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Effects of thermal oxidation on microwave-absorbing and mechanical properties of SiC_f/SiC composites with PyC interphase

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Abstract: The SiC_f/SiC composites containing PyC interphase were prepared by chemical vapor infiltration process. The influences of thermal oxidation on the complex permittivity and microwave absorption properties of SiC_f/SiC composites were investigated in the frequency range of 8.2−12.4 GHz. Both the real and imaginary parts of the complex permittivity decreased after thermal oxidation. The composites after 100 h thermal oxidation showed that reflection loss exceeded −10 dB in the frequency of 9.7−11.9 GHz and the minimum value was −11.4 dB at 11.0 GHz. The flexural strength of composites decreased but fracture behavior was improved obviously after thermal oxidation. These results indicate that the SiC_f/SiC composites containing PyC interphase after thermal oxidation possess good microwave absorbing property and fracture behavior.

Key words: SiC_f/SiC composites; thermal oxidation; dielectric properties; microwave absorbing; mechanical properties

1 Introduction

Microwave absorbing materials have attracted considerable attention because of its widespread applications in the fields of electromagnetic interference (EMI) shielding and radar cross section (RCS) reduction. Much interest has been focused on the magnetic absorbers filled polymers, which can effectively absorb microwave at room temperature but lose their advantages at high temperatures [1−3]. It is necessary to develop microwave absorbing materials which can work at high temperatures in oxidizing environment [4−6]. Although silicon carbide ceramics have many advantages used as high temperature microwaves absorbing materials, the low electrical conductivity limits their microwave absorbing application potential. In fact, heterogeneous elements doping and compositing with carbon materials are two effective methods to improve the microwave absorbing potential of SiC ceramic [7,8]. On the other hand, the inherent brittle fracture behavior of monolithic ceramics limits their application as load-carrying components. The SiC fibers reinforced SiC matrix (SiC_f/SiC) composites could display non-brittle fracture behavior through interphase design [9]. SiC_f/SiC composites were proposed as potential high temperature microwave absorbing materials, they do not show a good microwave absorbing performance due to its high complex permittivity, especially the imaginary part, which is mainly contributed by the continuous pyrolytic carbon interphase with high electrical conductivity and free carbon in SiC matrix or fibers [10−14]. Up to now, several methods have been proposed to improve the microwave absorbing properties of SiC_f/SiC. YU et al [12] proposed that the matrix fabrication atmosphere plays an important role in the decrease of complex permittivity of SiC_f/SiC composites. LIU et al [10] proposed that BN with low complex permittivity should be adopted as interphase of SiC_f/SiC composites instead of pyrolytic carbon. However, the complex permittivity of SiC_f/SiC composites can only be adjusted to some degree.

It is well known that the free carbon in SiC_f/SiC composites can be eliminated by thermal oxidation. While, the influences of thermal oxidation on dielectric and microwave absorbing properties of SiC_f/SiC composites are reported rarely. In the present work, the SiC_f/SiC composites containing PyC interphase were

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fabricated by chemical vapor infiltration (CVI) process. The effects of thermal oxidation on dielectric, microwave absorption and mechanical properties of SiC_f/SiC composites were discussed by testing its room temperature complex permittivity, reflection loss and flexural strength.

2 Experimental

2.1 Preparation of interphase and composites

The continuous KD-1 SiC fibers with diameter of 14 μm were provided by the National University of Defense Technology, China, and the fabric structure was 2.5D shallow straight-joint shown in reference [11]. The fiber volume fraction of the fabric was 40%. The PyC interphase and SiC matrix were fabricated by CVI process. The C_3H_6 was the gas precursor, and H_2 was the diluent gas of PyC interphase. The temperature and pressure of CVI-PyC were 800 °C and 7 kPa, respectively. The $SiCH_3Cl_3$ was the gas precursor of SiC matrix, and H_2 was used as carrier and diluent gases. The temperature and pressure of CVI SiC process were 1100 °C and 5 kPa, respectively. The SiC matrix infiltration time was 15 h.

2.2 Characterization

The microstructure of the composites was observed by a scanning electron microscope (SEM, S−4700, Hitachi, Japan). The complex permittivity in the frequency range of 8.2−12.4 GHz was measured by a vector network analyzer (VNA; E8362B) using rectangular waveguide method. The dimensions of test sample were 22.86 mm × 10.16 mm × 2 mm. The reflection loss was tested by the Naval Research Laboratory (NRL) arc method using sample with dimensions of 180 mm × 180 mm × 2 mm. The length and width directions were parallel to warp and weft directions, respectively. Three-point bending tests of SiC_f/SiC composites were performed at ambient temperature, with a crosshead speed of 0.5 mm/min and support span of 30 mm. The test was conducted following the general guidelines of ASTM standard C 1341, using five specimens. Tensile strength (σ_b) was calculated by

$$\sigma_b=3FL/(2bh^2) \quad (1)$$

where F is the load at a appoint of deflection of a load displacement curve in test, L is the support span length, b is the specimen width, and h is the specimen thickness.

3 Results and discussion

3.1 Microstructure of SiC_f/SiC composites

Figures 1(a) and (b) show the micrographs of cross section and Raman spectra of components of SiC_f/SiC composites containing PyC interphase, respectively. As can be seen from Fig. 1(a), the obvious PyC interphase is detected between fiber and matrix, and its thickness is about 100 nm. Figure 1(b) indicates that CVI-SiC matrix is rich in carbon. The typical D and G bands of Raman spectrum of free carbon are induced by disorder carbon and in-plane bond stretching of sp^2 carbon, respectively. In addition, two peaks of β-SiC are obvious in Raman spectrum of CVI-SiC [9,11,12].

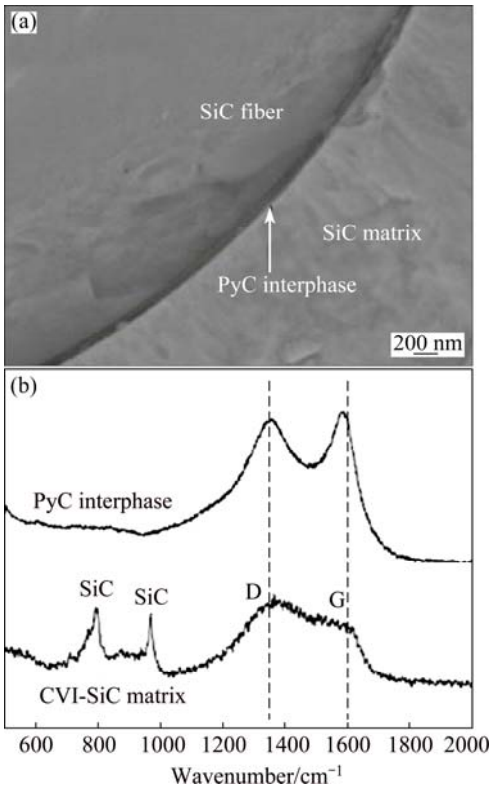

Fig. 1 SEM image of fracture surface morphology (a) and Raman spectrum (b) of SiC_f/SiC composites

3.2 Dielectric properties of SiC_f/SiC composites

Figures 2(a) and (b) display the real part (ε') and imaginary part (ε'') of permittivity of SiC_f/SiC composites after thermal oxidation at 900 °C for various time. The ε' decreases from 33 to 23 (at 8.2 GHz) with the oxidation time increasing from 0 to 100 h and decreases more rapidly with the increase in frequency. Meanwhile, slight difference is observed at the frequency of 9.5−12.4 GHz with the increasing oxidation time. The ε'' decreases sharply after thermal oxidation for 6 h, but the decreasing tendency is not obvious when oxidation time exceeds 6 h. Generally, the relation between alternating current conductivity (σ) and ε'' of the composites can be described according to Eq. (2):

$$\varepsilon''=\frac{\varepsilon_s-\varepsilon_\infty}{1+(\omega\tau)^2}\omega\tau+\frac{\sigma}{2\pi\varepsilon_0 f} \quad (2)$$

where f is frequency of electromagnetic wave, ε_0 is the

dielectric constant in vacuum, ε_s is the static permittivity, ε_∞ is the relative dielectric permittivity at the high frequency limit, ω is the angular frequency and τ is the relaxation polarization time [15]. The permittivity of pure SiC materials is relatively small. Based on the previous reports [16], the conductivity may also play an important role in the ε' of materials although their relation is not known well so far. It is believed that the typical conductivity of free carbon is much higher than that of pure SiC materials. So, the free carbon mainly determines the complex permittivity of SiC_f/SiC composites.

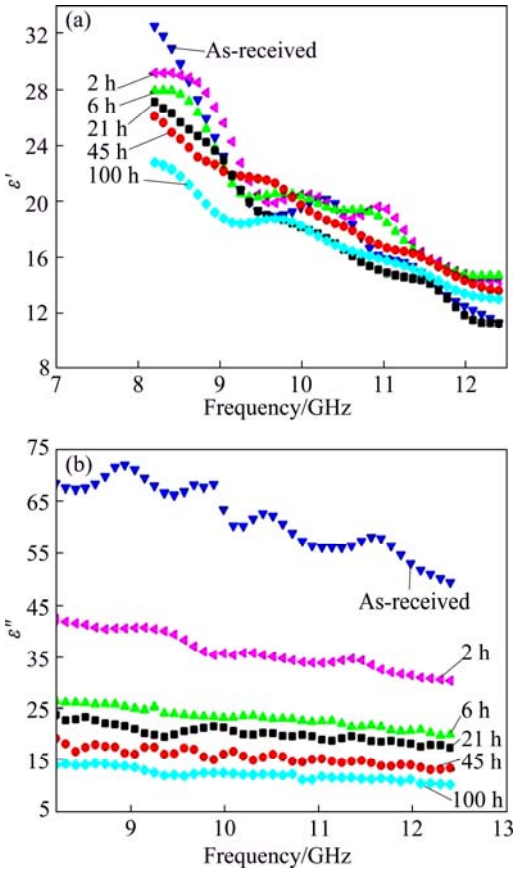

Fig. 2 Real (a) and imaginary (b) parts of SiC_f/SiC composites after thermal oxidation at 900 °C for various time

Table 1 shows the mass changes and room temperature conductivity after thermal oxidation at 900 °C for various time. The mass decreases by 2.99% after thermal oxidation for 2 h and increases slightly with the increasing oxidation time. After thermal oxidation for 2 h, the conductivity decreases sharply from 0.142 to 2.5×10^{-7} S/cm, then decreases slightly to 4.5×10^{-10} S/cm after oxidation for 100 h.

The porosity of SiC_f/SiC composites after thermal oxidation is shown in Table 1. There is an obvious increase in open porosity after thermal oxidation for 6 h. After thermal oxidation for 21 h, the porosity shows a slight decrease.

Table 1 Mass change, electrical conductivity and porosity of composites after thermal oxidation at 900 °C for various time

Oxidation time/h	Mass change/%	Electrical conductivity/(S·cm^{-1})	Porosity/%
As-received	–	0.142	9.0
2	−2.99	2.5×10^{-7}	9.5
6	−2.93	3.4×10^{-8}	10.0
21	−2.90	2.3×10^{-9}	10.2
45	−2.90	7.5×10^{-10}	10.1
100	−2.89	4.5×10^{-10}	9.9

There are three phenomena in the oxidation process of SiC_f/SiC composites with PyC interphase: consumption of carbon, formation of silica and diffusion of oxygen and carbon oxides along the pores. The oxidation reactions probably proceed as follows [17−20]:

$$2C+O_2=2CO \quad (3)$$

$$C+O_2=CO_2 \quad (4)$$

$$2SiC+3O_2=2SiO_2+2CO \quad (5)$$

$$SiC+2O_2=SiO_2+CO_2 \quad (6)$$

Figure 3 shows the schematic illustration of diffusion process of oxygen in SiC_f/SiC composites containing PyC interphase. The consumption of carbon and formation of silica could lead to mass loss and gain of SiC_f/SiC composites, respectively.

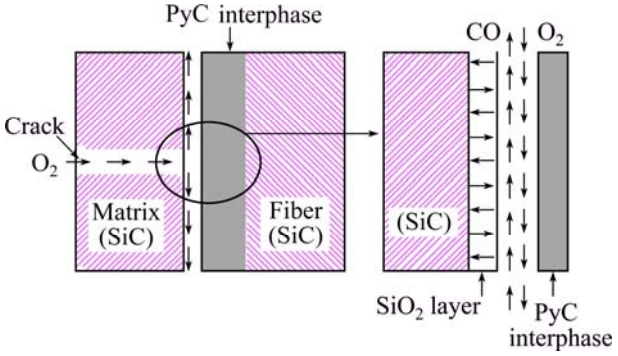

Fig. 3 Schematic diagram of diffusion process of oxygen in SiC_f/SiC composites

These results show that the oxidation of free carbon can lead to the mass loss and decrease electrical conductivity of SiC_f/SiC composites. The pores may be sealed by formation of silica and oxidation of carbon is inhibited after oxidation for too long time, which can increase the porosity first and then decrease. Consequently, there is a little change of ε'' when the oxidation time extends 6 h. And the decrease of ε' and ε'' should be attributed to the consumption of free carbon in SiC_f/SiC composites.

3.3 Microwave absorbing properties of SiC_f/SiC composites

Figure 4 shows the reflection loss (RL) of as-received and oxidized SiC_f/SiC composites at X band. It can be observed that the value of reflection loss of as-received composites is higher than −1 dB. The RL value of SiC_f/SiC composites decreases obviously with the increasing oxidation time. The peak values of composites after 2 and 6 h thermal oxidation are −5.1 dB at 8.2 GHz and −7.5 dB at 8.7 GHz, respectively. Also, the reflection loss below −10 dB (about 90% absorption) for composites after 100 h thermal oxidation is in the range of 9.7−12.0 GHz, a minimum RL value of −11.4 dB was obtained at 11.0 GHz.

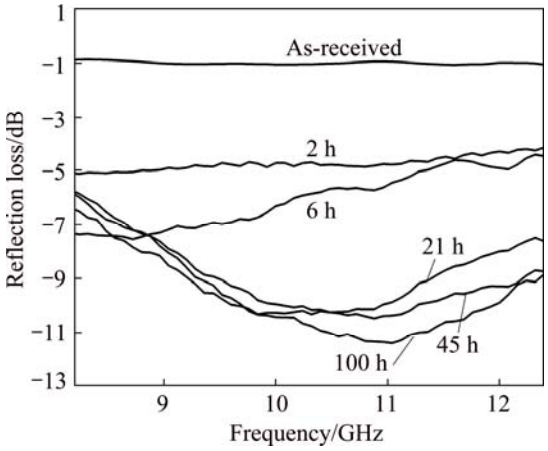

Fig. 4 Reflection loss of as-received composites and composites after thermal oxidation at 900 °C for various time

As the ideal microwave absorbing materials, they must satisfy two prerequisites: the impedance of free space and the material surface can match; and materials can absorb incident microwaves as many as possible inside of materials. The two prerequisites require the complex permittivity close to complex permeability and materials exhibit strong magnetic or/and dielectric loss, respectively. The relation between reflection loss and electromagnetic parameters of a material is usually illustrated as follows:

$$\mathrm{RL} = 20\lg\left|\frac{Z_{\mathrm{in}} - Z_0}{Z_{\mathrm{in}} + Z_0}\right| \tag{7}$$

$$Z_{\mathrm{in}} = Z_0\sqrt{\frac{\mu_{\mathrm{r}}}{\varepsilon_{\mathrm{r}}}}\tanh\left(\mathrm{j}\left(\frac{2\pi ft}{c}\right)\sqrt{\mu_{\mathrm{r}}\varepsilon_r}\right) \tag{8}$$

where Z_0 is the characteristic impedance of free space, Z_{in} is the input characteristic impedance at the absorber/free space interface, c is the velocity of light, t is the thickness of an absorber, ε_{r} and μ_{r} are the measured relatively complex permittivity and permeability, respectively [8].

In the present work, the composites are non-magnetic and μ_{r} is taken as 1.0. The thickness of all samples is 2 mm. So, the sample's reflection loss is determined only by its complex permittivity. For the as-received composites, the value of ε'' is about three times higher that of ε', meaning the obvious impedance mismatch between air and the composites. The microwave is reflected strongly on the surface of the as-received composites. So, the microwave absorbing property of as-received composites is very poor although its dielectric loss is strong. After thermal oxidation, the ε'' decreases obviously and almost keeps consistent with the ε', indicating that the impedance match characteristic was improved. The microwave reflection on the surface of composites should be reduced. Therefore, the microwave absorbing property of SiC_f/SiC composites was improved by thermal oxidation.

3.4 Mechanical properties of SiC_f/SiC composites

Figure 5 shows the typical stress−displacement curves and flexural bending strength of SiC_f/SiC composites after thermal oxidation at 900 °C for various time. It is observed that the fracture behavior of the as-received composites is brittle and the stress drops directly after its maximum value. After oxidation, the fracture behavior of the composites turns to ductile behavior after the fracture failure. While after thermal oxidation for 100 h, the fracture behavior of the composites exhibits brittle fracture again. Figure 6 shows the residual flexural bending strength of SiC_f/SiC composites after oxidation. The flexural strength of the composites decreases constantly with the extension of oxidation time. Figure 7 shows the fracture surface morphology of oxidized composites after bending test. It can be observed that the fracture surface of as-received composites is very plane and no pull out fibers can be seen in Fig. 7(a). For the composites oxidized for 2 h

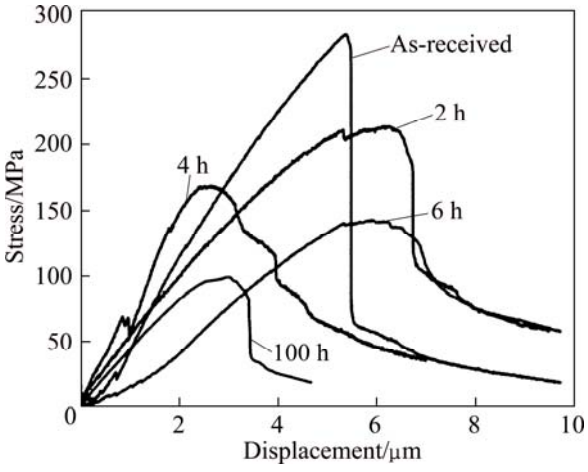

Fig. 5 Typical stress−displacement of as-received composites and composites after thermal oxidation at 900 °C for various time

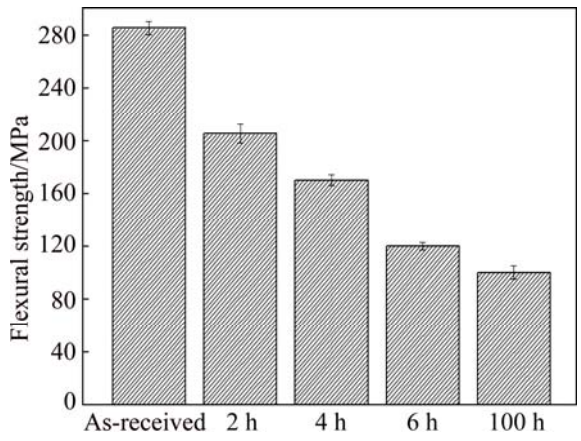

Fig. 6 Residual flexural strength of composites after oxidation at 900 °C for various time

shown in Fig. 7(b), obvious pull out fibers dominate the fracture surface indicating the weak fiber-matrix bonding. From oxidized composites, the obvious gap between fiber and matrix can be seen in Fig. 7(c). However, for the composites oxidized for 100 h, it can be seen from Fig. 7(d) that the pull out fibers are much shorter than composites oxidized for 2 h and 4 h.

It is well known that the fracture behavior and strength of continuous fiber reinforced ceramic matrix composites were determined mostly by the fiber matrix interface characteristic and fiber strength. After oxidation, the PyC interphase was consumed around the fibers, so the fiber−matrix bonding was weakened. The mechanism of debonding among the matrix and fibers and pull out of fibers can take place easily. However, the generated SiO_2 layer on the surface of the matrix makes the fiber−matrix bond strongly and bring about that the fibers cannot pull out easily when the oxidation time was too long. Therefore, the composites oxidized for 100 h exhibit brittle fracture behavior. The published literatures demonstrate that the used KD-1 SiC fiber was rich in carbon [14,21]. Both the consumption of free carbon and formation of silica layer can degrade the flexural strength of the SiC fibers [22,23]. Consequently, the decrease of in-situ strength of KD-1 SiC fibers after oxidation at 900 °C should lead to the decrease of residual strength of SiC_f/SiC composites.

4 Conclusions

Thermal oxidation was proposed to improve the microwave absorbing properties of SiC_f/SiC composites containing PyC interphase. The microwave absorbing potential was enhanced by improving the impedance matching characteristic between the composites and air and weakening the microwave reflectivity. The best reflection loss value of SiC_f/SiC composites after thermal oxidation reaches −11.4 dB, and its absorbing band is 2.3 GHz (RL<−10 dB). The flexural strength of composites decreased obviously but the fracture behavior was improved obviously after thermal oxidation.

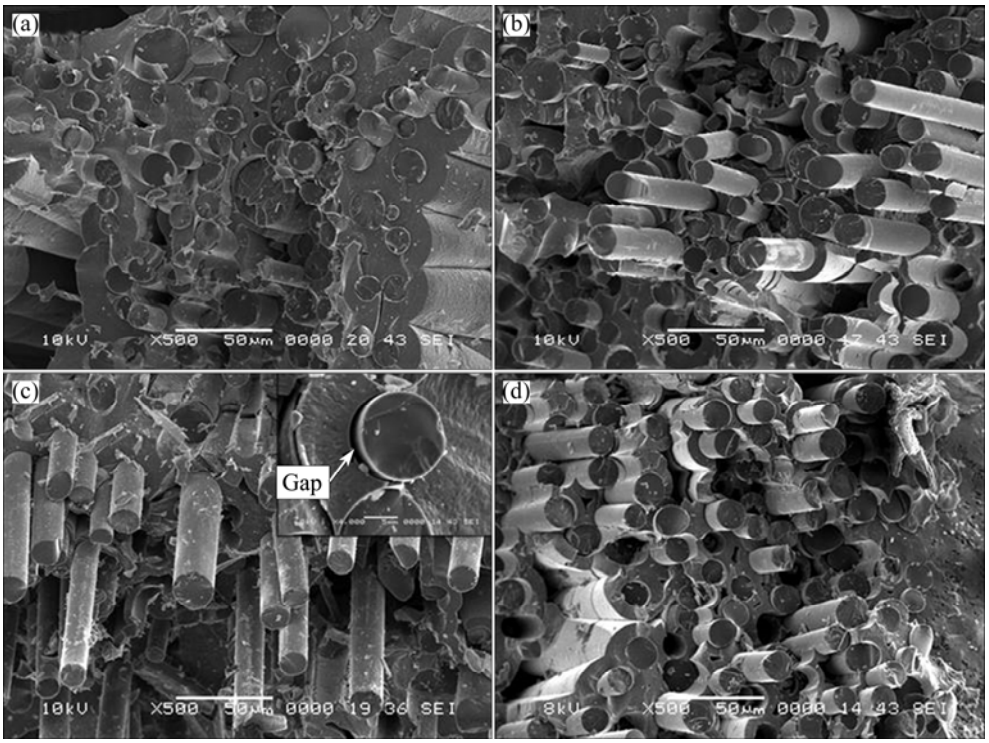

Fig. 7 SEM images of fracture surface of composites after bending test: (a) As-received; (b) Oxidized for 2 h; (c) Oxidized for 4 h; (d) Oxidized for 100 h

References

[1] QING Y C, ZHOU W C, JIA S. Dielectric properties of carbon black and carbonyl iron filled epoxy–silicone resin coating [J]. Journal of Materials Science, 2010, 45: 1885−1888.

[2] STERGIOU C A, LITSARDAKIS G. Electromagnetic properties of Ni and La doped strontium hexferrites in the microwave region [J]. Journal of Alloys and Compounds, 2011, 509: 6609−6615.

[3] MA F, QIN Y, LI Y Z. Enhanced microwave performance of cobalt nanoflakes with strong shape anisotropy [J]. Applied Physics Letters, 2010, 96: 202507.

[4] LI X M, ZHANG L T, YIN X W, FENG L Y, LI Q. Effect of chemical vapor infiltration of SiC on the mechanical and electromagnetic properties of Si_3N_4–SiC ceramic[J]. Scripta Materialia, 2010, 63: 657−660.

[5] SHI S L, LIANG J. The effect of multi-wall carbon nanotubes on electromagnetic interference shielding of ceramic composites [J]. Nanotechnology, 2008, 19: 255707.

[6] YIN X W, XUE Y Y, ZHANG L T, CHENG L F. Dielectric, electromagnetic absorption and interference shielding properties of porous yttria-stabilized zirconia/silicon carbide composites [J]. Ceramics International, 2012, 38: 2421−2427.

[7] LI D, JIN H B, CAO M S, CHEN T, DOU Y K, WEN B. Production of Ni-doped SiC nanopowders and their dielectric properties [J]. Journal of the American Ceramic Society, 2011, 94: 1523−1527.

[8] TIAN H, LIU H T, CHENG H F. Effects of SiC contents on the dielectric properties of SiO_{2f}/SiO_2 composites fabricated through a sol−gel process [J]. Powder Technology, 2013, 239: 374−380.

[9] IVEKOVIC A, NOVAK S, DRAZIC G. Current status and prospects of SiC_f/SiC for fusion structural applications [J]. Journal of the European Ceramic Society, 2013, 33: 1577−1589.

[10] LIU H T, TIAN H, CHENG H F. Mechanical and microwave dielectric properties of SiC_f/SiC composites with BN interphase prepared by dip-coating process [J]. Journal of the European Ceramic Society, 2012, 32: 2505−2515.

[11] DING D H, SHI Y M, WU Z H, ZHOU W C, LUO F, CHEN J. Electromagnetic interference shielding and dielectric properties of SiC_f/SiC composites containing pyrolytic carbon interphase [J]. Carbon, 2013, 60: 552−555.

[12] YU X M, ZHOU W C, LUO F, ZHENG W J, ZHU D M. Effect of fabrication atmosphere on dielectric properties of SiC/SiC composites [J]. Journal of Alloys and Compounds, 2009, 479: L1−L3.

[13] LIU H T, CHENG H F, WANG J, TANG G P. Dielectric properties of the SiC fiber-reinforced SiC matrix composites with the CVD SiC interphases [J]. Journal of Alloys and Compounds, 2010, 491: 248−251.

[14] DING D H, ZHOU W C, ZHANG B. Complex permittivity and microwave absorbing properties of SiC fiber woven fabrics [J]. Journal of Materials Science, 2011, 46: 2709−2714.

[15] YUAN J, SONG W L, FANG X Y, SHI X L, HOU Z L, CAO M S. Tetra-needle zinc oxide/silica composites: High-temperature dielectric properties at X-band [J]. Solid State Communications, 2013, 154: 64−68.

[16] CAO M S, SONG W L, HOU Z L, WEN B, YUAN J. The effects of temperature and frequency on the dielectric properties, electromagnetic interference shielding and microwave-absorption of short carbon fiber/silica composites [J]. Carbon, 2010, 48: 788−796.

[17] FILIPUZZI L, CAMUS G, NASLAIN R. Oxidation mechanisms and kinetics of 1D-SiC/C/SiC composites materials: I. An experimental approach [J]. Journal of the American Ceramic Society, 1994, 77: 459−466.

[18] NASLAIN R, GUETTE A, REBILLAT F, GALLETS L. Oxidation mechanisms and kinetics of SiC–matrix composites and their constituents [J]. Journal of Materials Science, 2004, 39: 7303−7316.

[19] NI D W, ZHANG G J, XU F F, GUO W M. Initial stage of oxidation process and microstructure analysis of HfB_2−20vol.% SiC composites at 1500 °C [J]. Scripta Materialia, 2011, 64: 617−620.

[20] XIANG Y, LI W, WANG S, CHEN Z H. Effects of the single layer CVD SiC interphases on the mechanical properties of the C/SiC composites fabricated by PIP process [J]. Materials Science and Engineering A, 2012, 558: 451−455.

[21] LIU H T, CHENG L F, WANG J, TANG G P, CHE R C, MA Q S. Effects of the fiber surface characteristics on the interfacial microstructure and mechanical properties of the KD SiC fiber reinforced SiC matrix composites [J]. Materials Science and Engineering A, 2009, 525: 121−127.

[22] TAKEDA M, URANO A, SAKAMOTO J I, IMAI Y. Microstructure and oxidation behavior silicon carbide fibers derived from polycarbosilane [J]. Journal of the American Ceramic Society, 2000, 83: 1171−1176.

[23] GAUTHIER W, PAILLER F, LAMON J, PAILLER R. Oxidation of silicon carbide fibers during static fatigue in air at intermediate temperatures [J]. Journal of the American Ceramic Society, 2009, 92: 2067−2073.

热氧化对有热解碳界面层的 SiC_f/SiC 复合材料吸波和力学性能的影响

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摘 要：采用化学气相渗透法制备含热解碳界面层的 SiC_f/SiC 复合材料，研究热氧化对复合材料在 8.2~12.4 GHz 波段的介电和吸波性能影响。复介电常数的实部和虚部在氧化后都降低。当氧化 100 h 后，反射损耗超过 −10 dB 的波段范围为 9.7~11.9 GHz，且反射损耗最小值在 11.0 GHz 时达到−11.4 dB。复合材料的弯曲强度在氧化后降低，但断裂韧性明显提高。结果表明：含热解碳界面层的 SiC_f/SiC 复合材料氧化后具有很好的吸波性能和断裂韧性。

关键词：SiC_f/SiC 复合材料；热氧化；介电性能；吸波；力学性能

(Edited by Xiang-qun LI)