

# NOVEL OXIDATION RESISTANT CARBON ALLOYS

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## Introduction

This work has aimed to synthesise boron-containing carbon alloys which are inherently self-protecting against oxidation via generation / regeneration of glassy coatings. Two approaches are described here. The first involves combining  $sp^2$  carbon with the isoelectronic and isostructural BN unit to produce a mesophase pitch precursor to C-BN alloys via borazarene pyrolysis. The second involves direct grafting of silicon<sup>1,2</sup> and boron onto a pitch fraction to yield C-Si-B alloy precursors. The oxidation behaviour of both alloy types is compared with that of corresponding non-boronated materials.

## Experimental

**Borazarene-based alloys:** Pyrolysis to 500°C of the borazarenes, 10-chloro-9-aza-10-boraphenanthrene or 2,2'-bis(dichloroborylamino)biphenyl, in the absence of moisture and presence of  $AlCl_3$  (0.2 - 1.0 mole ratio) gave black pitches (ca. 70% yield) which were further heat-treated to 1000°C, prior to characterisation by optical microscopy, electron energy loss spectroscopy (EELS) and oxidation studies in comparison with the analogous naphthalene-derived coke.

**Carbon-silicon-boron alloys:** A light fraction of A240 petroleum pitch (15.9g) was reacted with an equal weight of polydimethylsilane in a reactor which allowed the reaction vapour to be superheated to 650°C by recirculation through a tube furnace. The resulting C-Si alloy precursor (26.0g) was then reacted at up to 440°C with a boronation reagent *e.g.*, borane.pyridine complex (54.2g). The borane.pyridine reacted to produce a black solid product (62%). C-Si-B alloy precursors produced in this way were pyrolysed at 1200°C under nitrogen yielding black ceramic alloys. The alloys were characterised by thermogravimetric oxidation studies, EELS and X-ray diffraction. The oxidation residues were further characterised by X-ray photoelectron spectroscopy, secondary ion mass spectrometric (SIMS) depth profiling, optical & scanning electron microscopies and energy dispersive X-ray analysis.

## Results and Discussion

**Borazarene-based alloys:** Pyrolysis of, *e.g.*, 2,2'-bis(dichloroborylamino)biphenyl in the absence of  $AlCl_3$  produced an infusible isotropic resin. However, optical

microscopy of the alloy coke derived from precursor pyrolysis with an equimolar quantity of  $AlCl_3$  revealed a fine grained mosaic anisotropic texture. This indicated that the precursor had passed through a mesophase and that the presence of  $AlCl_3$  is essential to catalyse mesophase development<sup>3</sup>. Further studies on this system showed that isotropic material resulted, if the initial  $AlCl_3$  level was less than 0.2 mole ratio. EELS data indicate that the sample consists of carbon layers with isolated boron-nitrogen units<sup>4,5</sup>. Following heat-treatment to 1000°C, the C-BN coke showed a clear oxidation resistance advantage *cf.* the corresponding anisotropic naphthalene-derived coke, shown in figure 1 below.

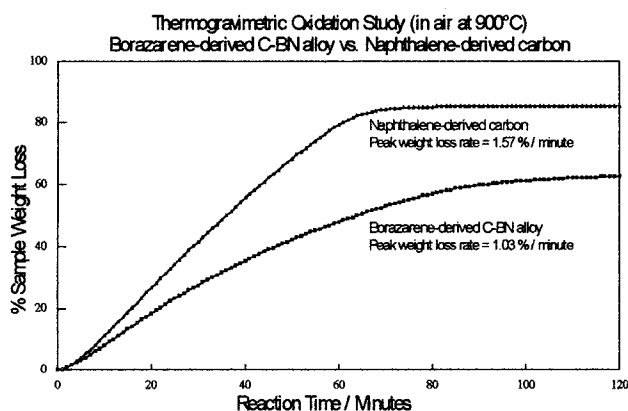


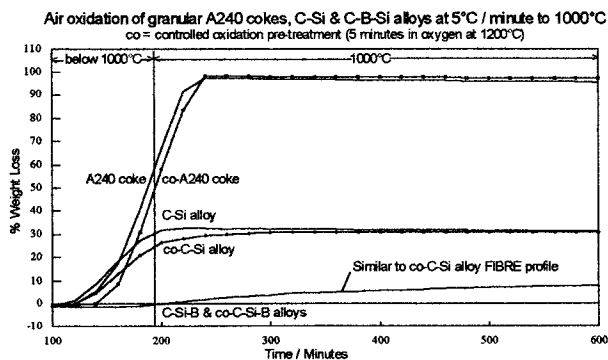
Figure 1. Oxidation of C-BN mesophase-derived alloy.

The advantage is observed despite alloy contamination with  $AlCl_3$ , which acts as an oxidation catalyst<sup>6</sup>.

**Carbon-silicon-boron alloys:** The product from the boronation of the C-Si alloy precursor gave a green flame test, confirming the presence of boron. EELS analysis shows that the product consists mainly of an amorphous structure with a low degree of order, (range < 1 nm). This contains turbostratic  $sp^2$  carbon,  $sp^3$  silicon,  $sp^2$  and  $sp^3$  boron in the abundance ratios  $C_{70} / Si_{20} / B_{10}$ , although some areas are Si-deficient.

The results of thermogravimetric oxidation studies are shown in figure 2 overleaf. The C-Si-B alloy shows some weight gain as the temperature approaches 1000°C, due to borosilicate formation. The alloy then loses just less than 10% of its original weight even after several hours at 1000°C. Visual inspection following oxidation revealed that

the black alloy granules were sintered together by the formation of a glassy phase.



**Figure 2.** Oxidation resistance of C-Si-B alloy compared with C-Si alloy and A240 coke.

In contrast, from 500°C (95 minutes) onward, the A240-derived coke and the C-Si alloy started to lose weight rapidly and had burned away completely, yielding ash and a silica relic respectively, shortly after 1000°C had been reached. For both the coke and the C-Si alloy granules, a controlled oxidation pre-treatment appeared to retard oxidation slightly, possibly since the most reactive sites were removed by this pre-treatment which delayed the onset of rapid attack in the main oxidation study. In contrast, earlier work<sup>7</sup> on the non-boronated alloy showed that the oxidation profile of the C-Si fibres after controlled oxidation was similar to the profiles of the C-Si-B alloy granules. This indicates some degree of shape sensitivity, possibly since the smooth C-Si fibre surfaces are coated more coherently than the surfaces of C-Si granules. Controlled oxidation of the C-Si-B alloy had no significant effect on its subsequent oxidation behaviour.

As also found in the earlier C-Si alloy work<sup>7</sup>, there is no evidence from optical and scanning electron microscopy studies to indicate a well-defined coating on the oxidised isotropic C-B-Si alloys. However, in further work on related C-Si-B alloys, energy dispersive analysis of X-rays suggests that the outer areas of oxidised alloy granules have higher oxygen levels and lower carbon levels than the core. X-ray photoelectron spectroscopy provides stronger evidence that the surface of these granules is modified by oxidation. This shows large increases in oxygen levels, smaller increases in boron and silicon levels and large decreases in carbon levels at the surface upon oxidation. SIMS depth profiling also provides strong evidence for a gradually varying composition. Over the first *ca.* 2µm from the surface, carbon content gradually increases and boron, silicon and oxygen abundances gradually decrease with increasing depth. These findings are consistent with the suggestion that oxidation of the granule surface produces a

borosilicate-rich protective zone whose composition changes gradually on traversing from surface to core. This could be expected to prove advantageous for a protective layer operating in a thermal cycle, as cracking due to thermal expansion mismatch for this system is less likely than if a clear interface existed between coating and core.

Further experiments have demonstrated that oxidation protection is maintained in the C-B-Si alloy system under thermal cycling conditions in dry air. In moist air a preformed borosilicate barrier still offers protection against oxidation but it appears that moisture prevents the initial formation of a coherent glassy protective layer, possibly *via* gasification of silicon and boron hydroxides.

## Conclusions

The borazarene pyrolyses described above provide the first ambient-pressure route to novel mesophase materials that yield optically anisotropic C-BN alloys with improved oxidation resistance, compared with mesophase-derived carbons. Boronated C-Si alloys have also been produced. These have excellent oxidation resistance, even when compared with the C-Si alloys upon which they are based and without the need for a controlled oxidation pre-treatment step. The improved oxidation resistance results from the formation of a borosilicate-rich outer zone, which has no clear interface with the C-Si-B alloy core.

## References

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