



ELSEVIER

Materials Science and Engineering A358 (2003) 298–303

**MATERIALS
SCIENCE &
ENGINEERING**

A

www.elsevier.com/locate/msea

Kinetic study by TGA of the effect of oxidation inhibitors for carbon–carbon composite

C.A.A. Cairo ^{a,*}, M. Florian ^b, M.L.A. Graça ^a, J.C. Bressiani ^c

^a Centro Técnico Aeroespacial, IAE, AMR, CEP: 12228-904 Sao Jose dos Campos, SP, Brazil

^b Instituto Tecnológico de Aeronáutica, ITA, CEP: 12228-900 Sao Jose dos Campos, SP, Brazil

^c Instituto de Pesquisas Energéticas e Nucleares, IPEN, Cx Postal 11049, CEP: 05422-970 Sao Paulo, SP, Brazil

Received 2 July 2002; received in revised form 3 April 2003; accepted 9 April 2003

Abstract

The corrosion by air oxidation of the carbon fiber reinforced carbon composites can be inhibited by adding glass-forming particles to the matrix during the impregnation process. The effectiveness of the inhibition is related to the formation, wetting and spreading of the glass on the carbon matrix. The glass acts as a blockage onto the carbon active sites forming a thin protection barrier against oxygen diffusion. This work intends to evaluate the influence of the reactivity of the composite components on the inhibition effectiveness obtained by the addition of boron carbide and amorphous boron to the carbon matrix. Bi-directional composites were obtained with carbon matrix derived from phenolic resin using both carbonized and graphitized carbon fibers. The oxidation resistance of the composites was carried out by a weight loss in a thermogravimetric analyzer and activation energy calculation through Arrhenius plot for oxidation in air. The inhibition effectiveness depended on the reactivity of the individual components of the composite.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Carbon–carbon composites; Oxidation inhibitors; Kinetic; Boron; Boron carbide

1. Introduction

The carbon fibers reinforced carbon composites (CRFC) have their use based on their high specific mechanical strength, resistance to the thermal shock and the retention of mechanical properties to temperatures above 2000 °C. That is why they are so used in the aeronautical industry and in the aerospace applications where most of the ceramic and metallic materials cannot be used.

In spite of their excellent mechanical properties at high temperatures, the use of the carbon–carbon composites in oxidizing atmospheres is limited severely because of the extensive corrosion by oxidation of this material at temperatures above 400 °C [1], as consequence of the catastrophic loss of their mechanical properties. For this reason, the application of an

antioxidant protection is necessary when one needs to enlarge the usefulness of these composites.

Compounds of boron and phosphorous present in the matrix of carbon are effective inhibitors of the graphite and carbon–carbon oxidation over a temperature range of 400–900 °C. The glass formed by the oxidation of these compounds possesses good wettability on the carbon and it spreads forming a fine layer that acts as an efficient barrier against the penetration of the oxygen [2,3]. This way, the oxidation is inhibited by the action of the glass, but not avoided. Growing amounts of glass are formed from the carbon matrix as it is being oxidized and, therefore, a certain amount of the matrix shall be oxidized before the oxidation inhibitors begin to act [4].

The effect of the inhibition in carbon–carbon composites can be obtained by the chemical modification of the matrix by the addition of glass formers ceramic particles with the resin during the process of impregnation of the pre-form of carbon fibers [4]. The efficiency of the inhibition is related to the formation and

* Corresponding author.

E-mail address: ccairo@iae.cta.br (C.A.A. Cairo).

wettability of the glass formed in the carbon matrix and also to the reactivity differences between the matrix and the carbon fibers of the composites, with the oxygen of atmosphere [5].

In this work an evaluation of the effectiveness of the inhibition of the oxidation of the carbon–carbon by the addition of particles of B_4C and amorphous boron, incorporated to the phenolic resin during the impregnation of two types of carbon fiber, was performed. The inhibition of the oxidation was evaluated by the weight loss of the composite for temperatures of up to $1000\text{ }^\circ\text{C}$ and by the activation energy involved in the oxidation process in each case. The differences in the inhibition effectiveness were related with the reactivity of the composite components with the oxygen.

2. Experimental procedure

2.1. Materials

Two woven of carbon of different origins are used as reinforcement material in the production of the CRFC 2D composite.

- Fiber of carbon twill, T-10 EKHO A manufactured by Ural-Ukraine, derived of the polyacrylonitrile precursor (PAN), carbonized, gramature 340 g m^{-2} , with a bunch of 3000 filaments and specific mass 1.48 g cm^{-3} .
- Fiber of carbon plain, T-300, manufactured by Torayca Carbon Fiber Co. Japan, derived from the PAN, stabilized, gramature 300 g m^{-2} , with a bunch of 6000 filaments and specific mass 1.75 g cm^{-3} .

Resin Resafen 8121 manufactured by Resana Ind. Quim. S/A in the form of a liquid phenolic resin, soluble in water, was used like a carbon matrix precursor. This resin presents the smallest viscosity value at the temperature of $110\text{ }^\circ\text{C}$ and it begins to gel around $120\text{ }^\circ\text{C}$ with increase of the viscosity, according to exhibition in Fig. 1. The viscosity was measured in a Brookfield viscometer, model DV II, using spindle no. 31 (6–12 r.p.m.).

The material glass formers added as inhibitors of the oxidation were:

- B_4C particles of Elektroschmeltzwerk Kempton GmbH, with average size of $2\text{ }\mu\text{m}$ and purity $>99\%$.
- Amorphous boron particles of Elektroschmeltzwerk Kempton GmbH, with average size of $0.5\text{ }\mu\text{m}$ and purity of 90% .

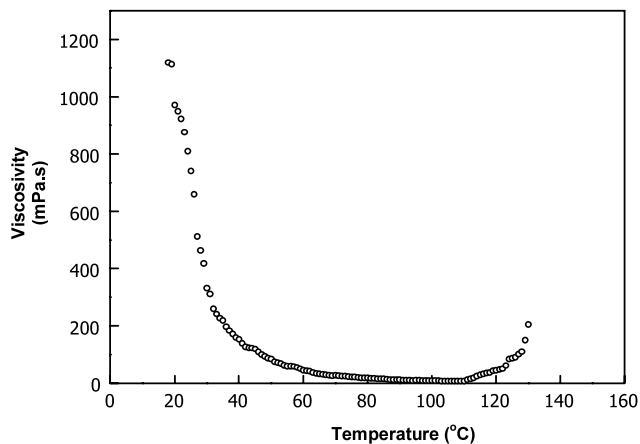


Fig. 1. Variation of the viscosity of the resin Resafen 8121 as a function of the temperature.

2.2. Methods

The fabrication of composite, arranged in 8 layers, included the manual impregnation with phenolic resin, previously mixed with amorphous boron and boron carbide in the proportion of 10% in resin weight. Each layer was put upon the previous in the same orientation and impregnated to complete the sequence of 8 layers.

Soon after, the resin was molded in autoclave, with application of pressure of 0.3 MPa in the temperature of $130\text{ }^\circ\text{C}$, at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. The composite was carbonized at $1000\text{ }^\circ\text{C}$ in atmosphere of argon, at a heating rate of $20\text{ }^\circ\text{C h}^{-1}$.

The composite manufactured with fibers of carbonized carbon Ural T-10 is named CCu, and the composite manufactured with stabilized fibers Torayca T-300, CCt.

The oxidation behaviour of the composite, as well as of its individual components, was evaluated by the weight loss in a DuPont 2100 thermogravimetric analyzer. Rectangular test specimens with $7.0 \times 3.5 \times 3.5\text{ mm}^3$ and estimated weight of 250 mg were previously dried at $200\text{ }^\circ\text{C}$ in atmosphere of nitrogen, cooled and then heated to the temperature of $1000\text{ }^\circ\text{C}$, under a constant flow of dry air ($<5000\text{ ppm}$ of humidity) of 100 ml min^{-1} with heating rate of $10\text{ }^\circ\text{C min}^{-1}$ [6].

The activation energy for the oxidation was calculated by the slope of the straight line in an Arrhenius plot that relates the logarithm of the reaction speed (% of mass loss), in the thermogravimetric analysis, with the inverse of the absolute temperature ($1/T$) [7].

The observation of the composite microstructure before and after the oxidation was accomplished by scanning electron microscopy in a Leo mod. 435 vpi.

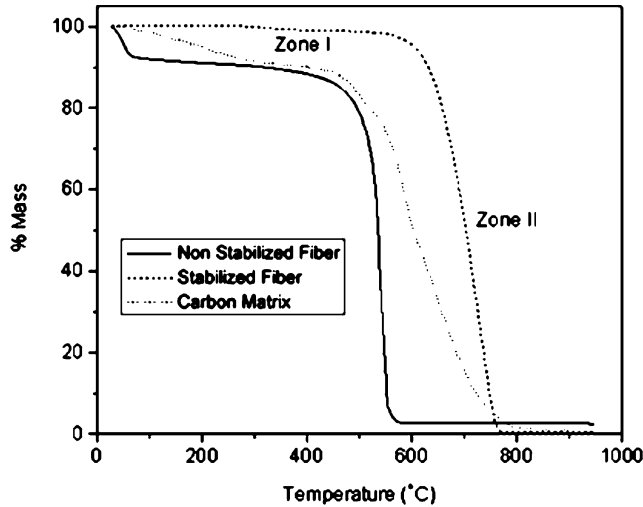


Fig. 2. Thermogravimetric analyses of the fibers and of the resin.

3. Results and discussion

Fig. 2 shows the results of the fibers and carbon matrix thermogravimetric analysis. It can be verified that the non-stabilized fiber was the first to be oxidized. Two regions can be observed with different reaction rates. In the region of low temperatures, zone I, the rate was controlled by the chemical reactivity of the carbon, while in the zone II, higher temperatures region, the rate was controlled by the diffusion of the reagent gas from the external surface to the reagent sites in the internal surface of the pores and for the chemical reaction in the active sites [8].

The activation energies (Q) calculated for the individual components are shown in the Table 1. The carbon fibers Ural T-10, at temperatures below 1000 °C, had a highly disordered structure, with open porosity and a superficial activity due to the incomplete connections of the structure, becoming them more reactive and more susceptible to the oxidation at low temperatures. The activation energy of those fibers is smaller than obtained for the graphitized fibers (T-300) that have lamellar

Table 1
Measured activation energy to oxidation for the components of the composite

Component	Region I Q (kJ mol ⁻¹ K ⁻¹) (temp. zone (°C))	Region II Q (kJ mol ⁻¹ K ⁻¹) (temp. zone (°C))
Ural fiber	108.86	–
T-300 fiber	120.20 (460–540)	163.03 (580–680)
Carbon matrix	144.32 (410–480)	87.09 (520–570)

structure. That structure is more compact and best organized, with a smaller amount of superficial defects.

The carbon matrix derived from the phenolic resin used in the thermogravimetric analysis was carbonized in a compact form with vitreous aspect and closed porosity, providing a smaller amount of active sites in the surface. In this case the activation energy is the highest for the range of low temperature (zone I). In the oxidation zone at higher temperatures, the surface pores are open for the oxidation and the diffusion of the reagent gas is facilitated by the turbostatic structure of the vitreous carbon, with strong optical isotropy. Carbons that present optical isotropy always have a larger exposed surface and, therefore a smaller resistance to the oxidation [9]. In the zone II the vitreous carbon is more reagent than the stabilized fibers (T-300).

The Ural T-10 fibers are totally gasified in the oxidation zone at low temperatures. The Arrhenius plots for the composite components are show in Fig. 3.

The activation energies calculated for the pure composite and with boron and B₄C particles are presented in the Table 2.

The fibers of the composite CCu underwent an expressive contraction during the carbonization process, practically debonding from the matrix (Fig. 4a). The debonding allowed the unprotected fibers to oxidize more quickly than the matrix, with an activation energy comparable that of the individual fibers in the region of low temperatures. The region of the debonding was a good pathway for the oxygen penetration. The weight loss was accentuated, suggesting that the fiber was totally gasified when the oxidation reaction reached the matrix. At this point, the activation energy going to values close those of the matrix of vitreous carbon.

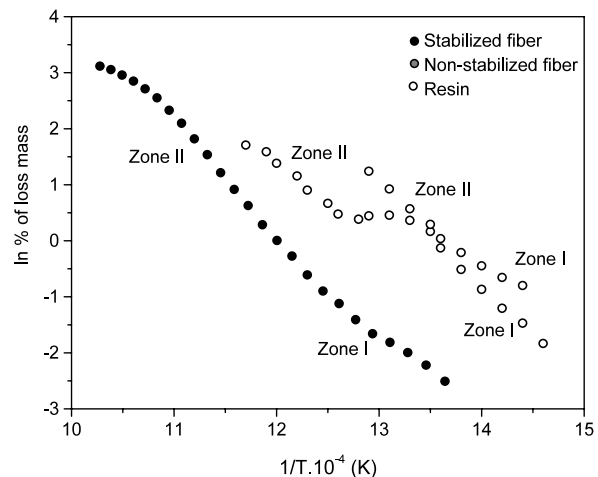


Fig. 3. Arrhenius plot of the components of the composite.

Table 2
Measured activation energy for the pure composites and inhibited with glass formers particles

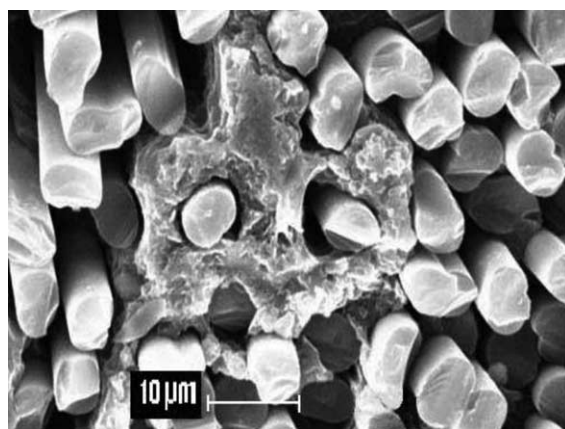
Composite	Region I Q (kJ mol ⁻¹ K ⁻¹) (temp. zone (°C))	Region II Q (kJ mol ⁻¹ K ⁻¹) (temp. zone (°C))
CCu	104.38 (360–470)	92.24 (470–560)
CCu 10% boron	173.21 (500–590)	71.47 (590–660)
CCu 10% B ₄ C	132.01 (430–550)	47.31 (550–640)
CCt	160.92 (520–590)	82.31 (590–690)
CCt 10% boron	25.16 (680–850)	108.86 (850–980)
CCt 10% B ₄ C	62.80 (630–710)	92.11 (830–950)

The carbon matrix of the CCt composite contracted more than the stabilized fibers so the interface fiber/matrix adherence was maintained. The fibers in the composite were completely covered and protected by the carbon matrix (Fig. 4b). However, the stresses generated

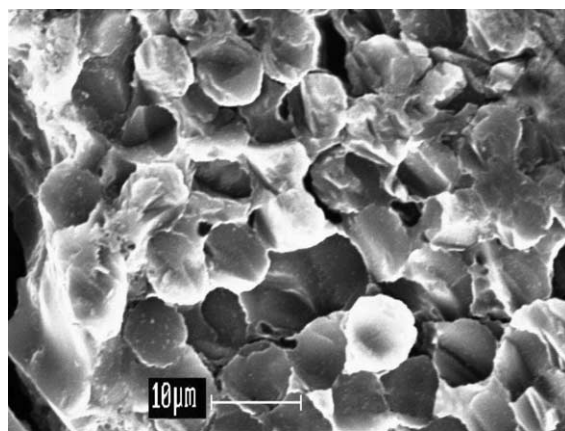
by the fibers contraction resistance acting at the matrix, results in microcracks formation. The oxidation happened preferentially at the active sites of the matrix opened by this microcracks, with energy values close to those of the individual matrix in both regions of low and high temperature.

The preferential oxidation of the matrix in the CCt composite yielded the glass formation by the reaction of the glass formers particles contained in the matrix with oxygen. The formed glass spread out and protected the surface of the fibers. This condition did not happen in the CCu composite, because when the matrix began to oxidize, a large part of the fibers was already gasified. Fig. 5a shows the skin of the carbon matrix that covered the fibers in the CCu composite without inhibitors and the spaces left by the gasified fibers. An area where the fibers were gasified and another protected by the glass can be seen in Fig. 5b.

In the CCt composite, Fig. 6, a glass layer protected the intact fibers. In this case, the formation of larger amounts of glass took place by the selective oxidation of the matrix. The glass spread out forming a protecting

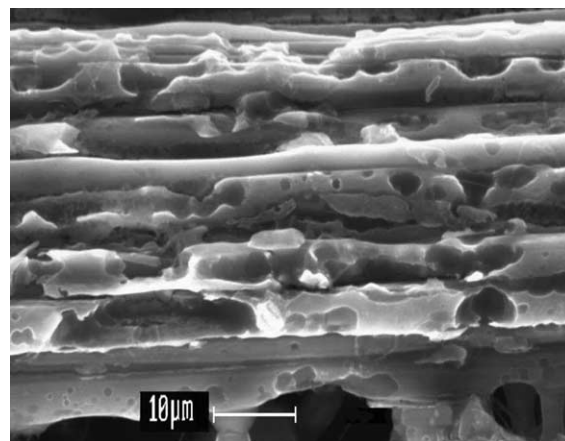


(a)

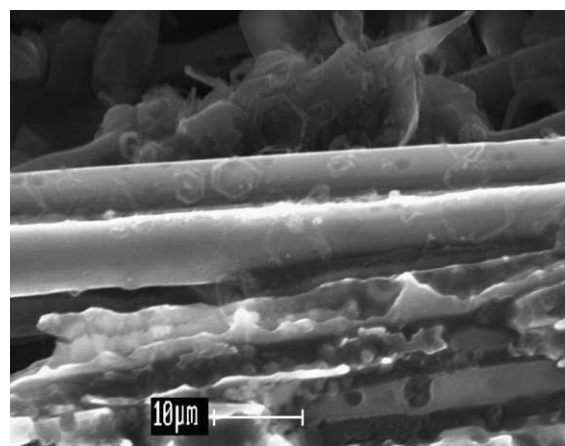


(b)

Fig. 4. Aspects of the adhesion between fiber and matrix in the composite (a) CCu and (b) CCt.



(a)



(b)

Fig. 5. Microstructure of the CCu composite after oxidation at 1000 °C, (a) CCu without inhibitors and (b) CCu+10% boron.

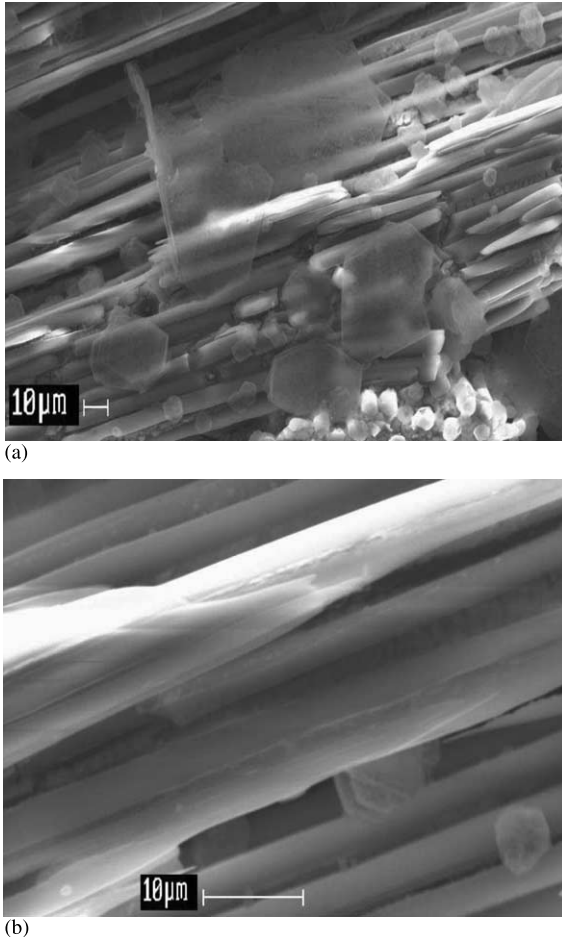


Fig. 6. Microstructure of the CCt+10% boron composite after oxidation at 1000 °C with weight loss of 15%: (a) glass formation starting from the matrix, and (b) fibers protected by the glass film.

film against the posterior penetration of the oxygen. In Fig. 6(a and b), fine plates of B_2O_3 are observed.

The advantage of the incorporation of glass formers particles is to produce growing amounts of protection

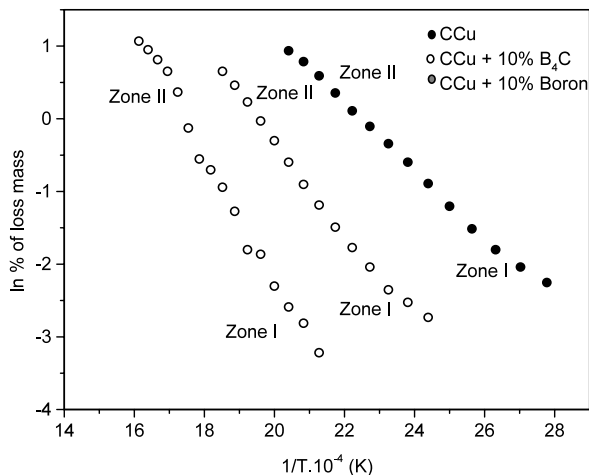


Fig. 7. Arrhenius plot of the CCu composite.

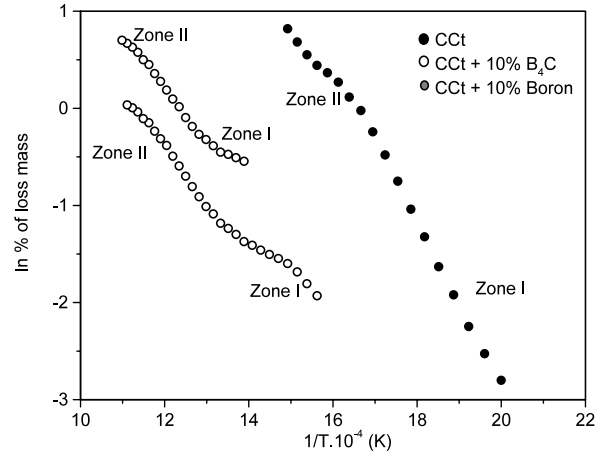


Fig. 8. Arrhenius plot of the CCt composite.

material as the penetration of the oxygen happens. This process results in the filling of the surface pores and formation of a coherent layer of glass.

Figs. 7 and 8 present Arrhenius plots of the inhibited composites. The activation energy obtained for the inhibited composites represents a value between the oxidation rates of the carbon with weight loss, and those of the boron and B_4C particles, that occur within the range 450–600 °C, with weight gain due to the formation of the boron glass (B_2O_3).

The effectiveness of the inhibition is indicated by the displacement of the oxidation curves to higher temperatures. The best inhibition was reached for the CCt composite with additions of amorphous boron. The action of glass as a barrier to the diffusion of oxygen is confirmed by the increase of the activation energy for the reaction of CCt+10% boron and CCt+10% B_4C in region II, which is the reaction stage controlled by the diffusion of the reagent gases. The reaction in this region happens at higher temperatures, when the whole particulate material is already transformed in glass.

4. Conclusions

Solid particles of boron and boron carbide are effective oxidation inhibitors for carbon–carbon composites. The addition of amorphous boron is more efficient because of its largest reactivity with the oxygen, promoting the formation of larger amounts of glass in lower temperatures. The inhibitor does not inhibit the oxidation, but it delays it, elevating the temperatures at the beginning of the process. The action of the inhibitor is based on the formation and spreading of the B_2O_3 glass and it is dependent on reactivity of the composite components, being more effective when the selective oxidation of the matrix that contains the particles

happens. The glass spreads and forms a protecting barrier against the diffusion of the oxygen in the temperature zone where the reaction is controlled by the gas reagent diffusion. In this temperature range the activation energy is larger.

Acknowledgements

The authors acknowledge the financial support for this research granted by FAPESP – 00/04573-5.

References

- [1] E. Fitzer, *Carbon* 25 (1987) 163.
- [2] D.W. McKee, C.L. Spiro, E.J. Lamby, *Carbon* 22 (1984) 507.
- [3] D.W. McKee, *Carbon* 26 (1988) 659.
- [4] J.E. Sheehan, in: B. John, D.D. Edie (Eds.), *Carbon–Carbon Materials and Composites*, Hoyes Publication, New Jersey, 1993.
- [5] C.A.A. Cairo, Ph.D. Thesis, University of São Paulo, 1998.
- [6] T.M. Wu, Y.R. Wu, *J. Mater. Sci.* 29 (1994) 1260.
- [7] R.F. Speyer, *Thermal Analysis of Materials*, Marcel Dekker, Inc, New York, 1994.
- [8] P.L. Walker, Jr., Rusinko, L.G. Frank, Jr., *Austin, Adv. Cat.* 11 (1959) 133.
- [9] H.W. Chang, S.K. Rhee, *Carbon* 16 (1978) 17.