SiC/yttrium silicate multi-layer coating for oxidation protection of carbon/carbon composites

HUANG JIAN-FENG
C/C Composites Technology Research Center, Northwestern Polytechnical University, Xi'an, Shannxi, 710072, People's Republic of China

ZENG XIE-RONG
Department of Materials Science, Shenzhen University, Shenzhen 518060, People's Republic of China

LI HE-JUN*, XIONG XIN-BO, FU YE-WEI, HUANG MIN
C/C Composites Technology Research Center, Northwestern Polytechnical University, Xi'an, Shannxi, 710072, People's Republic of China
E-mail: lihejun@nwpu.edu.cn

Carbon/carbon (C/C) composites are important engineering materials for high-temperature structural applications due to their low thermal expansion coefficient, low weight, high specific strength and modulus, high creep resistance and excellent thermal shock resistance. However, their susceptibility to air oxidation above 723 K represents one of the major technological obstacles preventing wider commercialization of C/C technology [1, 2]. This has led to research on the improvement of the oxidation resistance of C/C composites. During our investigations on this aspect, we have found that high temperature silicates such as mullite and zircon are promising candidate materials for oxidation protective coatings for C/C composites [3, 4]. Yttrium silicates are good oxidation resistant materials for high temperature applications because of their excellent properties such as high melting point and low oxygen infiltration. They have been suggested as a suitable outer coating layer for SiC based materials for the nearly equivalent thermal expansion coefficient to SiC, which results in good bonding to SiC materials [5]. But the bonding of yttrium silicates coating and SiC not only depends on the match of thermal expansion coefficient, but also relies on the preparation technology to a great extent The yttrium silicates coating for C/SiC composites produced by Webster with a slurry dipping process showed a spallation of the outer coating after oxidation in air at 1873 K for approximately 50 hrs due to the oxidation of SiC internal layer [6]. On the other hand, the Y_2SiO_5 coating for SiC-C/C prepared by Ogura using a thermal spray process exhibited perfectly good thermal shock resistance during the oxidation test [7], inferring that thermal spray is a suitable technique for preparing yttrium silicates outer coating.

The scope of the investigation reported here was to improve the oxidation resistance of C/C composites by pack cementation and plasma spray technologies with new SiC/gradient composition yttrium silicate mutilayer coatings. The SiO_2-Y_2O_3 powders of different compositions were synthesized, characterized, and applied to SiC-C/C composites by plasma spray to enhance the oxidation resistance of C/C composites.

Small specimens ($14 \times 10 \times 10$ mm^3) used as substrates were cut from bulk 2D-C/C composites with a density of 1720 kg/m^3. Before carrying out the pack cementation procedure, the specimens were hand-polished using 340 grit SiC paper, then cleaned with distilled water and dried at 353 K for two hours. SiC coating was prepared by a pack cementation process with Si, C, SiC, and Al_2O_3 powders in an argon atmosphere at 2073 K for 2 hrs. The preparation details were reported in document [3].

The SiO_2-Y_2O_3 powders for plasma spray in different compositions showed in Table I were synthesized at 1873 K for 3 hrs at ambient atmosphere in an electric furnace. The SiO_2 and Y_2O_3 commercially available powders are analytical grade, with the particle size from 5 to 25 μm. The multilayer coating structure was designed as is shown in Fig. 1. The yttrium silicate coating was deposited through the Plasmagyne SG-100 torch at the conditions shown in Table II. During thermal spray deposition, the gun, which was held vertically, was set to traverse in a reciprocating manner at a preset torch-substrate distance 100 mm, while the small SiC coated C/C samples were fixed in special tongs horizontally. The sample surface was first coated with $2SiO_2 \cdot Y_2O_3$ coating, then with $1.5SiO_2 \cdot Y_2O_3$, and $SiO_2 \cdot Y_2O_3$, in turn. Every surface of the sample was coated with yttrium silicate in the same manner, and every coating of yttrium silicate was deposited to a thickness of about 30 μm. The total thickness of the outer yttrium silicate coating was controlled as around 90 μm.

The as-coated specimens were placed upon a corundum support and heated at 1773 K in air flowing by natural convection in a corundum tube furnace to investigate the isothermal and thermal cycling oxidation behavior. Cumulative weight change of the samples after every thermal cycle from 1773 K to room temperature was measured by a precision balance and was reported as a function of time.

---

*Author to whom all correspondence should be addressed.

0022–2461

TABLE I The compositions of SiO_2:Y_2O_3 powders

Powder sample no.	Composition (mol ratio)
P1	$SiO_2:Y_2O_3 = 1:1$
P2	$SiO_2:Y_2O_3 = 1:1.5$
P3	$SiO_2:Y_2O_3 = 1:2$

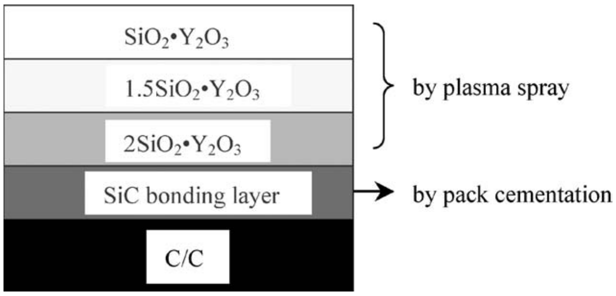

Figure 1 Schematic structure of the multilayer oxidation protective coating for carbon/carbon composites.

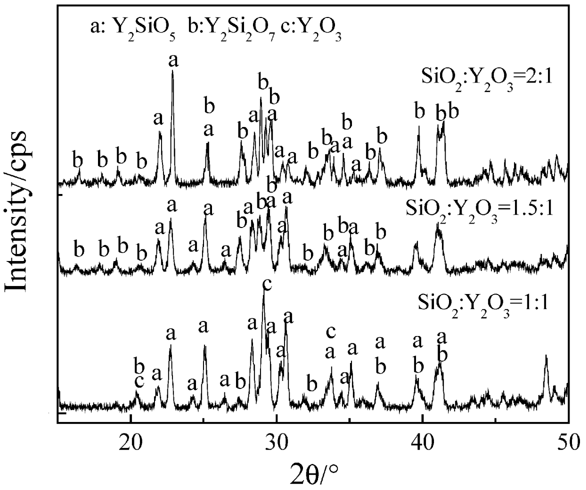

Figure 2 The XRD patterns of the as-synthesized yttrium silicate powders.

The crystalline structure of the synthesized yttrium silicate powder was measured with the Rigaku D/max-3C X-ray diffractormeter (XRD). The morphology of the as-prepared multilayer coatings was analyzed using JSM-5800 scanning electron microscope (SEM).

Fig. 2 shows the XRD patterns of the as-synthesized yttrium silicate powders. It reveals different phase compositions in different mol ratio of SiO_2:Y_2O_3. The major phase of Y_2SiO_5 and the minor one of $Y_2Si_2O_7$ and Y_2O_3 were observed when SiO_2:Y_2O_3 mol ratio is 1:1. With increase of SiO_2 content, the peak intensity of Y_2SiO_5 phase decreased, while that of $Y_2Si_2O_7$ phase increased. When SiO_2:Y_2O_3 mol ratio is 2:1, the phase of the synthesized powder is almost the $Y_2Si_2O_7$.

TABLE II Plasma spray condition

Spray torch	Plasmadyne SG-100
Plasma arc power	35 kW
Primary gas pressure (Ar)	0.42 MPa
Secondary gas pressure (He)	0.63 MPa
Spray distance	100 mm

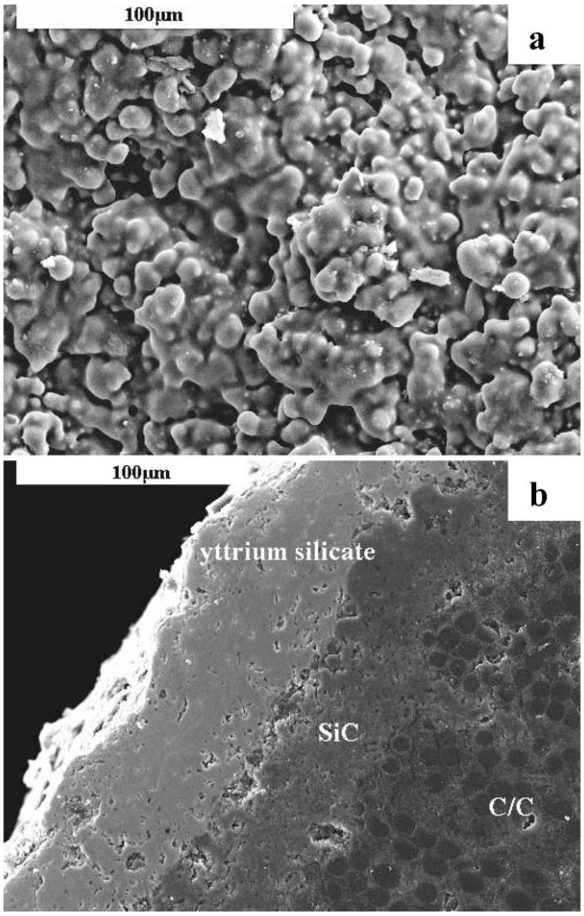

Figure 3 SEM micrographs of the as-prepared multilayer coating surface (a) and cross section (b).

Fig. 3a displays the typical surface morphology of the as-prepared sample; it is clear that the coating surface is composed of some small molten spherical particles. Some small holes are also visible on the coating surface, while no cracks are found. The cross section of the multicoating shows a perfect dense yttrium silicate coating with the thickness of around 90 μm and a SiC bonding layer with 50 μm in thickness. No obvious interfaces between the three different compositions yttrium silicates coatings are observed. No cross-coating cracks appeared due to the good match in coefficient of the thermal expansion between the SiC layer and yttrium silicate outer coating. In addition, some Si infiltrates into the C/C substrate to form a gradient SiC coating as seen in Fig. 3, which may result in excellent thermal shock resistance of the coating.

The results of the cyclic oxidation testing at 1773 K are reported in Fig. 4. The porous SiC coated C/C composite reaches almost 20% burn-off within 20 hrs. In the case of the gradient composition yttrium silicate coated SiC-C/C, no obvious weight loss of the coated sample was measured within 10 hrs oxidation at 1773 K. From 10 to 73 hrs, the weight loss of the sample gradually increases linearly, and the weight loss of the sample is only 1.93% after 73 hrs oxidation. The improvement of the oxidation resistance is owing to the gradient composition of yttrium silicate outer coating. Above 73 hrs, the weight loss rate increases quickly with time. In the experiment, we found that the yttrium silicate coating

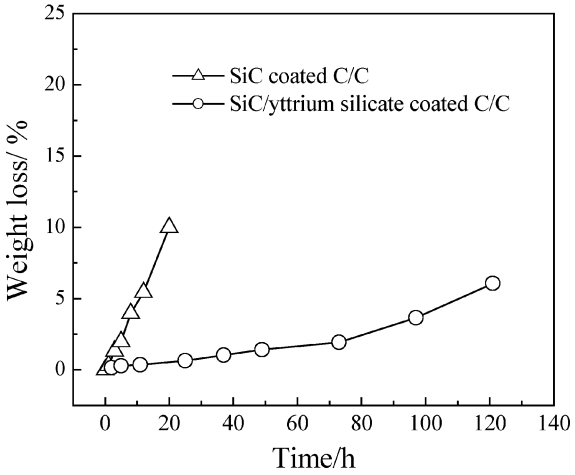

Figure 4 The isothermal oxidation curves of the C/C composites with a multilayer coating in air at 1773 K.

could react with the Al_2O_3 support gradually. After reacting with the support for some time, some big defects that could not be self-cured were generated. This may lead to the failure of the coating, which explained why the weight loss rate increases quickly above 73 hrs as shown in Fig. 4. By these analyses, the as-prepared multilayer coating may exhibit better oxidation resistance if another support that could not react with yttrium silicate is used during the oxidation examination. This needs further research.

Additionally, the sample has endured thermal cycling between 1773 K and room temperature nine times, and no cracks and destruction were found, from which it can be inferred that the coating has excellent thermal shock resistance. This is because of the formation of SiC gradient bonding layer and the good match of thermal expansion coefficient between yttrium silicate outer coating and SiC internal layer.

In conclusion, the SiC/gradient yttrium silicate multilayer coating produced by pack cementation and subsequently by plasma spray possesses excellent thermal shock resistance and can protect the C/C composites from oxidation perfectly at 1773 K for an extended period of time.

Acknowledgments

This work has been supported by the Foundation of Aeronautic Science of China under grant No. 03H53044 and the Foundation of Doctor's Degree of Chinese Ministry of Education under grant No. 20030699011 and the Foundation of Graduate students of Northwestern Polytechnical University.

References

1. J. E. SHEEHAN, K. W. BUESKING and B. J. SULLIVAN, *Ann. Rev. Mater. Sci.* **24** (1994) 19.
2. M. E. WESTWOOD, J. D. WEBSTER, R. J. DAY, F. H. HAYES and R. TAYLOR, *J. Mater. Sci.* **31** (1996) 1389.
3. J. F. HUANG, X. R. ZENG, H. J. LI, X. B. XIONG and M. HUANG, *Carbon* **41** (2003) 2825.
4. *Idem.*, International Conference on Carbon, July 6–10, 2003 (Oviedo, Spain, 2003).
5. Y. OGURA, M. KONDO, T. MORIMOTO, A. NOTOMI and T. SEKIGAWA, *J. Jpn Inst. Met.* **65** (2001) 13.
6. J. D. WEBSTER, M. E. WESTWOOD, F. H. HAYES, R. J. DAY, R. TAYLOR, A. DURAN, M. APARICIO, K. REBSTOCK and W. D. VOGEL, *J. Euro. Ceram. Soc.* **18** (1998) 2345.
7. Y. OGURA, M. KONDO and T. MORIMOTO, in Proc. Tenth Int. Conf. on Composite Materials, Whistler, British Columbia, Canada, Aug. 1995, edited by A. Poursartip and K. Street (Woodhead Publishing Limited, 1995) Vol. IV, p. 767.

Received 5 March
and accepted 28 May 2004