

The Use of Carboranes as Oxidation Inhibitors for Carbon-Carbon Composites

by

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Carbon-carbon composites have many beneficial properties for use in aerospace applications including their high specific strength and modulus at elevated temperatures. Unfortunately, they share with all carbon based substances a strong tendency to burn when heated in air. In order to exploit their good qualities, it is necessary to slow or prevent their oxidation during use.

There are two methods of protecting the composites, coating the composite and adding inhibitors directly to the resin. An effective coating must adhere well to the carbon-carbon material over a broad temperature range (0 - +1700 °C) Since the composites have very low coefficients of thermal expansion, this results in cracking and spalling of the coatings. Commercially available coatings try to overcome this problem by including some form of boric oxide glass to act as a sealant for these cracks.

The second method is to add inhibitors directly to the composite. Commercial inhibitors are usually based on boron carbide or pure boron along with other glass forming compounds. Since these materials are generally insoluble in the resins, they tend to settle out of the resin during heating, and there are problems with the undissolved material abrading the fibers during molding.

Molecular inhibitors could offer the same kind of protection, with the added advantage of being able to form a homogeneous solution with the resin. Since boron oxides are known to provide the desired kind of protection, molecular compounds based on boron seem reasonable candidates to test as inhibitors.

Dicarbadoodecaborane (12), more commonly referred to as "carborane", is a molecular compound with the chemical formula $C_2B_{10}H_{12}$. Carborane clusters have the shape of an icosahedron and exist in three isomeric forms depending on the relative positions of the two carbons in the cluster. (Figure 1) Derivatives are formed by

replacing the terminal hydrogens on either carbon or boron with other groups.

Carboranes have many properties to recommend their use as molecular inhibitors including a high mass percent boron and the ability to form solutions with the phenolic resins being tested. They are chemically very stable, resisting attack by strong acids or oxidizing agents and not decomposing thermally until $>600^{\circ}\text{C}$. The latter is an important consideration since the non-carbon components being expelled from the resin at lower temperatures can react with other additives and remain trapped in the composite. The carboranes release their borons only after the matrix has been reduce to essentially carbon, thus limiting the formation of compounds to carbide type substances.

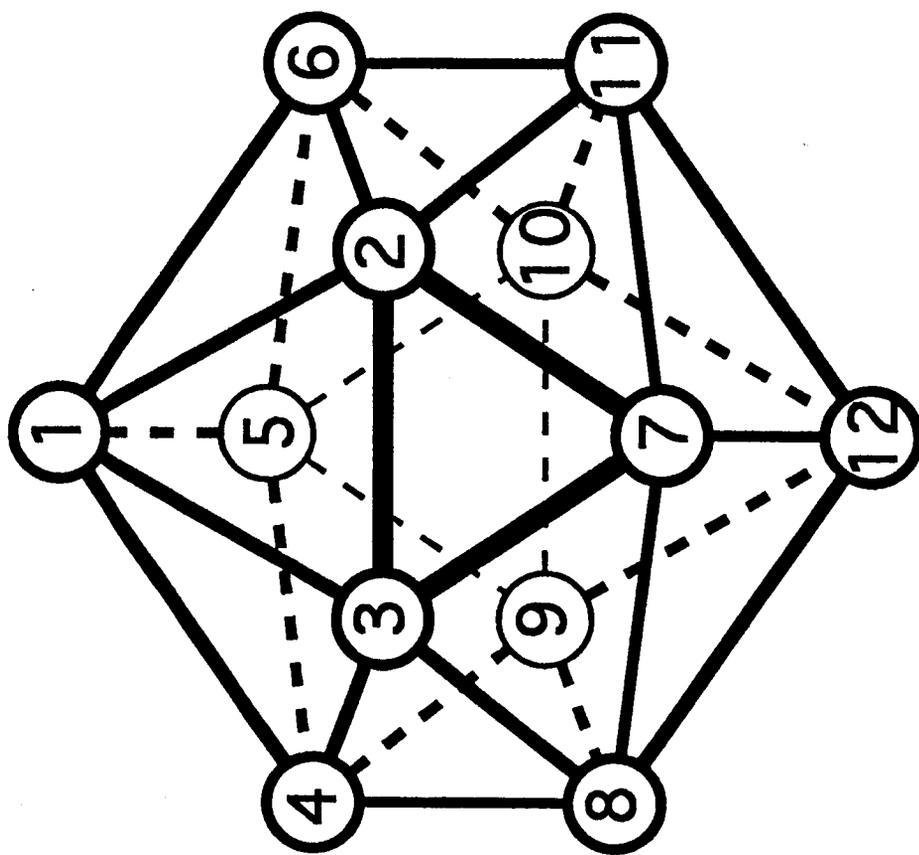
Samples containing from 5%-25% by mass of meta-carborane, 8%-17% by mass 1-methyl-ortho-carborane, 10% boron powder and the neat phenolic resin were prepared for testing. All the samples contained about 5 grams of resin, were cured in air and then pyrolyzed under nitrogen at $>850^{\circ}\text{C}$ to form a glassy carbon material. The pyrolyzed samples were cut into rectangular pieces and their rates of oxidation measured in a thermal gravimetric analyzer (TGA) in flowing air (20 torr), at temperatures of 700°C and 900°C . The results for representative samples are shown in Figures 2 & 3.

All the inhibited samples initially showed substantial reductions in the rate of oxidation compared to the uninhibited material. A more significant development became apparent only after the samples had been partially oxidized. The samples which originally had contained a high mass percent carborane continued to improve until their rates were less than 5% of that of the uninhibited material.

An examination of the oxidized samples using both a microscope and a scanning electron micrograph (SEM) demonstrated that all the inhibitors had responded to oxygen attack by forming partial coatings of boron oxides, but the surface of the sample which originally contained 10% boron powder showed many larger and deeper pits than any of the samples inhibited with carboranes. Clearly, the carboranes had done a better job of distributing their boron uniformly through out the matrix and so these samples showed much less damage on their exposed surfaces.

In conclusion, the carboranes have been shown to be excellent materials for obtaining high uniform loadings of boron inhibitors in glassy carbon materials and thus reducing their rates of oxidation. Further, there are is evidence that the use of substituted derivatives could provide more complete and thorough forms of protection.

Figure 1. Dicarbadodecaborane (12)



Three Isomers: 1,2 = Ortho-Carborane
1,7 = Meta-Carborane
1,12 = Para-Carborane

Figure 2.

Oxidation Rates of Pyrolyzed Resin Containing Various Inhibitors at 900 Celsius in Air

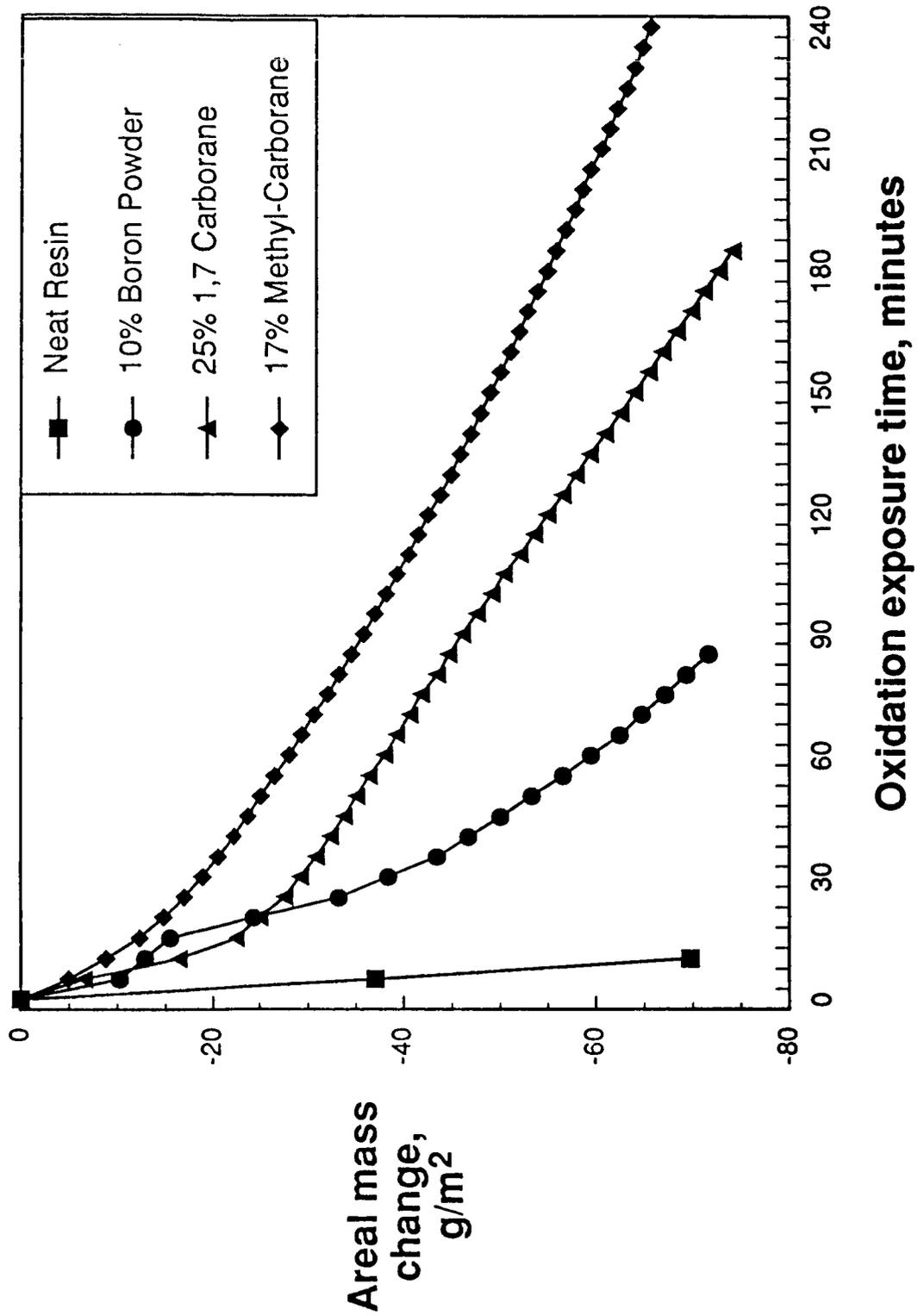


Figure 3.

Rates of Oxidation of Pyrolyzed Resin with Various Inhibitors at 700 Celsius in Air

