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Carbon/carbon composites derived from phenolic resin/silica hybrid ceramers

Part I *Oxidation resistance and morphological properties*

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A novel phenolic resin/silica hybrid ceramer fabricated via the sol-gel method was prepared. Hybrid systems with different inorganic contents were used as the matrix precursors to fabricate the silica containing carbon/carbon composites. Isothermal oxidation tests at temperatures ranging between 650°C and 750°C were employed to investigate how the oxidation resistance of the derived carbon/carbon composites is improved. Furthermore, the isothermal oxidation test results between 550°C and 615°C were used to calculate the activation energy of oxidation. Experimental results demonstrate that the silica containing carbon/carbon composites have a better oxidation resistance than those derived from pure phenolic resins. Meanwhile, morphological observations indicate that the oxidation of carbon fibers is retarded in the phenolic resin/silica hybrid derived carbon/carbon composites. *© 2001 Kluwer Academic Publishers*

1. Introduction

Organic/inorganic hybrid material fabricated through sol-gel technology represents a new class of materials developed in the recent decade [1]. Incompatible organic and inorganic components are mixed at the nanoscale to form molecular composites. The fabricated materials possess the advantages of both organic polymers and inorganic ceramics. These materials are termed "Ceramers" by Wilkes [2] or "Ormosils" by Schmidt [3]. Several polymers have been investigated as the organic phase of the hybrids such as polyimides [4, 5], polybutadiene and polydimethylsiloxane [6], phenolic resins [7], and so on.

Carbon fiber reinforced carbon matrix (C/C) composites are unique materials that possess excellent properties such as high specific strength, high toughness and light weight. Particularly, they can retain mechanical properties at temperatures above 2000°C and, hence, the C/C composites are attractive materials for use in rocket nozzles, disk brakes and thermal insulating elements [8, 9]. However, C/C composites are limited in that the carbon will rapidly oxidize under an oxygen environment at temperatures as low as 500°C [10]. Thus, a good oxidation protecting system is crucial in the development of C/C composites.

Two main classes of oxidation protection techniques exist for C/C composites. The first method involves coating a protective layer on the outer surface of C/C composites. The microstructure and oxidation resistance of SiC coated C/C composites have been described in our previous study [11]. The other method for improving the oxidation resistance of C/C composites is adding oxidation inhibitors. Mckee [12, 13] conducted a series of investigations on the inhibitors for modifying the oxidation resistance of C/C composites. Mun [14] also investigated the effects of combining various inhibitors in C/C composites. The above studies proved that adding inhibitors improves the oxidation resistance of C/C composites in certain temperature regions.

In our previous study [15], sol-gel method derived phenolic resin/silica hybrid ceramers have been employed as the matrix to prepare carbon fiber reinforced composites and to study the mechanical and thermal properties of the fabricated composites. According to those results, the phenolic resin/silica hybrid provides better thermal properties and higher stiffness than neat phenolic resins, furthermore, only microphase separation occurred between the organic and inorganic phases. Generally, phenolic resins are often used as the precursors of C/C composites and silica is a kind of oxidation inhibitor. The phenolic resin/silica hybrid contains both components and it should be possible to use the hybrids as the precursors to fabricate the novel silica containing C/C composites in one-step. Additionally, good compatibility between organic phenolic resin and inorganic silica ensures improved distribution of silica inside the

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TABLE I The materials used in this study

Materials	Description	Suppliers
Phenolic resin	PF-650 Resole type	Chang-Chun Plastics Co., Taiwan
Carbon fiber	PAN base, #3085 Plain woven	Mitsubishi Rayon Co., Japan
Tetraethyl orthosilicate (TEOS)	98.0%	Acros Organics Co., U. S. A

composites. Thus this study will focus on the oxidation resistance and oxidation morphologies of C/C composites derived from the phenolic resin/silica hybrids. Isothermal oxidation tests are conducted at several temperatures below 750 °C to study the improvement of the fabricated C/C composites. According to former investigations, oxidation inhibitors can only retard the oxidation rate of the C/C composites, and further protective coatings are necessary for better protection. However, the C/C composites prepared without surface treatment will not sustain higher oxidation temperatures. Thus, 750°C is chosen as the upper limit of the testing temperatures.

2. Experimental procedure

Table I lists the materials used in this study. The processing procedure of the carbon fiber reinforced phenolic resin/silica hybrid composites and the mixing ratio of phenolic resin and the sol-gel solutions are described in our previous work [15]. The nomenclature of the hybrids used in this study are presented as PXSY where P is phenolic resin, S is the sol-gel solutions, and X and Y are the mixing weight ratios of each mixture. For example, P80S20 is the mixture of 80 wt% phenolic resin and 20 wt% sol-gel solutions. The fabricated CF/hybrid composites are then carbonized at 1000°C under nitrogen atmosphere for 30 mins to form C/C composites.

The specimens with dimensions of 1.0 cm × 5.0 cm × 0.15 cm were used for the oxidation tests. The oxidation tests were conducted in a self-designed vertical TGA instrument under natural atmospheric convection. Measurements were conducted isothermally at temperatures between 550°C and 750°C. For temperatures below 615°C the oxidation rates are more uniform and the data were used to calculate the activation energy of oxidation utilizing the Arrhenius Equation.

The morphological properties of the oxidized C/C composites with different burn-out ratios and different temperatures were examined by scanning electron microscope (SEM) (JSM JEOL 840A, JEOL Company, Japan).

3. Results and discussion

3.1. Inorganic ingredients content and distribution

Fig. 1 presents the inorganic contents of the fabricated C/C composites. Compared with our previous data [15], the silica content within the materials are slightly higher after carbonization. This phenomenon is due to the phenolic resins that are degraded during carbonization, reducing the total weight of the composite. However, the change in silica content within the composites is less significant. Thus, the silica contents were increased after carbonization. Fig. 2 illustrates the distribution of inorganic residue in C/C composites based on different hybrid systems by SEM EDX mapping. The white points in the figures denote the Si atoms. The result demonstrates that the distribution of inorganic ingredients inside the fabricated C/C composites is homogeneous.

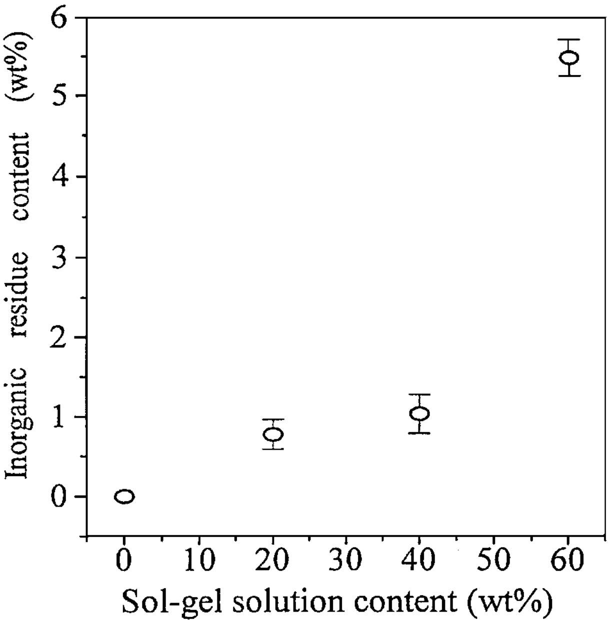


Figure 1 The inorganic residue contents in the fabricated composites.

3.2. Oxidation behaviors

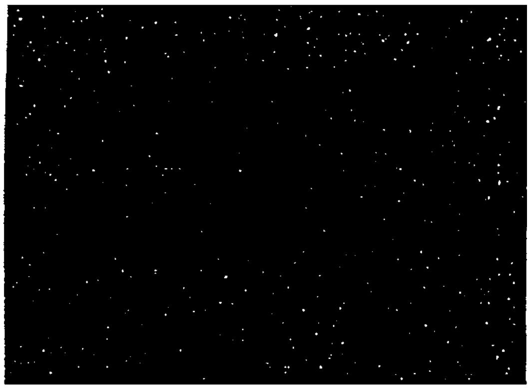
Fig. 3 presents summaries of the isothermal oxidation test results of C/C composites derived from pure phenolic resins at different temperatures. As the oxidation temperature increases, the time that the materials can remain without oxidation reduces. At isothermal temperatures between 650°C and 680°C, the oxidation rate changes at the burn-off level between 40% and 80%. When the oxidation temperature exceeds 700°C, a high oxidation rate is observed and the rate remains unchanged throughout the testing process.

Fig. 4 displays the isothermal oxidation curves of P80S20 hybrid derived C/C composites at different temperatures. When the oxidation temperature is 650°C and 665°C, the oxidation rates are slow and the oxidation rate remained unchanged. Meanwhile, when the temperature exceeds 680°C, the results also confirm the homogeneous oxidation rates but the rates are higher.

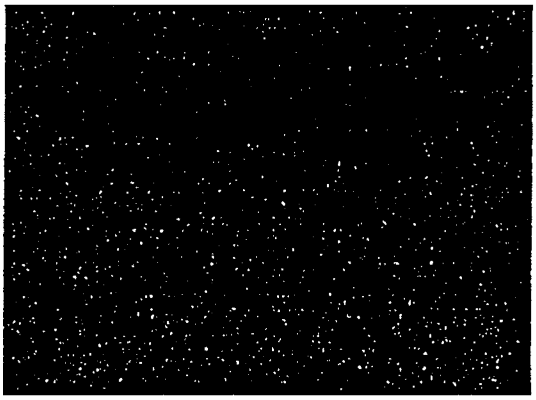
Fig. 5 presents the isothermal oxidation curves of P60S40 hybrid derived C/C composites at different temperatures. The oxidation curve at 650°C reveals a slow and homogeneous oxidation process. The oxidation rate changes at the 665°C oxidation curve. The transition ranges between the 55% and 80% burn-off level. At higher temperatures, higher and homogeneous oxidation rates can be observed.

Fig. 6 illustrates the isothermal oxidation curves of P40S60 hybrid derived C/C composites at different

P80S20 system



P60S40 system



P40S60 system

Figure 2 Distribution of inorganic residue in the materials with different hybrid systems.

temperatures. Similar results to those of P60S40 system are observed. Oxidation rates also change at the 665°C oxidation curves. The transition ranges between 25% and 55% burn-off level.

Comparing these results allows us to propose mechanisms for the oxidation process of the fabricated C/C composites. Since large specimens were used for this study, the surface area effect should be considered. The apparent oxidation rates should be controlled by both the oxidation temperature and the surface area of specimens. With a lower oxidation temperature or smaller exposed surface area, the oxidation rate is slow; while with a higher temperature or larger exposed surface area, the oxidation rate is faster. The oxidation behaviors of the phenolic resins and phenolic resin/silica hybrid derived C/C composites were investigated herein. For pure phenolic resin derived C/C composites, at temperatures below 680°C, the values of the slope of the oxidation curves are small before 40% burn-off level but then increase with testing temperature. This behavior indicates that the oxidation mechanism is controlled by the oxidation temperature. After 40% burn-off level the oxidation rate increases significantly, indicating that the surface area also influences the oxidation mechanism. Meanwhile, at temperatures above 700°C, the curves decrease with a higher and constant

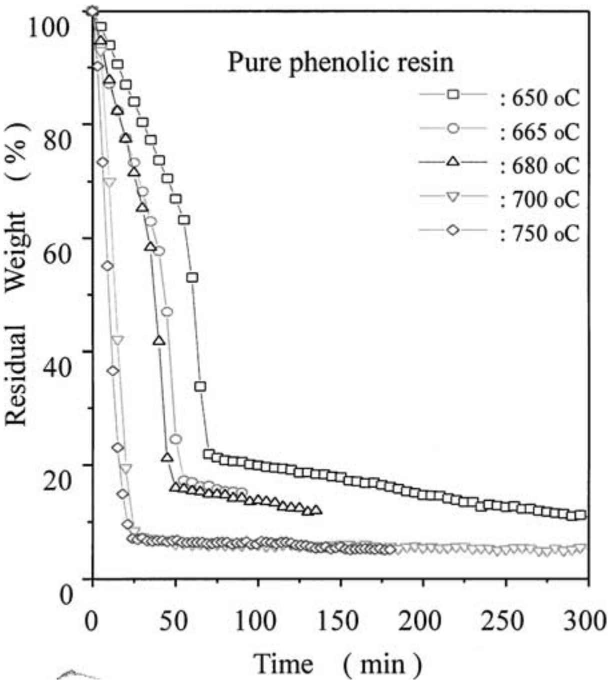


Figure 3 The isothermal oxidation curves for pure phenolic resins derived C/C composites at different temperatures.

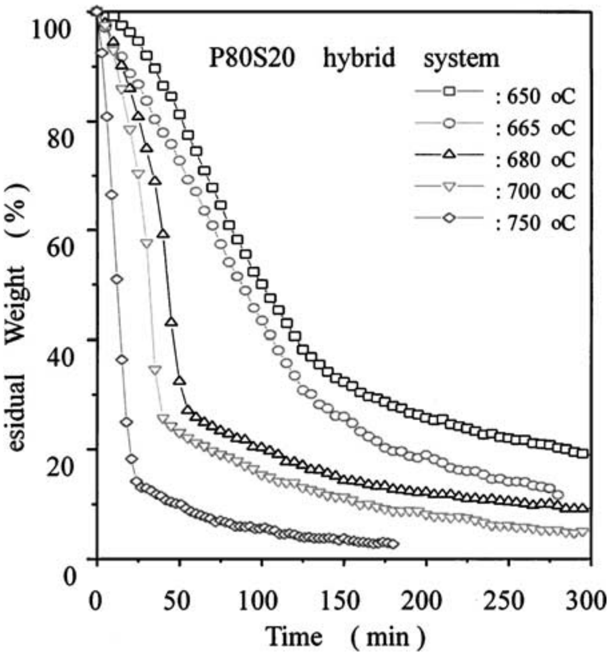


Figure 4 The isothermal oxidation curves for P80S20 derived C/C composites at different temperatures.

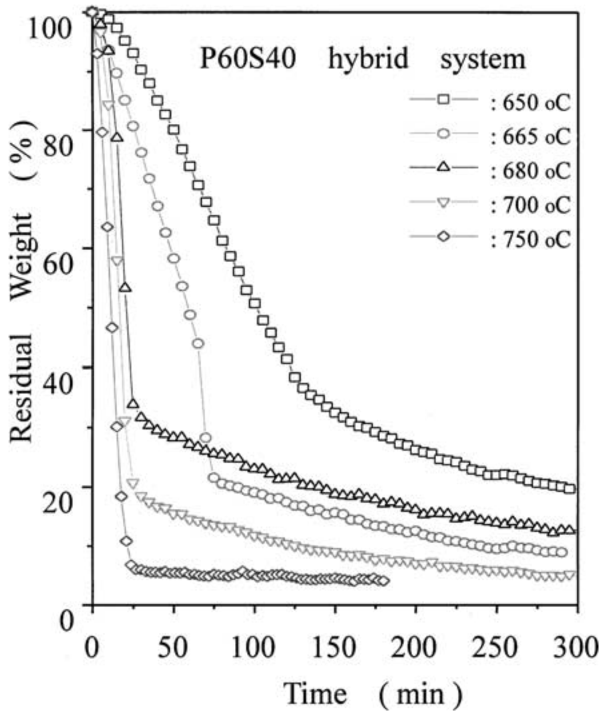


Figure 5 The isothermal oxidation curves for P60S40 derived C/C composites at different temperatures.

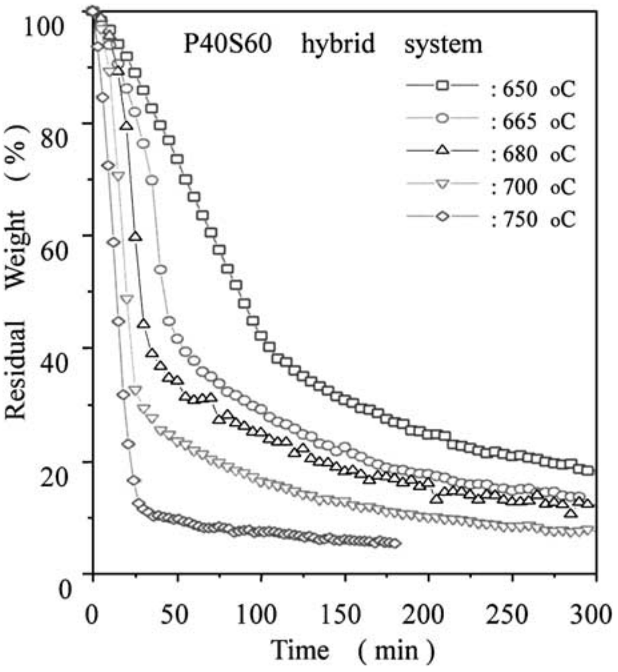


Figure 6 The isothermal oxidation curves for P40S60 derived C/C composites at different temperatures.

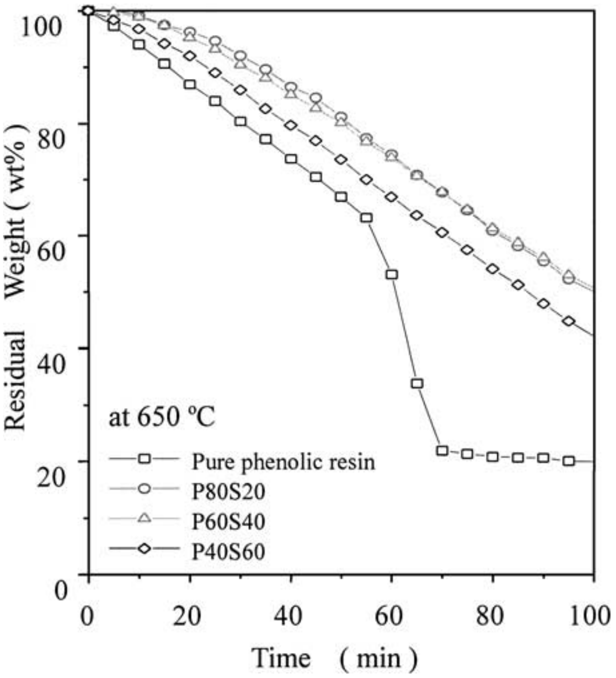


Figure 7 Comparison of the oxidation curves at 650°C for phenolic resins and hybrids derived C/C composites.

slope, implying that the oxidation temperature dominates the oxidation mechanism. Moreover, the interesting phenomenon that the rates in the second region of the low isothermal temperatures are similar to the rate under higher isothermal oxidation tests was observed. Thus even at low oxidation temperatures, if the exposed surface area reaches a critical value, the combined effect of specimen oxidation temperature and surface area will be equivalent to the high temperature effect. However, in this study, the surface areas of the oxidized specimens are difficult to measure when the burn-off level exceeds 10%, since the materials lose their integrity. Thus, the surface area effect proposed above is deduced based on the relevant literature [16].

For P80S20 hybrid derived C/C composites, two different kinds of oxidation curves with single slope and a transition temperature of 665°C clearly exist. This phenomenon demonstrates that the temperature effect dominates the mechanisms and the exposed surface area effect is insignificant. For the P60S40 and P40S60 hybrid systems, the combined effects are found at 665°C for the P60S40 system but are not obvious in P40S60 system. From these results, we can infer that the silica containing hybrids exhibit different oxidation behaviors to the pure phenolic resins derived C/C composites.

To confirm the improved oxidation resistance of the C/C composites fabricated by phenolic resin/silica hybrid ceramers, the oxidation curves of different hybrid systems and phenolic resins derived C/C composites at the same isothermal temperatures are compared. Fig. 7 displays the results with 650°C isothermal oxidation conditions. Obviously, all the hybrid derived C/C composites exhibit better oxidation resistance than those derived by pure phenolic resins. Fig. 8 presents the results of the isothermal oxidation test conducted at 700°C. The hybrid systems also show better oxidation resistance than pure phenolic resins and the P80S20 hybrid system is the best. Fig. 9 presents the results for the 750°C isothermal test conditions. Although the hybrids still show improved oxidation resistance, the effect is insignificant. Table II compares the time required to reach the 10% burn-off level for different C/C composites at different isothermal temperatures. Below 700°C, the phenolic resin/silica hybrid based C/C composites shows improved oxidation resistance, especially the P80S20 hybrid system. However, when the temperature exceeds 750°C, the effect is less significant.

Fig. 10 summarizes the Arrhenius type plots for all the materials in the temperature region between 550°C

TABLE II The time needed to reach 10% burn-off level for different C/C composites at different isothermal temperatures (min)

	650°C	655°C	680°C	700°C	750°C
Pure phenolic resin	16.0	8.2	8.2	5.8	3.2
P80S20	34.3	18.0	15.2	12.1	3.8
P60S40	30.7	14.7	11.1	7.7	3.9
P40S60	23.4	15.8	14.4	9.7	4.2

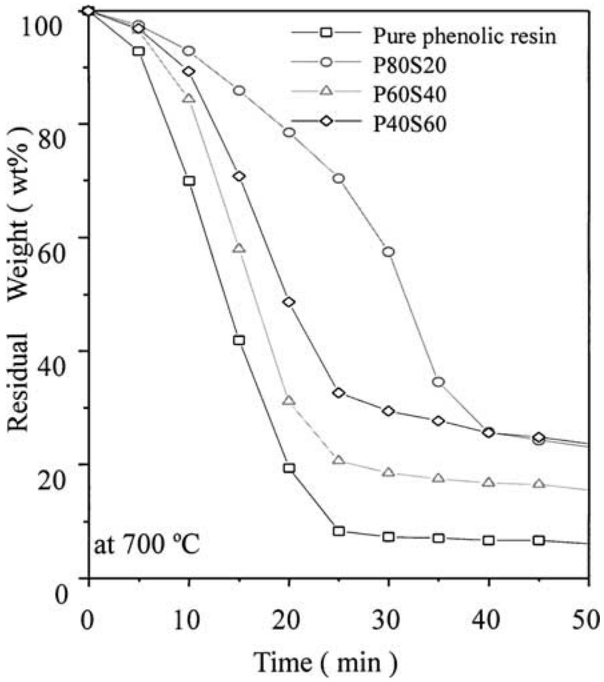


Figure 8 Comparison of the oxidation curves at 700°C for phenolic resins and hybrids derived C/C composites.

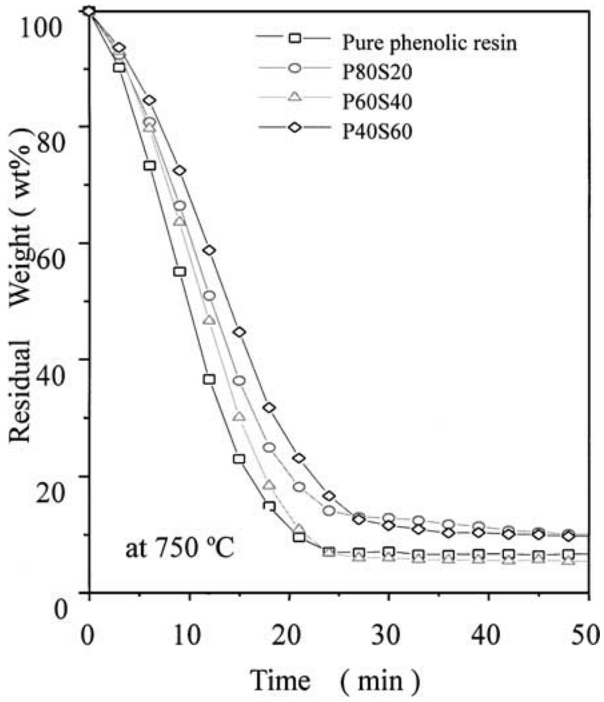


Figure 9 Comparison of the oxidation curves at 750°C for phenolic resins and hybrids derived C/C composites.

and 615°C. Obviously, the plots are linear. Table III summarizes the apparent activation energies of oxidation. The table indicates that the P80S20 and P60S40 hybrid systems have higher activation energies of oxidation. However, the activation energy of oxidation for P40S60 hybrid system is less than that of pure phenolic resins derived C/C composites.

TABLE III The apparent activation energy of oxidation of phenolic resin/silica hybrid derived C/C composites

Matrix composition	Activation Energy (KJ/mole)
Pure phenolic resin	252.50 ± 44.81
P80S20	371.39 ± 29.27
P60S40	301.47 ± 22.95
P40S60	180.08 ± 16.71

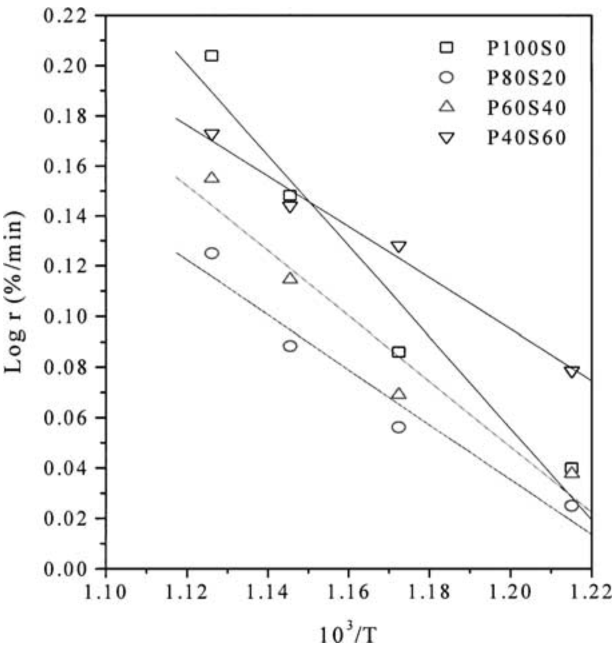
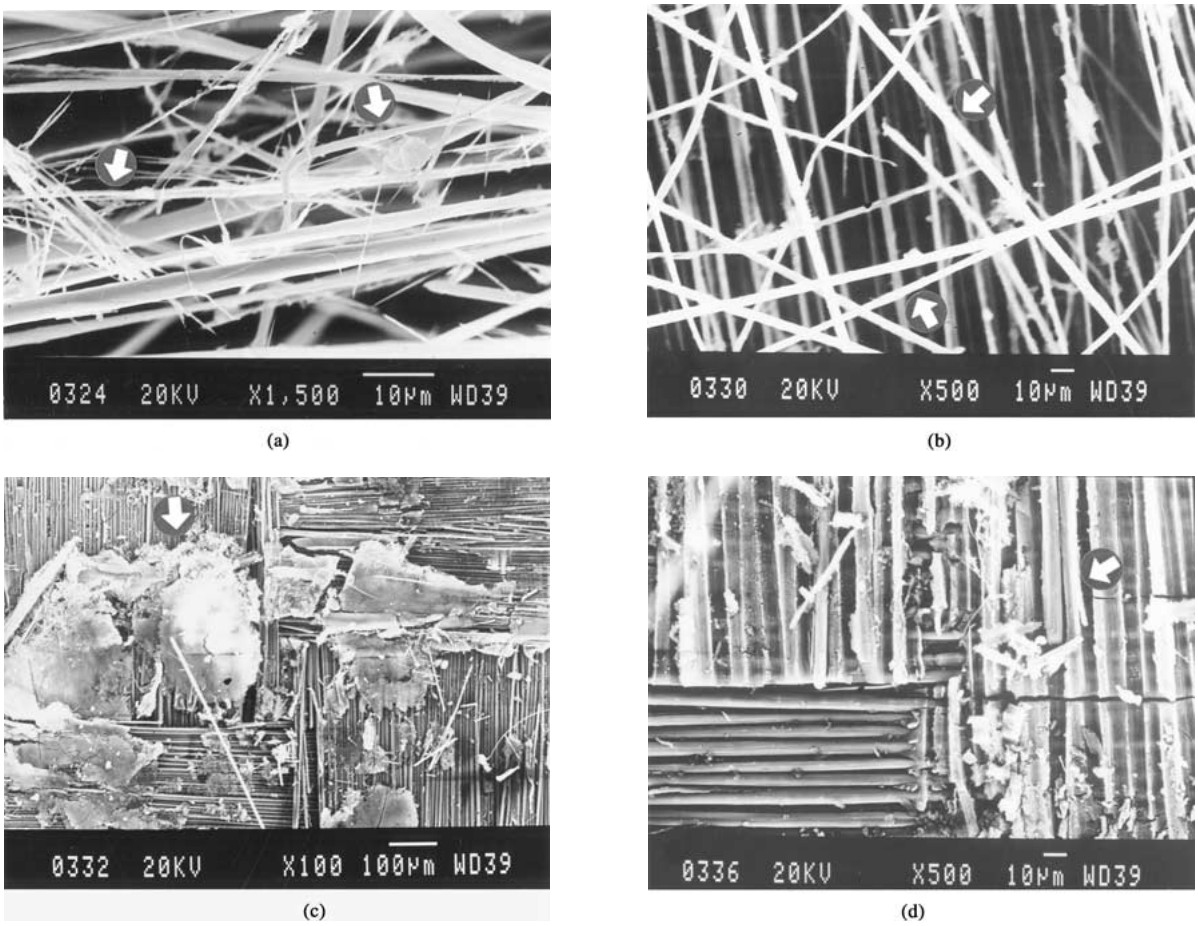


Figure 10 The Arrhenius plots of the fabricated C/C composites oxidized between 550°C and 615°C.

3.3. Morphological properties of oxidized specimens

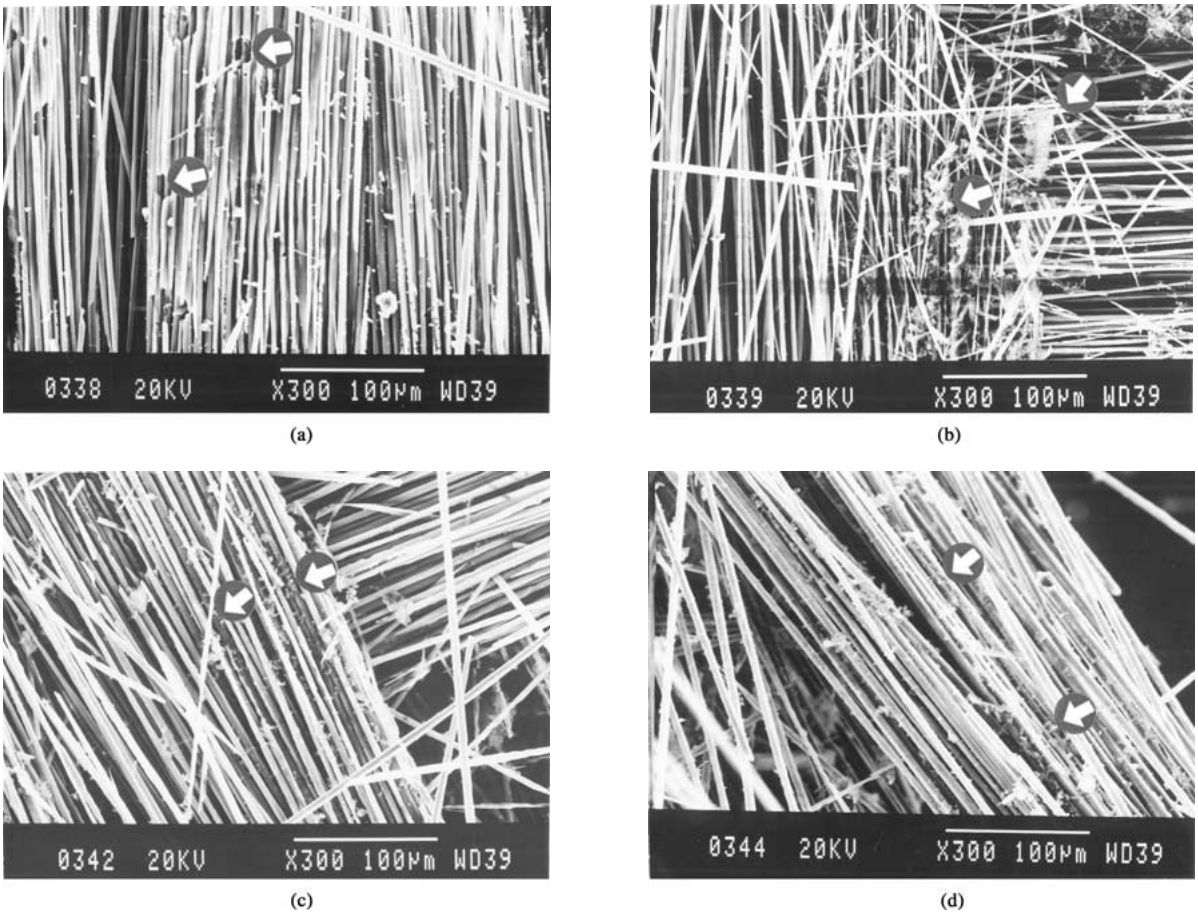
Fig. 11 presents the morphological properties of various C/C composites at various isothermal temperatures. Fig. 11a displays the reduction of fiber diameter for the pure phenolic resin derived C/C composites at 600°C. However, this phenomenon does not occur in the P80S20 hybrid system derived C/C composites tested at 700°C, as shown in Fig. 11b, where the fiber diameters are uniform. Furthermore, inorganic ingredients containing the matrix cover the fibers, as illustrated in Fig. 11c and d, representing the morphology of P60S40 hybrid system oxidized at 665°C and P40S60 hybrid system oxidized at 700°C, respectively. These comparisons confirm that even at higher temperatures, the hybrid ceramer derived C/C composites have better oxidation resistance than those derived from phenolic resin.

From the oxidation test results discussed above, at the 700°C isothermal temperature, P80S20 hybrid derived C/C composites show much better oxidation resistance than other systems, so the morphological properties for the materials under this testing condition were compared to clarify the reason for this phenomenon. The SEM photographs in Fig. 12 is the global observation of the C/C composites tested at 700°C for 15 min. At lower



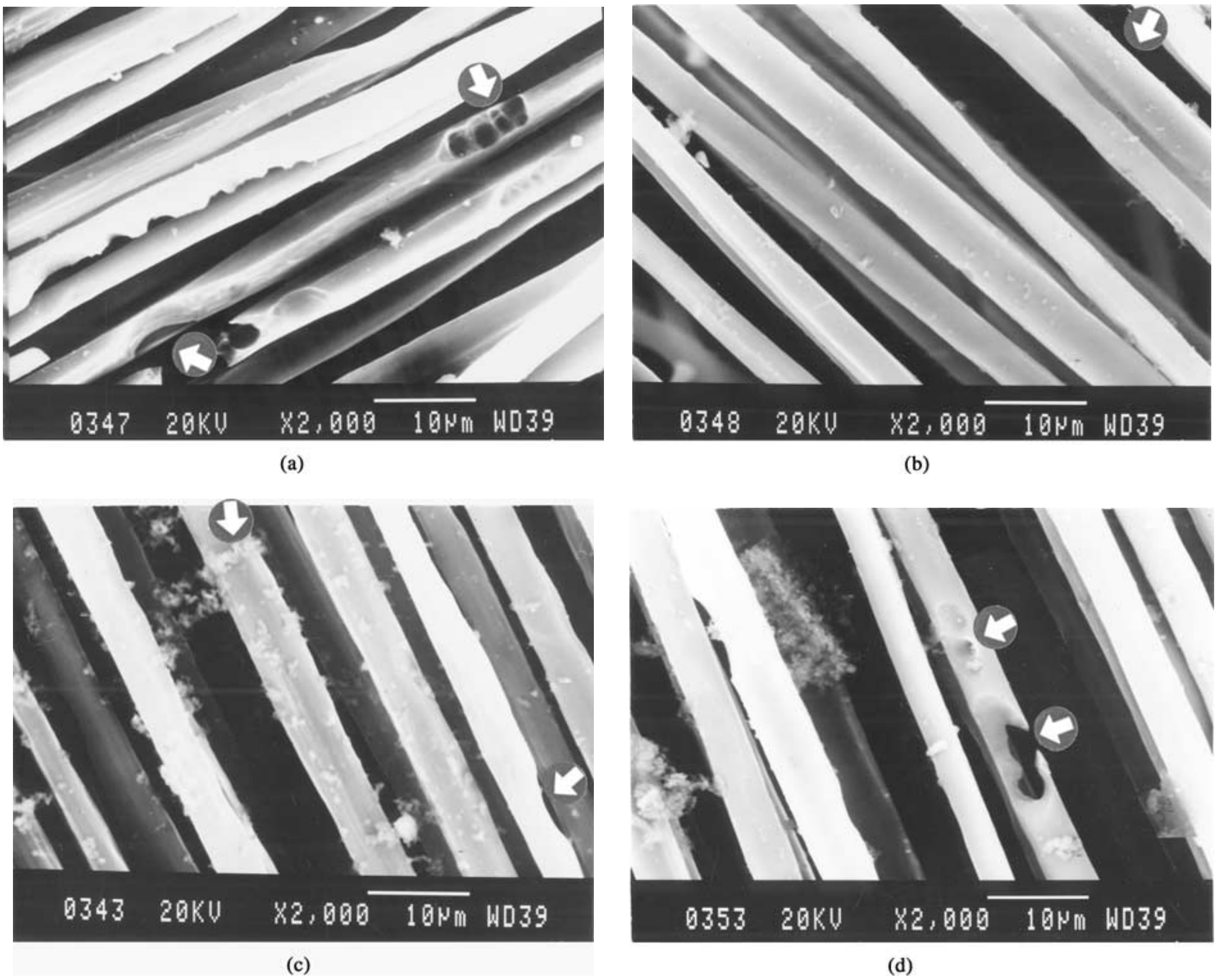
(a) (b) (c) (d)

Figure 11 SEM photographs of the oxidized specimens: (a) phenolic resin system at 600°C; (b) P80S20 system at 700°C; (c) P60S40 system at 665°C; (d) P40S60 system at 700°C.



(a) (b) (c) (d)

Figure 12 Morphological observations (lower magnification) of C/C composites oxidized at 700°C for 15 min: (a) pure phenolic resin system; (b) P80S20 system; (c) P60S40 system; (d) P40S60 system.



(a) (b) (c) (d)

Figure 13 Morphological observations (higher magnification) of C/C composites oxidized at 700°C for 15 min: (a) pure phenolic resin system; (b) P80S20 system; (c) P60S40 system; (d) P40S60 system.

magnification (×300), the oxidation of carbon fibers obviously occurs in the pure phenolic resins derived C/C composites, as displayed in Fig. 12a. For other hybrid systems, shown in Fig. 12b, 12c and 12d, respectively, pores from the oxidation could not be found. Furthermore, some fluff-like materials containing C, O and Si are observed on the fiber surface. Fig. 13 presents the microphotographs at a higher magnification (×2000). The oxidation induced pores can be found on the carbon fibers of pure phenolic resins derived C/C composites and the fiber surfaces are smooth with no matrix attached to them, as shown in Fig. 13a. Fig. 13b to 13d display the SEM microphotographs of phenolic resin/silica hybrid systems. Small species are dispersed on the fiber surfaces and the surfaces become irregular owing to partial oxidation. However, the pores caused by oxidation cannot be found, as shown in Fig. 13a. Furthermore, among the three hybrid systems investigated, the fibers of the P80S20 hybrid system show the least partial oxidation. Thus the difference between the oxidation behaviors of the hybrid systems in Fig. 8 should be controlled mainly by the delay of oxidation of carbon fibers. However, the influence of the fluff-like materials on the fiber surfaces of hybrid systems remain ambiguous and detailed investigation will be conducted later.

4. Conclusions

Phenolic resin/silica hybrid materials were employed as the matrix precursors for novel silica containing C/C composites. By changing the ratios of the hybrids, C/C composites with different contents of silica could be prepared. Isothermal oxidation investigations were conducted at between 650°C and 750°C to investigate the oxidation resistance of the fabricated materials. The data between 550°C and 615°C were employed to calculate the activation energy of oxidation. The Results demonstrate that the hybrid system derived C/C composites have better oxidation resistance than the phenolic resin derived C/C composites below 750°C. The activation energies of oxidation for the P80S20 and P60S40 systems are 371.39 and 301.47 kJ/mole, respectively. The values of both systems are higher than that of the phenolic resins system that is only 252.50 kJ/mole. From the morphological property investigations, the P80S20 system shows the best oxidation resistance among the three hybrid systems studied, since the fibers take longer to be oxidized. Furthermore, an oxidation mechanism combining the effects of exposed surface area and temperature was suggested. Although the oxidation temperature is low, if the exposed surface is sufficiently large, the oxidation rates will be similar to that of composites oxidized at higher temperatures.

Acknowledgments

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