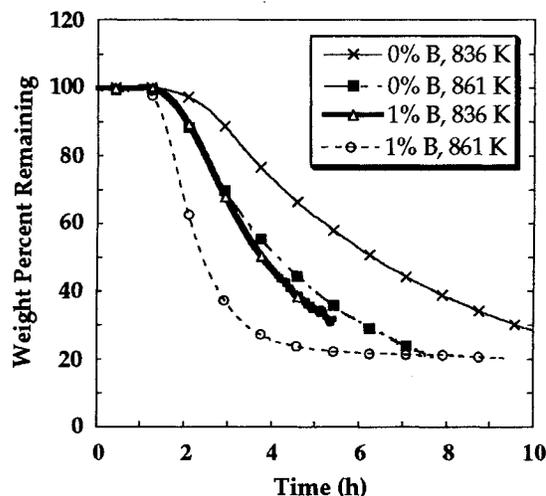


Figure 2. TGA plots for boron-free and boron-doped glassy carbon (0.1 MPa O₂).

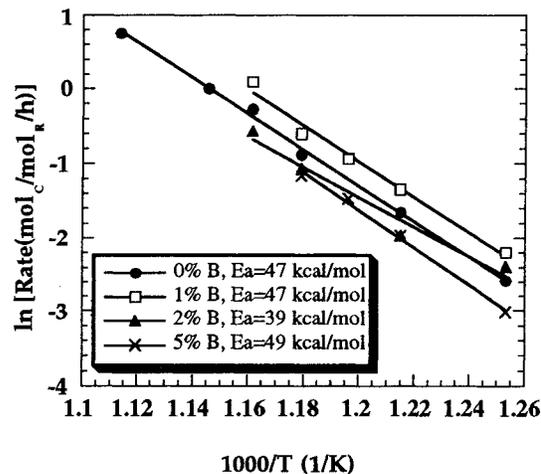


Figure 3. Arrhenius plots for boron-free Graphon and Graphon doped with 1-5% boron (0.1 MPa O₂).