

Corrosion behaviors of C/SiC composite under atomic oxygen environment

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Abstract

The C/SiC specimens were exposed in a simulated atomic oxygen (AO) environment to evaluate their properties in low Earth orbit. And found that AO bombardment can greatly affect the tensile strength of the uncoated C/SiC, while it has less influence on that of the SiC coated C/SiC. The microscopic observation found C/SiC degradation is mainly attributed to carbon fiber's dissipation by AO via SiC matrix cracks.

Keywords: C/SiC composite, Atomic oxygen, Tensile strength.

1. Introduction

Presently, carbon fiber reinforced silicon carbide (C/SiC) composite has being considered and developed as one type promising materials for several lightweight structures, thermal protect components, and hot structures of hypersonic propulsion engine aiming for aerospace applications [1–3]. Therefore, various environmental behaviors of C/SiC currently have being investigated in order to get some relevant key mechanisms preparing the coming practical applications [4–6].

The atomic oxygen (AO), predominant neutral particle in low Earth orbit (LEO), may causes violent degradations for mostly materials applied in space shuttle. [7–9] Although ordinary kinetic energy of AO is about 1000K, the orbit speed 7~8 km/h of the spacecraft makes AO with 5~8eV bombing energy, consequently actives some erosive reactions upon the bombed materials [10, 11].

While, there still has little knowledge about the AO influence on C/SiC composite, such as its tensile strength evolution under the AO environment.

2. Material preparation

The four-step three-dimensional braiding method was used to fabricate T300 carbon fiber (Toray, JPN) preform, braiding angle is 21° . Pyrolytic carbon (PyC) as interface and SiC as matrix were deposited into the braided preform by chemical vapor infiltration (CVI) technology. The volume fraction of carbon fiber is about 40%. The PyC was deposited at 900°C using a mixture gas of propylene (C_3H_6) and Ar with a constant ratio 0.5 ($\text{C}_3\text{H}_6/\text{Ar}$). For SiC matrix deposition, methyltrichlorosilane (MTS, CH_3SiCl_3) vapor was carried into reactor by H_2 gas at 900°C , in which H_2/MTS ratio is 10 and its typical pressure is 5 kPa. The as-received C/SiC substrate was machined into tensile strength test samples (Fig. 1). In addition, a chemical vapor deposition (CVD) SiC coat (about $100\mu\text{m}$ thick) was fabricated on some C/SiC samples to investigate SiC coat behavior. Density and porosity of those samples is about $2.0 \sim 2.21 \text{ g/cm}^3$ and $10.0\% \sim 12.2\%$, respectively.

3. Experimental facility

3.1. AO facility

The specimens were investigated in a ground based AO simulation facility at Lanzhou Institute of Physics. In experiment, a microwave resource stimulates O_2 by means of an antenna transmission system to generate oxygen plasma at vacuum environment. The O^+ in the plasma is accelerated by a permanent magnetic field to bomb a bias plate receiving an electron and neutralized to AO particle. The AO particles are reflected and oriented to the settled specimens. A silver oxide-quartz catalytic probe is used to measure the AO flux. Time of flight method was used to ascertain the AOs kinetic energy before their neutralizations by means of a quadrupole mass spectrometer and quartz crystal microbalance (QCM) system [12]. The produced AO energy is $8.4 \sim 10 \text{ eV}$ equal to that of the nature AO at LEO orbit. The maximum AO quantity in this work is $1.25 \times 10^{22} \text{ AOs/cm}^2$ equal to five year fluence in real LEO orbit [13].

3.2. Tensile strength test

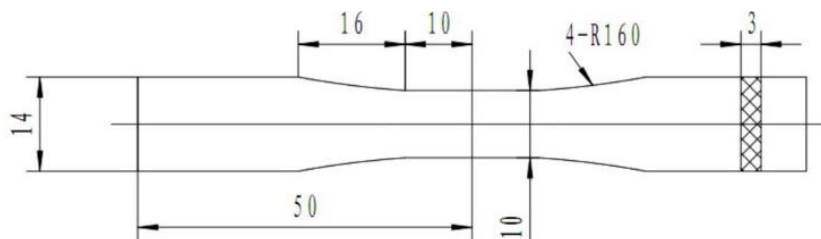


Fig. 1 The dimensions of tested specimen (unit, mm)

The specimens as the Fig. 1 described were investigated at room temperature on an Instron material mechanics testing system (Model 8801, Instron Ltd., High Wycombe, UK) with a loading rate of 0.05mm/min. And a contact extensometer with 25mm gauge length was used to measure strains under the applied loading. The received data were stored and processed by an industrial personal computer.

3.3. Microscopic analysis

The specimens pre or post-AO treatment were probed by 3D Color Laser Confocal Microscope (VK-9700, Keyence, Japan) and Scanning electron microscope (S-4200, Hitachi High-Tech. Corp., Tokyo, JPN) for characterizing C/SiC degradation process.

4. Discussion

4.1 The micro-morphology

In this work, a pair of paralleled tests was carried out for the un-coated C/SiC specimens and the SiC coated ones systematically to investigate its individual properties and compare their differences at the same AO environment.

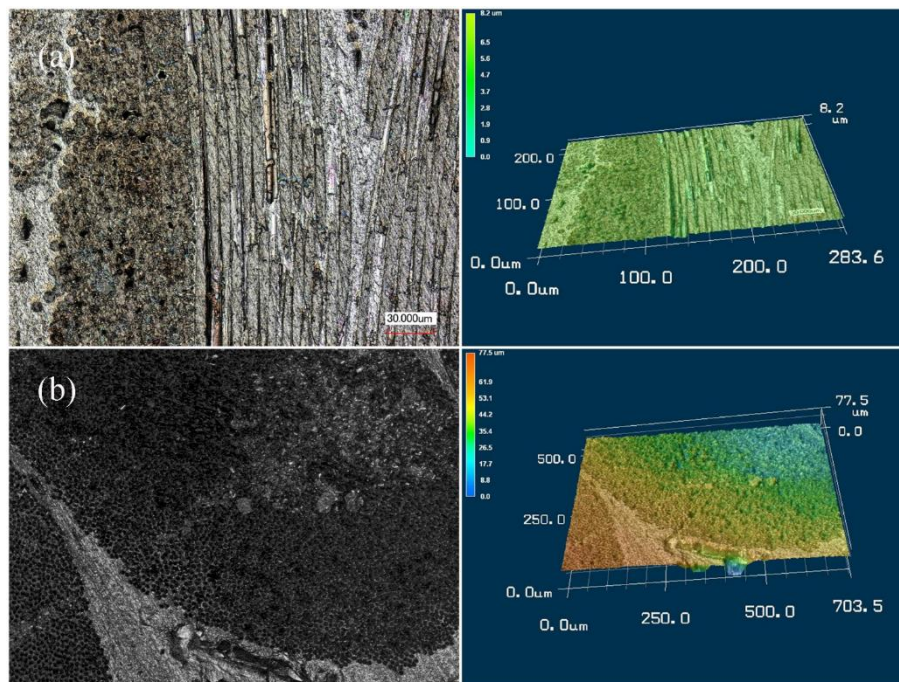


Fig. 2 Three-dimensional morphology of un-coated C/SiC (a. original b. after 5-year fluence AO treatment)

Fig.2 (a) shows the original 3D color surficial morphology and roughness of the un-coated C/SiC obtained by VK-9700 system. From the picture, carbon fiber bundles braided with different directions were displayed regularly on the specimen surface; its surface roughness is about 8.2 μm within the scanned area. After the AO experiment, the maximum roughness changed to 77.5 μm in the visional scope (Fig.2 (b)), in which left some SiC matrix holes and grooves because of the embedded carbon fibers were disappeared in some certain depth. The carbon fiber should be oxidized into CO or CO₂ according to previous reports [14, 15].

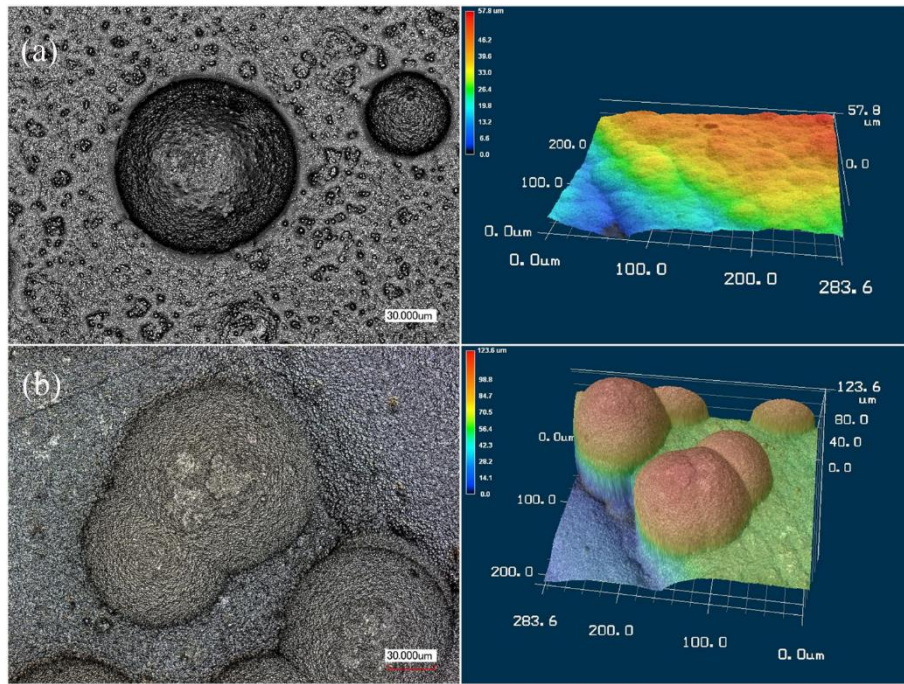


Fig.3 Three-dimensional morphology of SiC coated C/SiC (a. original b. after AO treatment)

The exterior SiC coat acted as protective barrier is commonly used to improve ceramic matrix composite stability under may harsh environments [16, 17]. Therefore, it is essential to get more information about the SiC coated C/SiC behavior subjected to AO bombing. The Fig.3 (a) displays the surficial situation of the original SiC coated C/SiC specimen, in which some SiC crystal caps exhibit on the specimen. After AO bombing, some oxidized remark appeared on the SiC crystal top (Fig.3 (b)). The surficial roughness turned to 123.6 μm from the original 57.8 μm . Fujimoto K et al. found some cavities lied on the AO bombarded Si-C.C profile although which is slighter than that of the C/C composite. Liu X et al. considered a “SiC active oxidation” of generating gaseous SiO by AO particle as the reason why the specimen surface can be changed in vision [18].

4.2 The flexural property

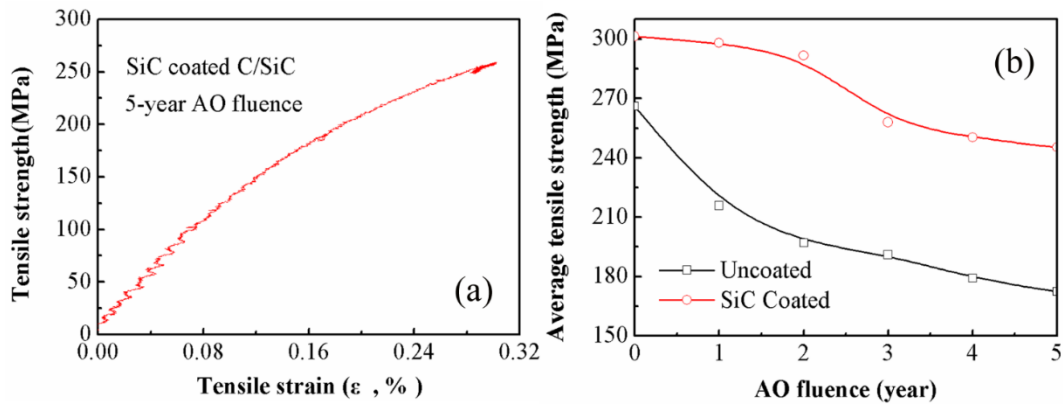


Fig. 4 The tensile strength versus strain curve of SiC coated C/SiC (a) and un-coated C/SiC specimen after 5-year AO treatment

The tensile strength is one of important mechanical parameters related to material engineering applications. A typical tensile strength versus strain curve was shown in the Fig.4 (a), after 5-year AO fluence bombardment, mechanics respond of the SiC coated C/SiC specimen still keep its non-linear characteristic.

The Fig.4 (b) described the average tensile strength tendency depending on the AO fluence. At least 10 specimens were tested in each testing point. The SiC coated C/SiC specimens have a higher average strength than that of the uncoated specimens, and suffered a weaker strength damage comparing to the uncoated ones.

Tab. 1 The tensile strengths and its distribution for C/SiC before and after 5-year AO treatment

Specimens		Min		Max		Average		Standard deviation	
		σ , MPa	ϵ , %	σ , MPa	ϵ , %	σ , MPa	ϵ , %	σ	ϵ
Un-coated	Pre-AO	230	0.28	300	0.54	266.0	0.41	30.49	0.04
	Post-AO	134	0.26	249	0.37	172.4	0.32	36.02	0.10
Coated	Pre-AO	257	0.35	332	0.55	301.4	0.45	27.23	0.06
	Post-AO	190	0.32	310	0.38	258.5	0.35	48.63	0.07

The detailed strength data after AO treatment were listed in the Tab.1. For un-coated C/SiC specimens, the average tensile strength is 266 MPa, with the standard deviation of 30.49. After 5-year AO treatment, its average tensile strength abridged to 172.4 MPa, reduced 35.18% from the original. Their tensile strength should be undermined by the dissipative oxidation of the load-bearing carbon fiber in the AO environment, as the Fig.2 shown.

For SiC coated C/SiC specimens, after AO tested, the average tensile strength decreased to 245MPa from the original 301.4 MPa, about 18.71% reduction. And their strength values displayed a wider distribution as its standard deviation is increased to 48.63 from the 27.23.

4.3 The AO erosion mechanism

To reveal the basic principles of AO erosive approaches for C/SiC specimens, the SEM tool was used to observe their microscopic evolutions.

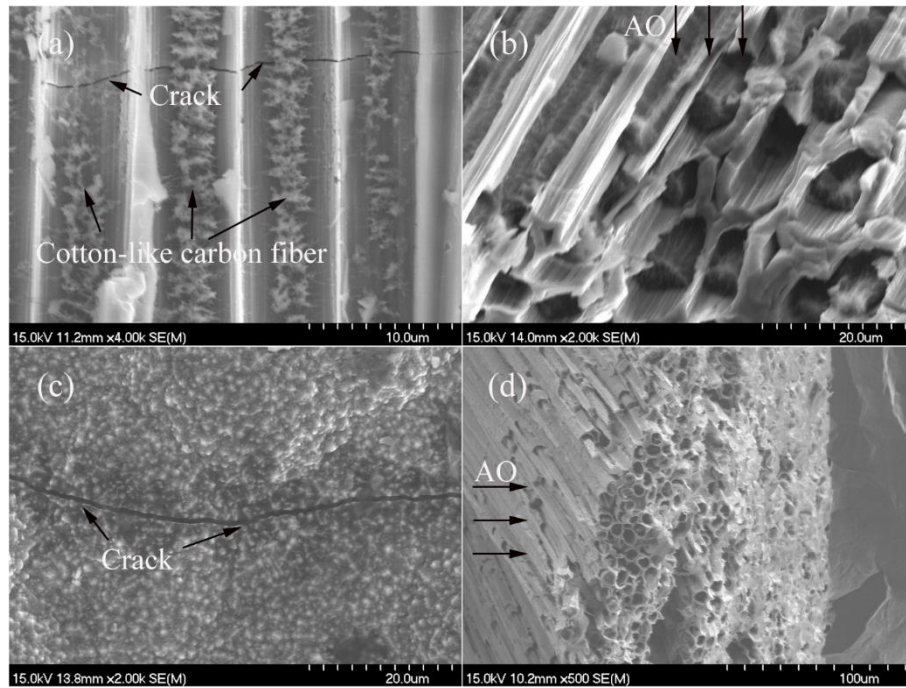


Fig.5 The microscopic image of specimen after 5-year fluence AO treatment
(a. un-coated C/SiC specimen and b. its fractured cross-section c. SiC coated C/SiC specimen and d. its fractured cross section)

From the Fig. 5(a), carbon fiber almost disappeared totally on uncoated specimen surface, with some carbon fiber ashes left on the bottom of the SiC grooves, and there are some cracks oriented perpendicular to carbon fiber direction, which usually originated by the mismatch of coefficient of thermal expansions (CTE) between SiC matrix and carbon fiber [19]. It is to say that the surface fibers will be gradually lost its normal function of burdening force, as well as another function of restraining the surficial crack propagation under applied loading. In the Fig. 5(b), the broken cross-section exhibited some carbon fibers corroded by AO particles. Apparently, AO particles can penetrate surficial cracks inwards and corrode the inner fibers of the composite.

From the Fig. 5(c) some CTE mismatch induced cracks also exhibited on the SiC coated C/SiC. In the fractured cross section (Fig.5 (d)), there are some AO eroded carbon fibers displayed on the bottom of the pulled-out carbon fiber bundles. So, it can be determined that the AO can damage SiC coated C/SiC through cracks on the C/SiC composite.

In this study, C/SiC composite including un-coated and SiC coated specimens were investigated in AO simulation environment, and some usable results can be concluded.

5. Conclusions

- The un-coated C/SiC specimens suffered a serious tensile strength degradation after 5-year fluence AO treatment, which abridged in 35.18%. While, that of the SiC coated C/SiC was about 18.71% reduction after the same AO erosion.
- For un-coated C/SiC, not only surficial carbon fibers but also the carbon fibers embedded in SiC matrix can be eroded by AO particles via the patch of cracks induced by CTE mismatch, and the latter erosion mechanism is also suitable to SiC coated C/SiC specimen.
- The C/SiC degradation in AO environment attributes to carbon fiber's damage. Fabricating SiC coat on specimen is an effective method to improve C/SiC ability confronting AO bombing, and non-oxide ceramic fiber is fundamental guarantee for preparing anti-AO ceramic composite.

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References:

- [1] 'Carbon Fiber Reinforced CMC for High - Performance Structures', W. Krenkel, International Journal of Applied Ceramic Technology, 1, 2, pp188-200, 2004.
- [2] 'CMC thermal protection system for future reusable launch vehicles: Generic shingle technological maturation and tests', T. Pichon, R. Barreateau, P. Soyris, A. Foucault, J.M. Parenteau, Y. Prel, S. Guedron, ACTA ASTRONAUTICA, 65, 1-2, pp165-176, 2009.

- [3] 'Evaluation of ultra-high temperature ceramics for aeropropulsion use', S.R. Levine, E.J. Dpilab, M.C. Halbig, J.D. Kiser, M. Singh, J.A. Salem, *Journal of the European Ceramic Society*, 22, pp2757–2767, 2002.
- [4] 'Effects of frequency and environment on fatigue behavior of an oxide-oxide ceramic composite at 1200 𐀀 C', M.B. Ruggles-Wrenn, G. Hetrick, S.S. Baek, *International Journal of Fatigue*, 30, 3, pp502–516, 2008.
- [5] 'Oxidation of Carbon Fiber-Reinforced Silicon Carbide Matrix Composites at Reduced Oxygen Partial Pressures', E.J. Opila, J.L. Serra, *Journal of the American Ceramic Society*, 94, 7, pp2185–2192, 2011.
- [6] 'Tensile properties and damage evolution in a 3D C/SiC composite at cryogenic temperatures', X. Liu, L. Cheng, L. Zhang, N. Dong, S. Wu, Z. Meng, *Materials Science and Engineering: A*, 528, pp7524–7528, 2011.
- [7] 'Surface molecular degradation of 3D glass polymer composite under low earth orbit simulated space environment', F. Awaja, J.B. Moon, S. Zhang, M. Gilbert, C.G. Kim, P.J. Pigram, *Polymer Degradation and Stability*, 95, 6, pp987–996, 2010.
- [8] 'Low earth orbit space environment simulation and its effects on graphite/epoxy composites', J. Han, C. Kim, *Composite Structures*, 72, 2, pp218–226, 2006.
- [9] 'Investigation of degradation mechanisms in mechanical properties of polyimide films exposed to a low earth orbit environment', H. Shimamura T. Nakamura, *Polymer Degradation and Stability*, 95, 1, pp21–33, 2010.
- [10] 'Atomic-oxygen undercutting of protected polymers in low earth orbit', B.A. Banks, A. Snyder, S.K. Miller, K.K. De Groh, and R. Demko, *Journal of spacecraft and rockets*, 41, 3, pp335–339, 2004.
- [11] 'Material selection guidelines to limit atomic oxygen effects on spacecraft surfaces', D. Dooling, M.M. Finckenor, NASA/TP–1999–209260, 1999.
- [12] 'A fast atomic oxygen beam facility with in situ testing/analysis capabilities', H. Kinoshita, J. Ikeda, M. Tagawa, M. Umeno, N. Ohmae, *Review of Scientific instruments*, 69, 6, pp2273–2277, 1998.

- [13] H Du, Z.H. Ye, Handbook of Space environment for LEO spacecraft, National Defense Industry, Bei Jing(1996).
- [14] 'Degradation of carbon-based materials due to impact of high-energy atomic oxygen', K. Fujimoto, T. Shioya, K. Satoh, International Journal of Impact Engineering, 28, 1, pp1-11, 2003.
- [15] 'Effects of atomic oxygen irradiation on the surface properties of phenolphthalein poly(ether sulfone)', X. Pei, Y. Li, Q. Wang, X. Sun, Applied Surface Science, 255, 11, pp5932-5934, 2009.
- [16] 'Damage mechanisms of SiC-coated C/C composites subjected to cyclic loading in combustion gas environment', C. Liu, L. Cheng, H. Mei, X. Luan, H. Huang, Materials Science and Engineering: A, 486, 1-2, pp511-516, 2008.
- [17] 'Oxidation resistance of highly porous CVD-SiC coated Tyranno fiber composites', N. Cocera, N. Esparza, I. Ocaña, J.M. Sanchez, Journal of the European Ceramic Society, 31, 6, pp1155-1164, 2011.
- [18] 'Erosion Behavior of C/SiC Composites in Atomic Oxygen', X. Liu, L. Cheng, L. Zhang, X. Yin, N. Dong, D. Zhao, Z. Hong, Z. Li, International Journal of Applied Ceramic Technology, 10, 1, pp168-174, 2013.
- [19] 'Comparison of the mechanical hysteresis of carbon/ceramic-matrix composites with different fiber preforms', H. Mei, L.F. Cheng, CARBON, 47, 4, pp1034-1042, 2009.