

Xiaoqi Zhu, Zheng Yang, Hejun Li, Mokuang Kang

Department of Materials Science and Engineering
Northwestern Polytechnical University
Xi'an, Shaanxi, 710072, P.R.China

INTRODUCTION

Although carbon/carbon composites (c/c) fabricated from high strength carbon fibers exhibit attractive mechanical properties when heated in vacuum or in an inert atmosphere to temperatures exceeding 2000°C, a main obstacle to their high temperature structural application is their susceptibility to oxidation by ambient air [1].

McKee et al. reported a series of studies on carbon matrix modified materials which were applied to improve oxidation resistance [2]. There are some other papers and reports concerning the matrix modification by chromium and boron carbide [3,4]. However, the composites could not withstand oxygen attack when the temperature exceeded 1000°C. The most popular method of solving this problem is to introduce coatings [5]. But some problems remain to be solved because of cracks which are caused by the difference of thermal expansion of matrix and coatings.

In this study, attention is paid on the composites' inner self-protection as well as outer protection. Additives are introduced into matrix to enhance its oxidation resistance and thermal expansion coefficient. A multilayer coating on the surface of c/c is applied to accommodate not only the thermal expansion mismatch but also the chemical reactivity between coating and matrix. The weight loss curves of unmodified and modified coated c/c at various temperature are measured and discussed.

EXPERIMENT

There are four kinds of specimens, 1#—c/c composites with SiC coating, 2#—modified c/c with SiC coating, 3#—modified c/c with sealed SiC coating, 4#—modified c/c with sealed SiC and ZrO₂ coating. The c/c specimens are two dimension and fabricated by conventional technology but modified by additives such as B₂O₃, SiC and SiO₂. SiC ceramic coating is produced on the surface of c/c composites by cementation. The specimens are contacted with a particular composition, which is heated and maintained between 1500°C and 2000°C in argon atmosphere for a period to form SiC coating having the desired thickness on the c/c surface. The optimal thickness is about 50 μm, which is

determined by several factors including the time-temperature profile (TTP). The TTP should be arranged as the step curve to get suitable thickness. The sealing technology for SiC coating is used to decrease the weight loss percentage significantly. ZrO₂ coatings are introduced into the anti-oxidation system of c/c by plasma spraying. The compactness of structure is improved and the internal stress is relieved after heat treatment. The coating structure has been optimized. One sealing base layer is introduced between SiC layer and ZrO₂ layer, which can seal the crack in coating as well as improve the bonding strength greatly [6]. The weight loss curves are measured by thermal scale.

RESULTS AND DISCUSSION

The results from specimen 1# and 2# (figure 1) show that the burning rate is constant at low temperature and initial oxidizing stage (the weight loss percentage is less than 20%). At second stage, the burning rate is also constant, but higher than the first one (the weight loss percentage is between 20% and 70%). At third stage, the weight loss percentage has logarithmic relationship with time (the weight loss percentage is higher than 70%). The burning rate of 2# was found to be significantly less than 1#, which means modification can greatly enhance the oxidation resistance of c/c. Their Arrhenius curve are shown as figure 2. It is found that the first stage of Arrhenius curve is composed of two broken lines. The values of activation energy of these four parts of specimen 1# are 158 KJ/mol, 82 KJ/mol, 79 KJ/mol and 22 KJ/mol respectively. The transition temperature is 1125°C. Values of activation energy of specimen 2# are 159 KJ/mol, 83 KJ/mol, 81 KJ/mol and 24 KJ/mol respectively. The transition temperature is 1200 °C.

The weight loss percentage of sealed SiC coating and sealed SiC + ZrO₂ coating (for specimens 3# and 4#) are less than 1.2% and 1% after 10 hours oxidizing at 1500 °C. The whole burning rate is constant. Their values of activation energy are 162 KJ/mol and 166 KJ/mol [6].

Different activation energy means different rate-determining mechanism. The whole oxidation process can be divided into three stages. The value of activation energy at initial stage is about 160 KJ/mol

and the burning rate is constant. In this case, diffusion rate is higher than reaction rate and there is no gradient of oxygen concentration in the diffusion tunnel. Therefore reaction is uniform over the specimen. The burning rate of this stage is determined by the reaction rate.

At the second linear oxidizing stage, the reaction rate increases with temperature, even higher than diffusion rate. In this stage burning rate not only depends on reaction but also depends on the diffusion process in coating and matrix. The activation energy here is from 70 KJ/mol to 100 KJ/mol. Higher energy value corresponds to more effect from chemical reaction, while lower value corresponds to more effect from diffusion process.

At the last stage, there exists a logarithmic relationship between weight loss percentage and time. After many holes and cracks have been formed, the process is almost completely controlled by the diffusion process. The activation energy of this stage is below 30 KJ/mol. It can be demonstrated by calculation that the diffusion process of the reacted gas and product gas through the interfacial gas layer is the slowest process compared with other diffusion processes and becomes the rate-determining process.

CONCLUSIONS

The oxidation process of protected c/c can be divided into three stages. At initial linear stage, the burning

rate is constant and determined by the oxidizing reaction rate. The value of activation energy is about 160 KJ/mol. At higher temperature stage, the burning rate is also constant and is not only determined by chemical reaction, but also by diffusion of O₂, CO and CO₂ through coating and matrix. The value of activation energy is between 70 KJ/mol and 100 KJ/mol. The lower value means more effect from the diffusion. At final stage, the burning rate is determined completely by the diffusion process. The weight loss percentage has logarithmic relationship with time and is controlled by the diffusion through interface layer between coating and matrix. The value of activation energy is less than 30 KJ/mol.

The value of activation energy reflects the effectiveness of coating. Higher transition temperature means that coating remains effective at a higher temperature. The transition temperature gives useful information concerning the temperature at which the burning rate determining mechanism changes [6].

REFERENCES

1. Krishan, L. *Carbon*, **26**, 217 (1988)
2. D.W. McKee, *Carbon*, **26**, 664 (1988)
3. C.T. Ho, et al, *Carbon*, **28**, 818 (1990)
4. Hannache M., *J.Mater.Sci.* **19**, 202 (1984)
5. J.E. Sheehan, *Carbon*, **27**, 709 (1989)
6. Xiaoqi Zhu, Ph.D. Thesis (1995), NPU

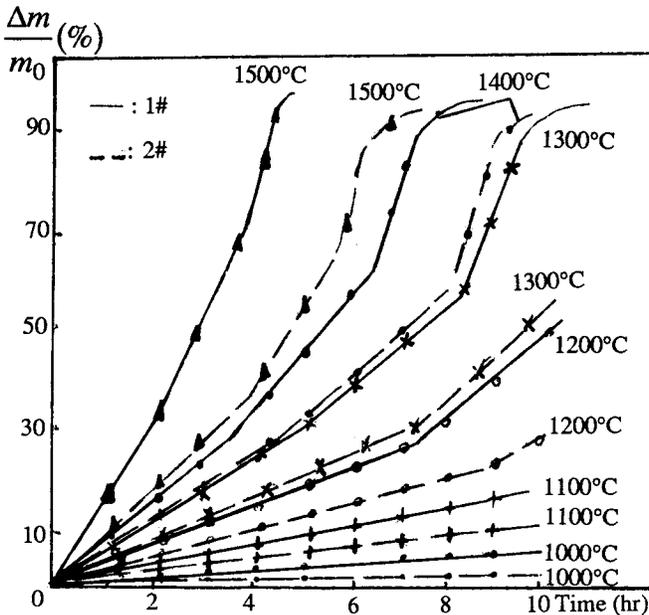


Figure 1 Weight Loss Percentage Curves of Specimen 1# and 2#

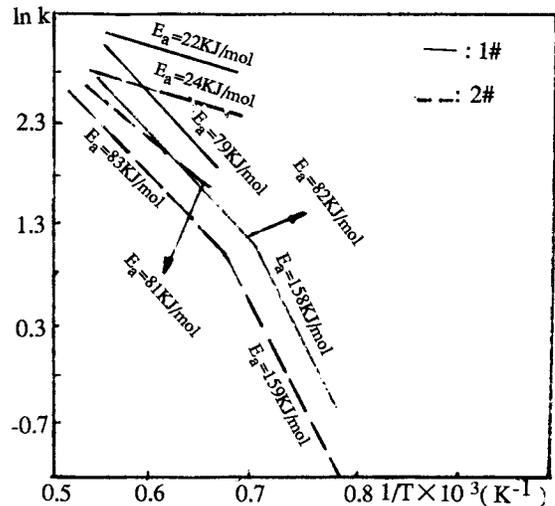


Figure 2 Arrhenius Curves of Specimen 1# and 2#