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A study of the effects of various inhibitors in C/C composites

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The oxidation behaviour of carbon/carbon composites, with the addition of various inhibitors, has been studied using thermodynamic analysis and microscopy. The effects of ZrB_2, B, SiB_4, tetraethylorthosilicate (TEOS), tributylphosphate (TBP) and additions of treatment with H_3PO_4 were compared using L_8 orthogonal array table and analysed by the ANOVA-TM program.

1. Introduction

Carbon/carbon (C/C) composites are attractive materials for use in applications requiring strength, toughness and light weight at high temperatures. In an inert atmosphere or in a vacuum, carbon fibres retain their strength, stiffness and other mechanical properties to temperatures exceeding 2000 °C [1]. A serious drawback, however, is that carbon in any form reacts rapidly with oxygen, at temperatures as low as 500 °C. Many efforts are therefore being expended in attempts to improve the oxidation resistance of carbonaceous materials at elevated temperatures. Unfortunately, although a large number of chemical species are known to catalyse the oxidation of carbon [2], very few materials have been identified as oxidation inhibitors. In recent studies, certain phosphorus [3] and boron [4] additives and halogen compounds [5] have been found to be effective in reducing the rates of carbon oxidation in air below 1000 °C, apparently by blocking the active sites on the carbon surface where oxidation normally occurs. In most previous work, the effects of additives on the inhibition of the oxidation C/C composites have been studied individually rather than in combination. In this study various inhibitor-treated C/C composites have been fabricated by a conventional liquid impregnation technique to evaluate the relative importance of inhibitors at temperatures below 1200 °C.

The results were analysed using the temperature for 20% weight loss as the characteristic value in a $L_8 2^7$ orthogonal array table for the experimental design [6]. The effects of ZrB_2, B, SiB_4, TEOS, TBP additions and a H_3PO_4 treatment using weight loss measurements on the oxidation of C/C composites were investigated. The data was processed by the analysis of variance with the help of the ANOVA-TM program to identify the factors most effective in inhibiting the oxidation of C/C composites in air.

2. Experimental procedure

The 2 Dimensional prepregs used in this study were obtained from Sun-Kyung Co., Korea. The T300 polyacrylonitrile (PAN)-based carbon fibres (Toray Co., Japan), and the phenolic resin (Novolac type) were densified into carbonized C/C composites by Kang-Nam Hwa-Sung Co., Korea. The physical properties of 2D-prepregs which were used to fabricate 2D-C/C composite are shown in Table I. The inhibitors used to increase the oxidation resistance of C/C composites were of reagent grade quality; B (submicron: Alfa products), ZrB_2 (325 mesh: Alfa products), SiB_4 (325 mesh: Alfa products), TEOS (Aldrich Chemical Co.), TBP (Aldrich Chemical Co.) and H_3PO_4 (Junsei Chemical Co.).

The inhibitor-treated C/C composites were fabricated by the process shown in Fig. 1. In the C/C composite of the desired composition, the powder mixtures were formed by spraying with the experimentally designed composition of B, ZrB_2, and SiB_4 on the surface of 2D woven 8 harness/satin preimpregnated weaves. The individual weaves were laid up to form a composite and loaded into a press with heated platens. The composite was processed by the heat/press schedule shown in Fig. 2.

The composites were imbedded in an abundance of carbon black powder and heated at 0.2 °C min^{-1} to

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TABLE I The characteristics of 2D-woven fabric prepreg used for C/C composites

Fibre type	Filament No.	Woven type	Resin used	Resin content
T300	3000	8H/satin	Phenolic resin	33 wt%

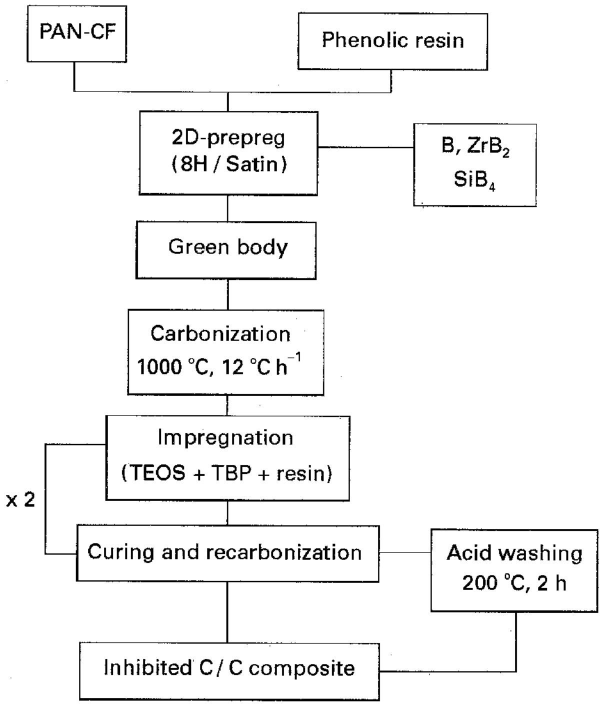

Figure 1 Flowchart for inhibitor-treated C/C composites of fabrication.

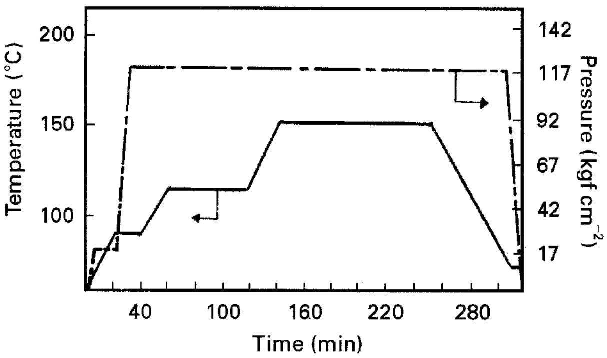

Figure 2 Temperature and pressure profile for greenbody fabrication.

TABLE II Factors and levels used for C/C composites

Sign	Factors	Level 1	Level 2
A	ZrB_2	1 wt%	2 wt%
B	B	1 wt%	2 wt%
C	SiB_4	1 wt%	2 wt%
D	TEOS	1 wt%	2 wt%
E	TBP	1 wt%	2 wt%
F	H_3PO_4 treatment	Yes	No

1000 °C in a box furnace (SYBRON/Thermolyne) for carbonization. After furnace cooling to room temperature, the composites were impregnated with the phenolic resin mixtures, which had desired compositions of TEOS, TBP and methanol, and subsequently carbonized. The impregnation and carbonization processes were repeated following the procedure shown in Fig. 1. The compositions of the impregnants based on the designed levels of the orthogonal array ($L_8 2^7$) are shown in Table II. In the above process, the pores in the composite were filled by the vacuum-pressure impregnation technique. The vacuum was maintained at 1 torr and the chamber was replenished by nitrogen gas at a force of 20 $kgf\,cm^{-2}$ to increase the efficiency of the impregnation.

Any remaining oxidation catalysts, such as Na, K and Ca were removed from the C/C composites by a H_3PO_4 treatment for 2 h at 200 °C, after which the samples were dried for 1 h at 100 °C in a vacuum oven.

The oxidation behaviours of C/C composite treated with inhibitors were tested by measuring weight loss of the specimens in air as a function of temperature using a RIGAKU Thermoflex thermal analyser during a linear temperature rise at a rate of 20 $°C\,min^{-1}$ up to 1200 °C. In this study, the temperature required for 20 wt% burn-off was used as the characteristic value for the analysis of variance in the experimental design.

3. Results and discussion

The bulk densities and porosities of the eight samples were measured for comparison with reference, untreated C/C composite, following the method in ASTM C-20 [7]. Table III shows that the measured densities ranged from 1.45 to 1.49 $g\,cm^{-3}$ after the third stage of carbonization, which are similar to densities reported earlier for the untreated C/C composite [8].

Thermogravimetric analysis (TGA) tests were performed for untreated and inhibited C/C composites respectively. The weight changes as a function of temperature in Fig. 3 show that the inhibitor-treated samples are more oxidation resistant than the untreated C/C composite. In this analysis, the characteristic oxidation temperature for the experimental design analysis was defined as 20 wt% burn-off temperature because temperature differences at 20 wt% burn-off are easy to differentiate. The characteristic oxidation temperature for the treated samples were 60 to 133 °C higher than that of the untreated samples.

Table IV shows ANOVA (analysis of variance) results, where *Df*, *S*, *V*, *F*, *S'*, and *rho*% stand for degrees of freedom, sum of squares, variance, *F* value, pure sum of squares, and percent contribution, respectively. B (boron), D (TEOS) and E (TBP) factors in the table are pooled to the error term because they show minor

TABLE III Bulk density ($g\,cm^{-3}$) and porosity (%) of third-carbonized C/C composites

	Reference	1	2	3	4	5	6	7	8
Bulk Density	1.466	1.456	1.464	1.478	1.496	1.481	1.485	1.463	1.489
Porosity	12.18	13.30	13.63	13.53	8.35	11.34	11.06	12.38	10.12

TABLE IV ANOVA table of 20% oxidation temperatures of C/C composites

Source	Pool	*Df*	*S*	*V*	*F*	*S'*	*rho%*
A	[N]	1	450.00000	450.00000	26.73268	433.16667	6.31
B	[Y]	1	40.50000	40.50000			
C	[N]	1	840.50000	840.50000	49.93070	823.66667	12.00
D	[Y]	1	8.00000	8.00000			
E	[Y]	1	2.00000	2.00000			
F	[N]	1	4324.5000	4324.5000	256.90104	4307.6667	62.74
G	[N]	1	1200.5000	1200.5000	71.31685	1183.6667	17.24
e1	[N]	0	0.00000				
e2	[N]	0	0.00000				
(e)		3	50.50000	16.83333		117.83332	1.72
Total (raw)	[–]	7	6866.0000	980.85714			

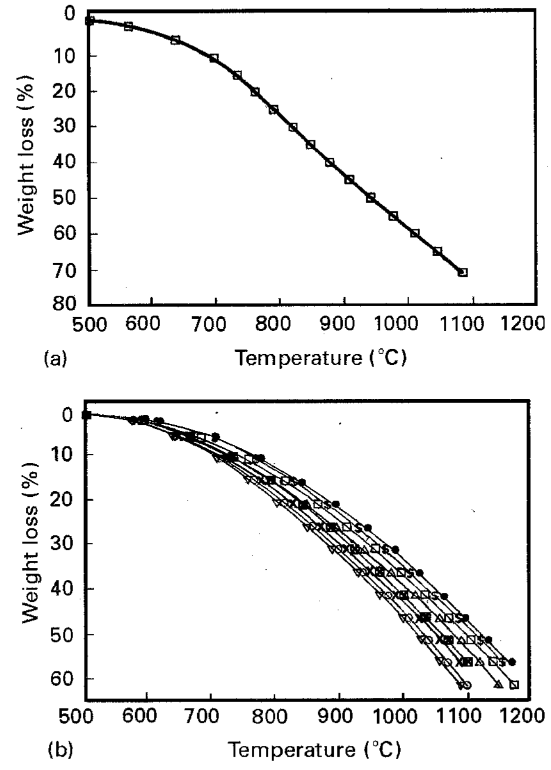

Figure 3 Oxidation curves of C/C composites in air with a linear temperature increase of 20 °C min^{-1}. (a) Untreated C/C composite; (b) inhibitor-treated C/C composites. Experiment numbers $ 1, ∇ 2, ○ 3, ● 4, □ 5, △ 6, × 7, ⊠ 8.

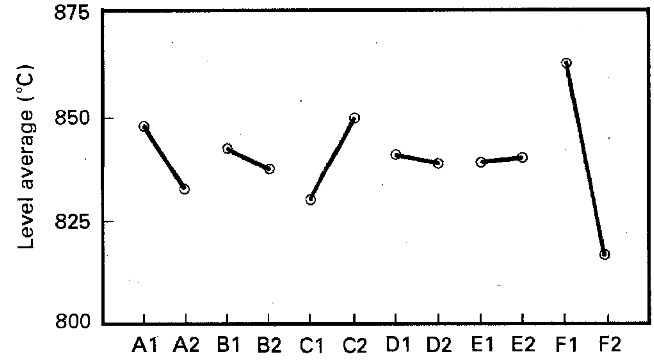

Figure 4 Variation of level averages with different levels (A, B, C, etc.: factors, 1, 2: levels for each factor).

effects on the oxidation protection. According to the analysis, the phosphoric acid treatment has the most effect on the inhibition of the C/C composites compared with other additives. The relative contribution of phosphoric acid washing is about 63%, while SiB_4 shows only 12% increase. In addition, ZrB_2 additives show a detrimental effect on oxidation resistance. This is because the melting point of ZrB_2 is so high that at the fabricating temperature of 1000 °C, ZrB_2 may not react with carbon but exists as particles to increase the surface area oxidation.

Fig. 4 shows the ANOVA level average plot for characteristic temperatures of individual factors with the changes of the levels. For example, addition of ZrB_2 decreases the oxidation resistance while the addition of SiB_4 increases oxidation resistance. Of the inhibitors used in this study 1 wt% ZrB_2, 1 wt% SiB_4, 1 wt% TEOS, 2 wt% TBP and phosphoric acid treatment most effectively improved the oxidation protection under 1000 °C.

To examine the inhibition mechanism, the untreated and inhibited C/C composite samples were examined using scanning electron microscopy (SEM) after various stages of oxidation in air. Fig. 5 shows that in the untreated sample the matrix was preferentially oxidized (Fig. 5b) followed by gasification of carbon fibres (Fig. 5c and d), resulting in the thinning of fibres (Fig. 5e and f). Apparently the oxidation proceeds more rapidly in the matrix, which had undergone thermal treatment at 1000 °C, rather than in the carbon fibres treated at temperatures above 2000 °C. Fig. 6 shows the morphological changes of

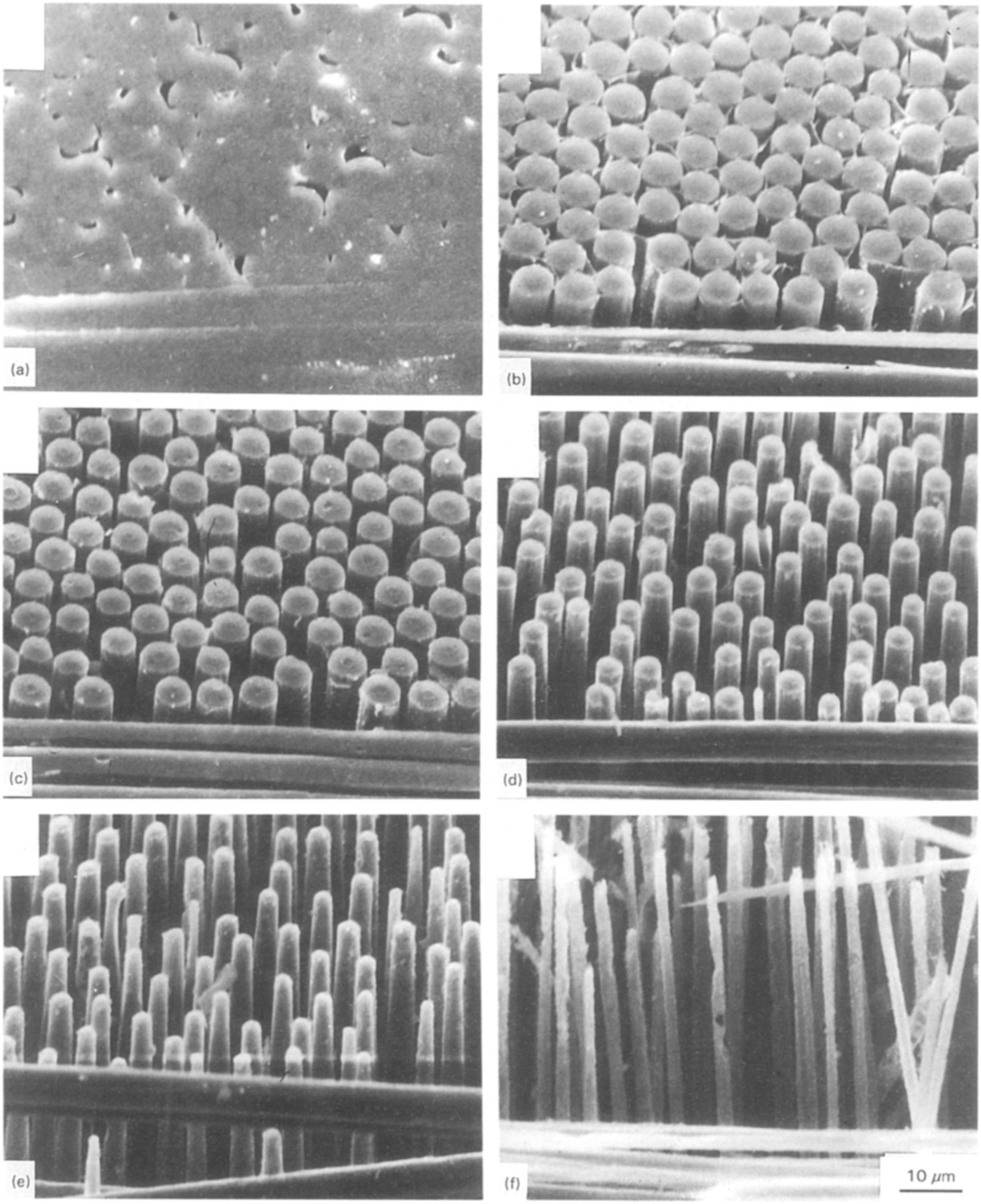

Figure 5 SEM micrographs of untreated C/C composite after varying degrees of oxidation in air. (a) Unoxidized; (b) 3%, (c) 6%, (d) 10%, (e) 20%, (f) 30% burn-off.

inhibitor-treated C/C composites. Oxidation appears to lead progressively to the formation of nuclei of inhibitors on the surfaces of fibres and matrix (Fig. 6c). Increasing temperature, the number of the fine nuclei increase until they coalesce to form a film on the surface as shown in Fig. 6d and e. The formation of continuous film on the C/C composite surface is presumably due to the migration of the glass formed from the Si, B, and P-containing inhibitors. The film becomes thicker and changes into globular form as the carbon fibres become thinner (Fig. 6f).

The elemental composition of the protective films marked in Fig. 6e was investigated using an auger electron spectroscope (AES: $E_p = 5\,\text{kV}$). The spectrum shown in Fig. 7 shows that the film is a glassy material composed of P–Si–B–O. This material is well known as the oxidation protection material of C/C

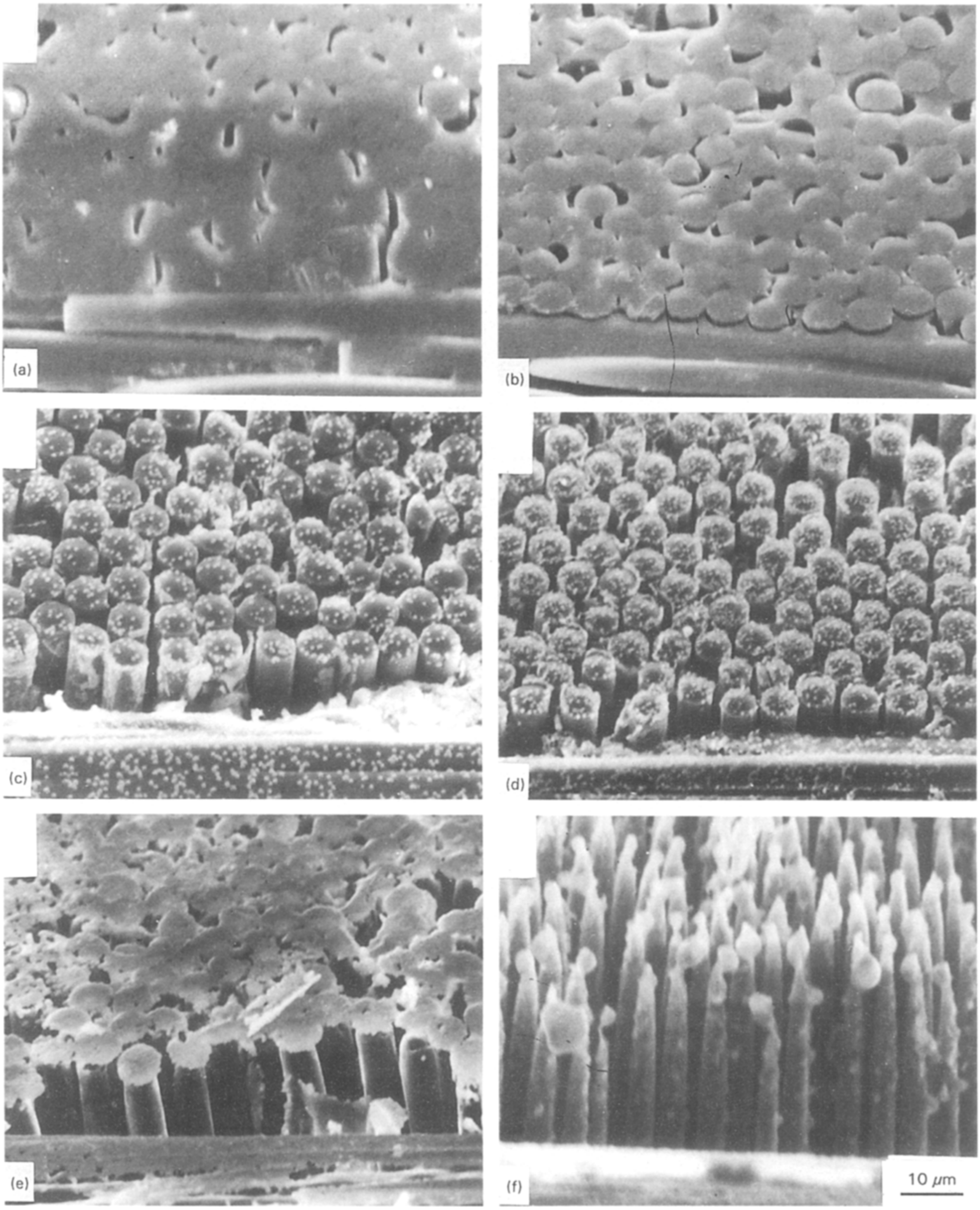

Figure 6 SEM micrographs of phosphoric acid-treated C/C composite after varying degrees of oxidation in air. (a) Unoxidized; (b) 3%, (c) 6%, (d) 10%, (e) 20%, (f) 30% burn-off.

composites, because the glass melts and flows to coat surfaces and fill cracks, and thus provides a barrier against oxygen ingress. Interestingly, elemental Zr could not be found from the protective film, which agrees with the analysis result that ZrB_2 has a detrimental effect on oxidation protection. Furthermore, SiB_4 is more effective in oxidation resistance than B, TEOS or TBP because it produces Si and B simultaneously to form borosilicate glass.

4. Conclusions

According to the experimental analysis of the inhibitors in C/C composites, the following conclusions could be drawn.

1. The oxidation temperature for 20 wt% burn-off during heating at 20 °C min^{-1} in air can be increased by a maximum of 133 °C with respect to untreated C/C composites, by adding the optimum composition of inhibitors.

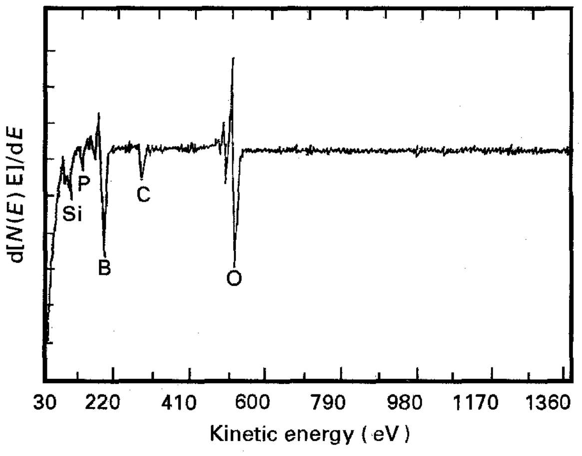

Figure 7 AES spectrum of oxidized surface of phosphoric acid-treated C/C composite.

2. The analysis of the results indicate that the phosphoric acid treatment is the most effective among inhibitors added in this study.
3. The inhibited C/C composites are protected from oxidation by the formation of a glassy thin film of P–Si–B–O.

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