JOURNAL OF MATERIALS SCIENCE 29 (1994) 1260–1264

Methodology in exploring the oxidation behaviour of coated-carbon/carbon composites

WU TSUNG-MING, WU YUNG-RONG
Materials R&D Center, Chung Shan Institute of Science and Technology, Lung-Tan, Taiwan 325

The aim of this study was to develop a useful method of analysing the oxidation behaviour of coated-carbon/carbon (coated-C/C). A few experiments were needed to explore the oxidation rate of coated-C/Cs at various temperatures, and the activation energy of oxidation in each temperature interval was determined simultaneously. Combining theoretical analysis of the values of the activation energy and the temperature at which the mechanism changes, allows specification of the quality of the protective coating. The concept of the integrity of the coating layer is also explained from the theory of mass transportation. This analytical procedure offers a method of distinguishing the effectiveness of coated-C/Cs by different processes. The mechanism of oxidation at each temperature interval is also specified.

1. Introduction

The development of carbon/carbon composites (C/Cs) has attracted a lot of attention owing to their excellent mechanical properties at high temperatures. Among the objects of the extensive studies on C/Cs, the elevation of their oxidation resistance is important. As C/Cs are easily oxidized when the temperature exceeds 500 °C, a surface coating is necessary to isolate the C/C matrix from oxygen attack. There are reports concerning the processing of refractory coatings, such as silicon carbide, silicon nitride and boron oxide [1–4], and their effectiveness in elevating the oxidation resistance of C/Cs. Almost all of the studies investigate the oxidation rate of a coated sample in specified circumstances, while they seldom explain the oxidation mechanism. It is also difficult to compare the reported data due to their different testing environments, Luthra [5] has demonstrated that all channels contribute to oxidation in a coated-C/C. The oxidation processes include gas-phase diffusion across the boundary layer, diffusion through cracks, diffusion through the protection layer and chemical reaction between oxygen and C/C at the interphase. The present work aims to describe an analytical procedure to qualify the oxidation resistance of coated-C/Cs under severe circumstances, and the mechanism of the oxidation is also specified. A quantitative description on the oxidation resistance of coated C/Cs is theoretically derived via a differential method by using thermogravimetric analysis (TGA).

2. Experimental procedure

The C/C samples were manufactured by the Chung Shan Institute of Science and Technology (CSIST), Taiwan, with the fibre preforming followed by cycles of pitch impregnation/pyrolysis in a hot-isostatic-press (HIP) process [6]. SiC was used to coat the C/C samples by dipping them in a silicon slurry and then reaction sintering in a graphite furnace at 1600 °C for 4 h as described elsewhere [7]. The colour of the coating layer changed from grey to light green as the silicon-carbide coating was produced.

The measurement of the oxidation rate of SiC-coated-C/C was carried out by TGA, on a CAHN 2000 TGA, under a controlled atmosphere. As the reaction of coated-C/Cs with air (oxygen) is a typical solid–gas reaction, the oxidation rate was influenced by the flow pattern of the gas phase in the reactor, which must be controlled accurately during the rate measurement. The flow rate of compressed air was kept constant at 100 c.c. min^{-1} during the testing. The humidity of air was automatically determined by the pressure of the compressor and it was kept at a constant value. The coated samples were suspended by a fine Pt/Rh13% wire along the axis of the tube of the vertical furnace. The wire passed through a small hole in the top cover of the tube to connect with the balance unit of the TGA, as shown in Fig. 1. To avoid the shielding of the C/C surface and to keep the sample in homogeneous flowing air, a fine wire was used to suspend the sample instead of a platinum crucible. The opening in the tube top cover was minimized to prevent disturbances caused by natural convection of the atmosphere, by speedy flow rate of the outlet gas. Natural convection would cause a turbulent flow of the gas and thus distort the result of the oxidation-rate measurement of the C/Cs.

The oxidation rate was then calculated and converted to a unit of weight loss per unit time per unit surface area, mg $\mathrm{h}^{-1}\,\mathrm{cm}^{2}$. The surface area was used as a calculation basis, since oxidation of C/C is a

0022–2461 © *1994 Chapman & Hall*

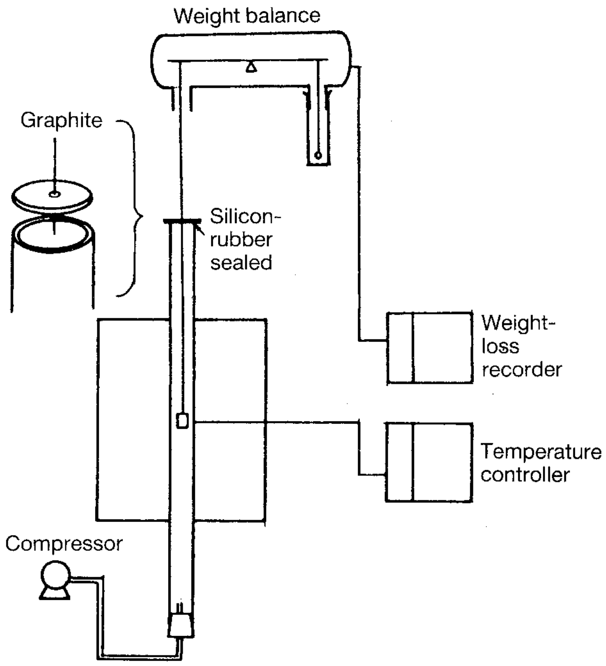

Figure 1 The TGA instrument and its accessory installation.

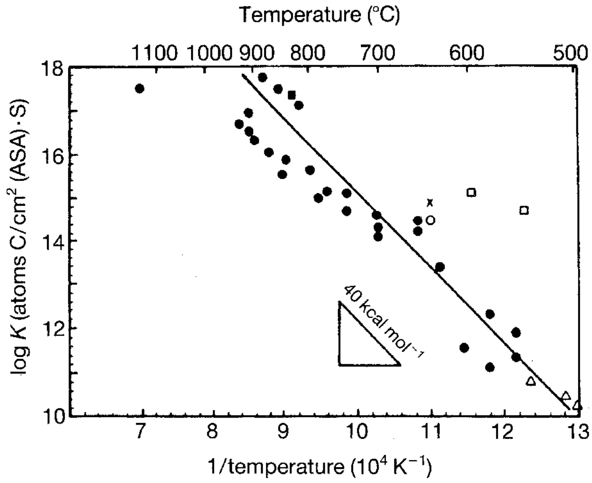

Figure 2 A compilation of the specific oxidation rates of carbon/graphite materials. (●) [10], (△) [11], (□) [12], (×) [13], (○) [14], and (■) [15].

solid–gas reaction in which mass transport of oxygen plays a key role in the performance of the oxidation. Basing the oxidation rate on unit areas eliminates the inconsistencies due to geometrical factors of the samples. An Arrhenius plot of the oxidation rate was then used to find the activation energy of the oxidation at each temperature interval.

Morphology observation of the surface of the coating layer and its cross-section was conducted by scanning electron microscopy (SEM), on a Philips 515 SEM. The crystallography of the coated SiC was identified by a Philips 7028 diffractometer.

3. Results and discussion

3.1. Theory

The oxidation of carbon materials has been widely studied and reported since 1959 [8]. The mechanism and its activation energy have also been accurately described. The mechanism changes with the temperature; chemical reactions occur at low temperatures, carbon-matrix diffusion at medium temperatures and boundary-layer diffusion at elevated temperatures. The respective activation energies are 40 kcal mol^{-1}, 25 kcal mol^{-1} and 2–5 kcal mol^{-1}. We have compiled some of the related research of the oxidation of C/Cs and found that there are no apparent differences between C/Cs and carbon materials, as shown in Fig. 2 [9–15]. The result can be used to judge the oxidation phenomena of coated-C/Cs. Whenever the activation energy of oxidation of coated-C/Cs is the same as that of carbon, it can be said that microcracks exist in the coating layer, and the C/C matrix is exposed to the atmosphere. In other words, a perfect coating on the surface of C/Cs will have a different activation energy of oxidation when it encounters an oxygen attack. The activation energy of oxidation in such a case is then determined by the oxidation of SiC. Fortunately, SiC oxidation has also been studied intensively, and a value of about 28 kcal mol^{-1} is commonly quoted [16]. The activation energy then becomes an indicator of the oxidation mechanism of coated-C/Cs. The existence of microcracks in the coating layer can be determined from the value of the activation energy.

3.2. Description of the coating layer

C/C can be easily distinguished from its carbon matrix and carbon-fibre bundle. The appearance becomes homogeneous after a SiC coating is applied to the surface. A SiC coating layer on the surface of a C/C composite is shown in Fig. 3. There are no visible microcracks under a microscope on a well-processed coating. On the other hand, a visible microcrack will cause fatal oxidation when the sample encounters severe circumstances, and the coating will fail to protect the C/C composite.

The crystal structure of the coating layer is identified as a hybrid of SiC/Si, as illustrated in Fig. 4. A graphite structure in the C/C matrix is also found, due to the thinness of the coating layer. The intertransport of carbon and silicon becomes difficult after SiC is formed, and so the SiC layer grows by less than a few tens of micrometres in a reasonable sintering time. We have found previously that the existence of unreacted silicon in the coating layer is useful in enhancing the oxidation resistance of the coated C/C composite. This may be due to the melting of silicon at high temperatures which seals the microcracks in the coating layer and so stops the transportation of oxygen, but the real mechanism is not clear yet [9].

3.3. Oxidation measurement

The oxidation rate was measured by a differential method by TGA. The recording curve of weight versus time in the TGA recorder was used to derive the differential oxidation rate at a specified temperature. Whenever the temperature and gas profile reach a

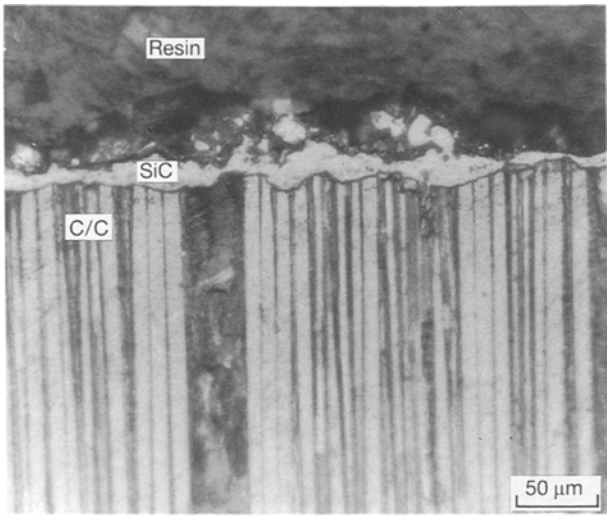

Figure 3 A micrograph of the cross-section of a SiC-coated carbon/carbon composite.

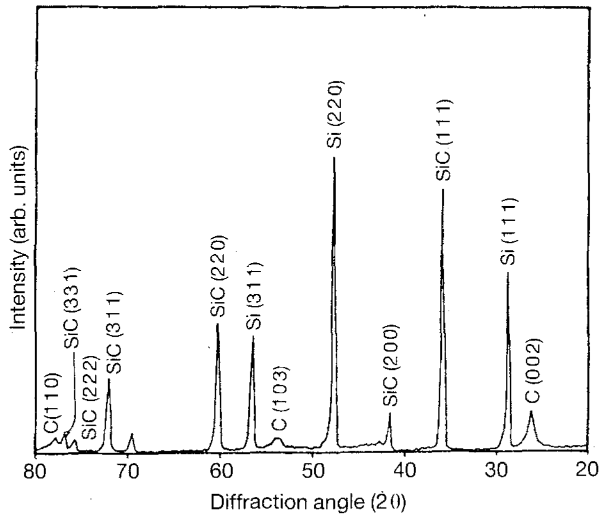

Figure 4 An XRD pattern for a SiC coating on the surface of carbon/carbon composite.

steady state in the furnace tube, the slope of the time–weight curve is a constant. The rate of oxidation is therefore determined by the slope of the time–weight curve. The advantage of a differential method in measuring the oxidation rate is that the state of the measured sample remains in a near-virgin condition after a few milligrams of weight loss, and the sample can be used for further measurement at another temperature. This assumption is believed to be valid because the mass variation during the overall measurement never exceeds 2% of the total weight. Besides, a cycling measurement at various temperatures can also prove the assumption that the oxidation rate is a function of temperature instead of its measuring history. Complete rate data can be obtained for analysis by using a few samples or even a single sample if the weight loss during measurement is not too severe. A double check on the measured data can be conducted by repeat measurements at each temperature to confirm the oxidized sample is in a near-virgin state after the measurements. The oxidation rate of the SiC-coated sample is shown in Fig. 5. The activation energy of oxidation is found by calculating the slope of the curve in an Arrhenius plot. A value of 23.5 kcal-mol^{-1} in the interval 600–920 °C was found. This value corresponds to the mechanism of oxygen transport [17]. The value of 4.1 kcal mol^{-1} at temperatures higher than 920 °C corresponds to boundary-layer diffusion of oxygen, as reported by Walker and co-workers [11, 17].

3.4. Kinetics phenomena

As described in the previous section, the oxidation of the SiC-coated C/C is controlled either by a chemical reaction or by oxygen diffusion through a boundary layer in the temperature region 600–1200 °C. The overall oxidation phenomena is similar to the oxidation of carbon. In other words, the "exposed surface" of the C/C is the main site of the oxidation reaction. A reasonable explanation of this result is that a micro-crack forms in the coating layer. The microcrack is induced by the thermal mismatch when the coated sample cools down from the processing temperature of 1600 °C to room temperature [18]. Thermal-stress analysis also supports this viewpoint [9].

The temperature of the transition from oxygen transport to boundary-layer diffusion denotes the highest temperature at which the coating layer remains valid in inhibiting the overall oxidation. The transition temperature is an indicator of the effectiveness of the coating layer. The physical meaning of the variation of the transition temperature is analysed in Fig. 6. The shifting of the transition temperature from T_1 to T_3 suggests an increase in the thickness of

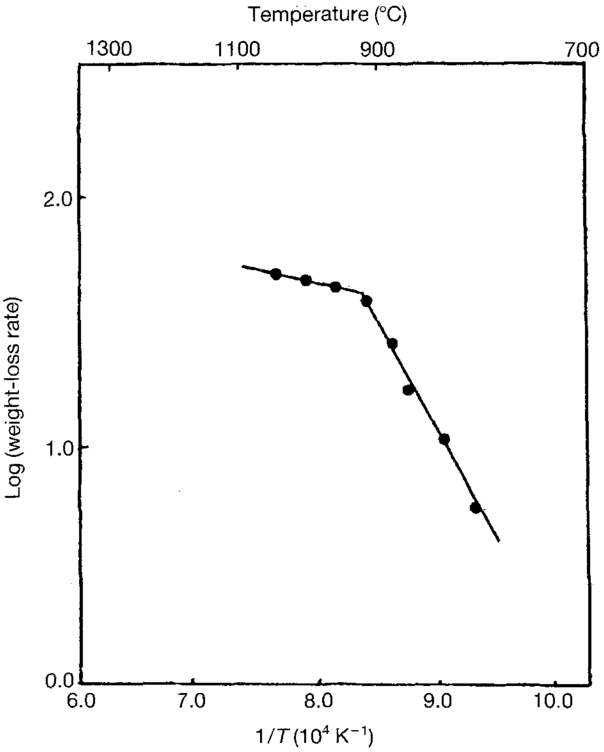

Figure 5 The oxidation rate of a SiC-coated carbon/carbon composite (the weight-loss rate has units of $\text{mg}\,\text{h}^{-1}\,\text{cm}^{-2}$).

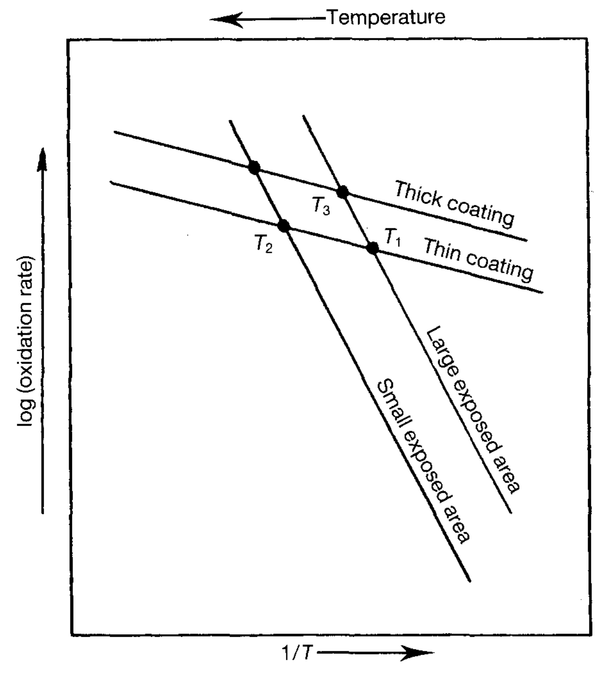

Figure 6 A schematic diagram of the shift in the transition temperature.

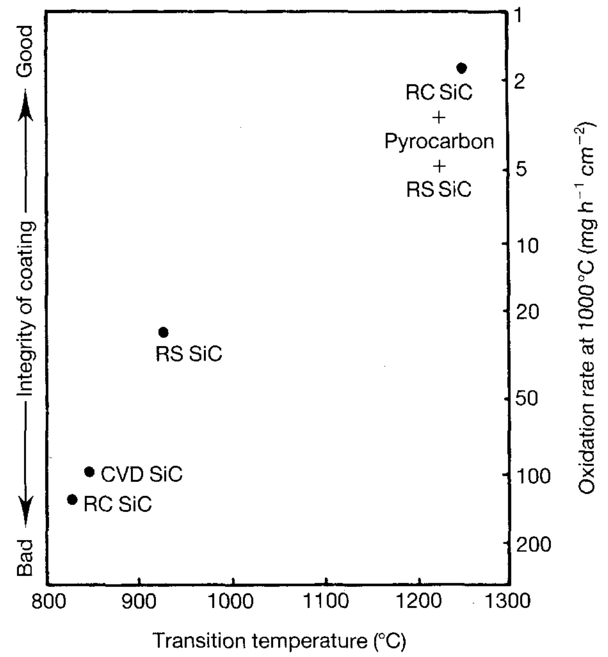

Figure 7 The degree of integrity and the transition temperature of different coating procedures for the protected carbon/carbon composite: RS, reaction sintered; RC resin converted, and VD, chemical vapour deposited.

the coating layer, which lengthens the transport path and decreases the overall oxidation rate. Whereas a shift from T_1 to T_2 suggests that a small area is provided for oxidation, and so the oxidation rate decreases. An optimized coating combination is to have a coating with the property of a higher transition temperature and a lowered oxidation rate, simultaneously.

The oxidation of coated C/C composites mainly takes place at the uncoated site of C/C composites, as described above. The oxidation rate is totally determined by the oxygen partial pressure, reaction temperature and site area. The difference in oxidation resistance of coated C/C composites reflects a difference in the "exposed" area of the uncoated carbon matrix. The oxidation rate measured under the same atmosphere is then an index of the quality of the coating layer. A plot of the oxidation rates versus transition temperature is shown in Fig. 7, with some reported data also [6]; the results obtained in the present work are denoted as reaction sintered (RC) SiC. It was found that a higher transition temperature is always accompanied by a lower oxidation rate. We propose a concept called the integrity of the coating, indicated on the left-hand-side ordinate. The better integrities of the coating layer mean that most of the area of the C/C composite is protected, while bad integrities indicate that much of the surface area of the C/C composite is unprotected owing to microcracking of coating layer. As the integrity of the coating also shifts the transition temperature of oxidation to higher values, T_1 to T_2 in Fig. 5, different coating processes may be compared by measuring the oxidation rate at the same atmosphere, and the transition temperature then becomes another indicator of the quality of the protection coating.

3.5. Comparison with the traditional method of TGA

In measuring the oxidation rate of the coated C/C composites by TGA, a curve of residual weight versus varying temperature at a fixed rate is commonly used [19, 20]. A typical result is shown in Fig. 8. The rate of oxidation is frequently taken from the curve by a first-order differentiation. The disadvantage of such procedure is that the differential calculation can offer only a little useful data. The lack of gas-phase control and the great variation of the sample sizes during the testing procedure also prevent comparisons. A different rate of temperature variation also changes the profile of the weight–temperature curve. The convection of the gas phase becomes important after the temperature is raised, and the mass-transfer phenomena

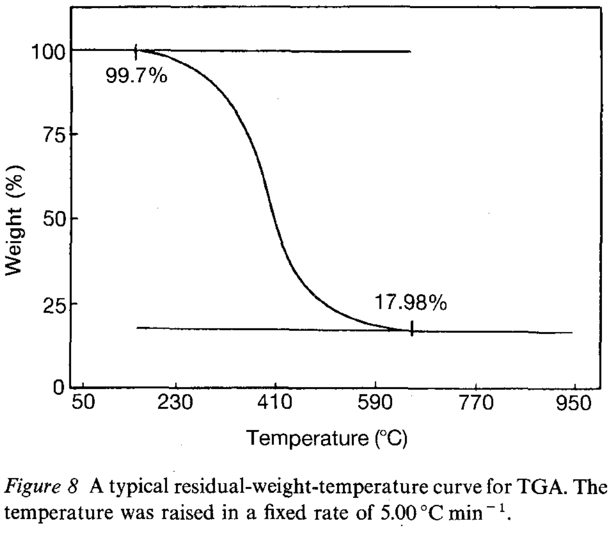

Figure 8 A typical residual-weight-temperature curve for TGA. The temperature was raised in a fixed rate of 5.00 °C min^{-1}.

is affected. Some studies calculate the activation energy of the oxidation from data like that shown in Fig. 8. There is an essential error in the physical meaning of the activation energy because the measured oxidation rate never corresponds to the same basis [19, 21]. The depletion of the reactant available at lower temperatures often causes an incorrect statement of the zero rate at elevated temperatures, a differentiation at 900°C in Fig. 8. The analytical method used in our work never gets into such a mess, and a useful conclusion could be reached by determining the rate data accurately. This analytical method is also applicable to the cases where there is difficulty in preparing the sample, such as in expensive alloys.

4. Conclusion

An effective method in evaluating the oxidation resistance of C/C composites was developed. A method of testing the oxidation resistance of coated C/C composites by TGA was also established. A shifting of the oxidation mechanism was found after analysing the oxidation rate versus reciprocal-temperature curve. The temperature of this mechanism shifting is an indicator of the quality of the protection coating. A quantitative description on the oxidation rate of coated C/C composites was also established.

References

1. P. EHRBURGER, F. LOUYS and J. LAHAYE, *Carbon* **24** (1986) 495.
2. E. FITZER, in "Sintering key papers", edited by S. Somiy and Y. Moriyoshi, (Elsevier, 1990) p. 203.
3. R. D. VELTRI, US patent 4472476, 18 September (1984).
4. D. M.SHUFORD, US patent 4465771, 14 August (1984).
5. K. L. LUTHRA, *Carbon* **26** (1988) 217.
6. T. M. WU, W. C. WEI and S. E. HSU, *Chinese J. Mater. Sci.* **22** (1990) 70.
7. Idem. *Carbon* **29** (1991) 1257.
8. P. L. WALKER Jr, F. RUSINKO Jr and L. G. AUSTIN, "Advanced Catalyst", Vol. 11 (Academic Press, New York, 1959) p. 133.
9. T. M. WU, PhD thesis, National Taiwan University, (1991).
10. P. L. WALKER Jr, *Carbon* **28** (1990) 261.
11. I. M. K. ISMAIL and P. L. WALKER Jr, *ibid.* **27** (1989) 549.
12. H. W. CHANG and R. M. RUSNAK, *ibid.* **17** (1979) 407.
13. P. EHRBURGER, F. LOUYS and J. LAHAYE, *ibid.* **27** (1989) 389.
14. J. LAHAYE, F. LOUYS and P. EHRBURGER, *ibid.* **28** (1990) 137.
15. L. E. JONE, P. A. THROWER and P. L. WALKER Jr, *ibid.* **24** (1986) 51.
16. Z. ZENG, R. E. TRESSLER and E. SPEAR, *J. Electrochem. Soc.* **137** (1990) 854.
17. P. L. WALKER Jr, M. SHELET and P. A. ANDERSON, in "Chemistry and physics of carbon", Vol. 4, edited by P. L. Walker Jr, (Marcel Dekker, 1968) p. 287.
18. T. M. WU, W. C. WEI and S. E. HSU, *J. Euro. Ceram. Soc.*, **9** (1992) 351.
19. S. M. GEE, J. A. LITTLE, *J. Mater. Sci.* **26** (1991) 1093.
20. D. W. MCKEE, C. L. SPIRO and E. J. LAMBY, *Carbon* **22** (1984) 285.
21. T. M. WU, *J. Mater. Sci. Lett.* **11** (1992) 1005.

Received 29 September 1992
and accepted 16 August 1993