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Effect of boron carbide particle addition on the thermomechanical behavior of carbon matrix silicon carbide particle composites

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Carbon-matrix composites are important for lightweight high-temperature structures. However, carbon suffers from the tendency to be oxidized. Due to its superior oxidation resistance, silicon carbide is used in combination with carbon, whether it is a part of the matrix or a part of the reinforcement [1,2]. Due to its tendency to inhibit the oxidation of carbon through the gettering of oxygen, boron carbide and other boron compounds are also used in combination with carbon [3–5]. The combined use of silicon carbide and boron carbide in a carbon-matrix composite provides a dual mechanism of oxidation protection [6–13]. Furthermore, this combined use results upon oxidation in a protective SiO_2-rich borosilicate layer with a self-healing property [14–16].

Although the oxidation inhibition ability of boron carbide as indicated by thermogravimetric analysis is well-known, the effect of boron carbide on the thermomechanical behavior has received relatively little attention [3,6,7]. Therefore, this letter is focused on this effect by providing a comparison between carbon-matrix SiC particle composites with and without boron carbide particle addition.

The carbon-matrix composites were prepared by mixing mesophase particles (<60 μm) with α-SiC particles (15 μm, from Navarro, Cuenca, Spain), optionally together with B_4C particles (<10 μm, from Aldrich, Madrid, Spain), by ball-milling for 1 h, followed by uniaxial pressing at room temperature and 60 MPa (except for 40 MPa for the carbon matrix without SiC or B_4C) in a steel mold of size 50×10×5 mm. After demolding, the compact was heated to either 1000 or 1450 °C at a rate of 1 °C/min, held at the maximum temperature for 1 h in a nitrogen flow of 60 ml/min, and then furnace cooled. The compositions of the samples are shown in Table 1.

Mesophase particles of size <500 μm were prepared by extraction of semicoke (obtained by pyrolysis under an inert atmosphere of an aromatic petroleum residue, as supplied by Repsol-YPF, Madrid, Spain) with toluene at 100 °C (a temperature close to its boiling point) for 2 h and a solid/solvent mass ratio of 1/20. The extraction product was filtered and washed with toluene (100 °C, solid/solvent mass ratio of 1/10, 15 min). The filtrate was dried in vacuum at 100 °C for 12 h. The dry powder was then ground to a size of less than 60 μm for use in making the carbon-matrix composites. The powder was binderless polyaromatic mesophase, with the properties shown in Table 2.

The oxidation resistance of the carbon matrix and its composites were tested by thermogravimetric analysis using the Model TGA7 analyzer of Perkin-Elmer. Heating

Table 1
Compositions of carbon-matrix composites made at 1000 and 1450 °C

	With SiC		With SiC and B_4C	
	1000 °C	1450 °C	1000 °C	1450 °C
Wt.% SiC	22.5	22.8	21.6	22.1
Wt.% B_4C	0.0	0.0	6.0	6.2
Vol.% SiC	11.9	12.6	11.7	12.5
Vol.% B_4C	0.0	0.0	4.1	4.4

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Table 2
Properties of mesophase powder used in making carbon-matrix composites

Extraction yield (wt.%)	46
Toluene insoluble (wt.%)	90
NMP insoluble (wt.%)	66
β-Resins (wt.%)[a]	24
Mesophase content (wt.%)[b]	5
Volatile matter (wt.%)	14
$CH_{aromatic}/CH_{aliphatic}$ ratio	0.66
C (wt.%)	93.8
H (wt.%)	4.5
N (wt.%)	0.02
C/H ratio	1.75
Density (g/cm^3)[c]	1.300

[a] β-Resins refer to the NMP soluble component in the toluene insoluble. The weight fraction of β-resins is given by the difference between the toluene insoluble and the NMP insoluble (i.e., 99–66=24).

[b] Determined by microscopy, which only detected mesophase particles that exceeded 1 μm in size.

[c] Measured by helium gas impregnation and gas pressure measurement.

from room temperature to 1000 °C was conducted in air at a rate of 10 °C/min. In addition, the oxidation resistance was studied by measurement of the specimen (10.0×8.5×3.5 mm) dimension in the stress (thickness) direction during compression at a constant stress of 206 kPa in air at either 300 or 500 °C for 800 min, using the Model TMA7 thermomechanical analyzer equipped with a quartz cylindrical probe of diameter 4 mm.

For investigating the effect of temperature on the dynamic compressive behavior, the dynamic mechanical analyzer (Model DMA7, ASTM D4065-94) was used during heating in air from 35 to 500 °C and subsequent cooling, both at a rate of 2 °C/min, under uniaxial compression using a quartz cylindrical probe of diameter 10 mm and a controlled frequency of 1.00 Hz. The storage modulus was measured as a function of temperature on rectangular specimens (10.0×8.5×3.5 mm). The heating rate was selected to prevent any artificial damping peaks which may be caused by higher heating rates. The stress used (a static stress of 11 kPa, superimposed on a stress amplitude of 11 kPa) was large enough so that the specimen deformation exceeded 5 μm.

The microstructure, as revealed by observation of the fracture surface by scanning electron microscopy (SEM), is shown in Fig. 1 for the carbon-matrix SiC particle composite heat treated at 1450 °C. The bright particles (as large as 3 μm) in Fig. 1 are SiC. The dark regions (as large as 20 μm) are the carbon matrix. The black regions (as large as 3 μm, just a few) are pores. Observation of the composite containing both SiC and B_4C particles failed to distinguish between B_4C particles and the carbon matrix, because boron and carbon are close in atomic weight. Observation of the sample without SiC or B_4C showed that the carbon grains ranged from 2 to 25 μm in size.

Table 3 summarizes the results on the thermal behavior. As also shown by the relative weight versus temperature

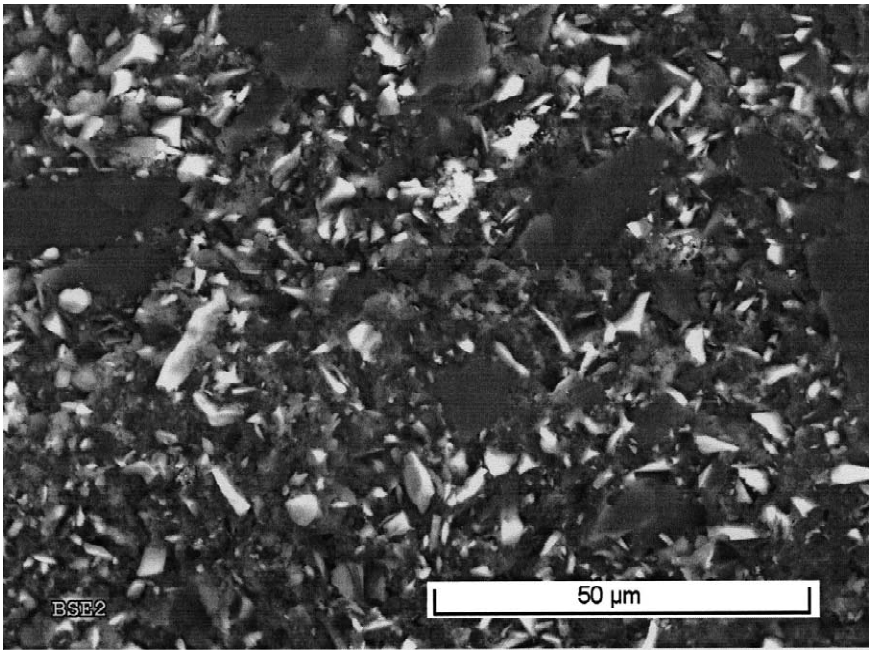

Fig. 1. SEM photograph of the fracture surface of composite with SiC, heat treated at 1450 °C.

Table 3
Thermomechanical behavior of the carbon matrix and its composites made at 1000 and 1450 °C

	Carbon matrix		With SiC		With SiC and B_4C	
	1000 °C	1450 °C	1000 °C	1450 °C	1000 °C	1450 °C
Total weight (%) at 700 °C	26	87	52	85	66	87
Total weight (%) at 850 °C	0	4	23	27	36	52
Carbon weight (%) at 700 °C	26	87	38	81	53	82
Carbon weight (%) at 850 °C	0	4	1	5	11	33
Storage modulus (MPa)[a]	7.4±0.2	9.9±0.4	3.2±0.2	4.1±0.4	3.8±0.2	3.5±0.3

[a] In the temperature range from 35 to 500 °C.

(Fig. 2a) and the relative thickness versus time at 500 °C (Fig. 2b), the oxidation resistance is best for the composite containing both SiC and B_4C, intermediate for that containing only SiC, and worst for the carbon matrix by itself.

The TGA result in Fig. 2a shows that the boron carbide addition is effective for enhancing the oxidation resistance above about 700 °C. However, the TMA result in Fig. 2b shows that it is effective even at 500 °C. This means that oxidation can cause a dimensional decrease under compression without a measurable weight loss. The TMA result at a constant temperature of 300 °C shows essentially no thickness change, as expected from the absence of oxidation at such a low temperature. This observation supports the notion that the thickness decrease at 500 °C (Fig. 2b) is due to oxidation.

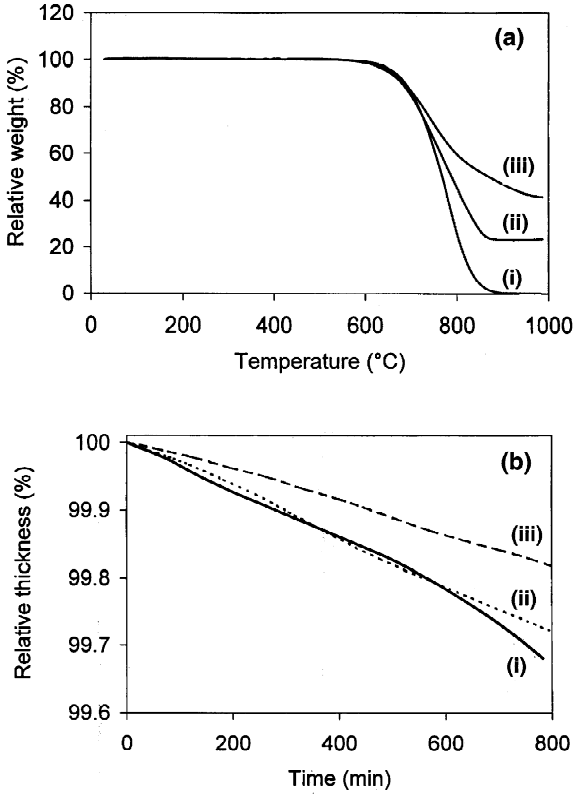

Fig. 2. Behaviors of (i) carbon matrix, (ii) composite with SiC, and (iii) composite with SiC and B_4C, all heat treated at 1450 °C. (a) Relative weight versus temperature during heating in air at 10 °C/min. (b) Relative thickness versus time in air at a constant compressive stress of 206 kPa and a constant temperature of 500 °C.

As shown by the carbon weight in Table 3, the B_4C addition significantly enhances the oxidation resistance at 850 °C for both heat-treatment temperatures of 1000 and 1450 °C, but enhances the oxidation resistance at 700 °C only for the heat-treatment temperature of 1000 °C. In contrast, Fig. 2b shows that the B_4C addition enhances the oxidation resistance at 500 °C for the heat-treatment temperature of 1450 °C. This again indicates the higher sensitivity of TMA than TGA to the detection of oxidation. Nevertheless, the TGA result in Table 3 shows that B_4C is most effective at higher temperatures and that it is more effective when the carbon is poorly ordered.

Table 3 also shows that heating at 1450 °C during fabrication results in higher oxidation resistance than heating at 1000 °C for the carbon matrix as well as the composites; this is expected since the carbon matrix is known to become more ordered as the heat-treatment temperature increases.

The compressive storage modulus does not show any significant or systematic temperature dependence up to 500 °C. It is reduced by the addition of SiC, with little further reduction, if any, upon the further addition of B_4C, whether the heat-treatment temperature is 1000 or 1450 °C (Table 3). The effect of SiC is probably due to the detrimental effect of the interface between the carbide particles and the carbon matrix. The essential absence of effect of B_4C implies that modulus measurement is less sensitive to oxidation than strain measurement.

Heating at 1450 °C during fabrication results in a higher modulus than heating at 1000 °C for the carbon matrix as well as the composites; this is expected since the carbon matrix is known to become more ordered as the heat-treatment temperature increases.

In summary, boron carbide particle addition to carbon matrix silicon carbide particle composites increases the oxidation resistance in air, even at temperatures as low as

500 °C, as shown by the strain at a constant compressive stress of 206 kPa for materials heat-treated at 1450 °C. Weight loss is less sensitive to oxidation than strain; it shows that boron carbide addition helps the oxidation resistance above 700 °C. Nevertheless, boron carbide addition is more effective at higher temperatures and for materials made at a lower heat-treatment temperature. The storage modulus is less sensitive to oxidation than the strain; it essentially does not change upon heating up to 500 °C, and is essentially not affected by the boron carbide addition.

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