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Influence of pyrolytic carbon coatings on complex permittivity and microwave absorbing properties of Al_2O_3 fiber woven fabrics

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Abstract: The pyrolytic carbon (PyC) coatings were fabricated on Al_2O_3 fiber fabrics by the method of chemical vapor deposition (CVD). The microstructures of Al_2O_3 fibers with and without PyC coatings were characterized by SEM and Raman spectroscopy. The influence of deposition time of PyC on the DC conductivity (σ_d) of Al_2O_3 filaments and complex permittivity of fabrics at X band (8.2−12.4 GHz) were investigated. The values of σ_d and complex permittivity increase with increasing deposition time of PyC. The electron relaxation polarization and conductance loss were supposed to be contributed to the increase of ε' and ε'', respectively. In addition, the reflection loss (RL) of fabrics was calculated. The results show that the microwave absorbing properties of Al_2O_3 fiber fabrics can be improved by PyC coatings. The best RL results are for 60 min-deposition sample, of which the minimum value is about −40.4 dB at about 9.5 GHz and the absorbing frequency band (AFB) is about 4 GHz.

Key words: complex permittivity; pyrolytic coating; Al_2O_3 fiber fabric

1 Introduction

Growth of interest in stealth technology applied to reducing the radar cross-section surface of military vehicles has promoted the investigations of microwave absorbing materials. Ceramic fibers, such as SiC fibers [1−5], carbon fibers [6,7] and glass fibers [8], have been investigated intensively as structural microwave absorbing materials at high temperature. The ceramic fibers woven fabrics as microwave absorbing materials are attracting more and more attention because of their light mass, high environmental durability and thermal stability [9−11]. Although the commercially available Nextel series of Al_2O_3 fibers produced by Minnesota Minning and Manufacturing Corporation (3M) have received much interest as reinforcement [12−15] in continuous fiber ceramic composites (CFCCs), the reports on complex permittivity and microwave absorbing properties on Al_2O_3 fibers are rare. It has been recognized that the PyC is one of the best interphase materials for the CFCCs. However, the investigations were mostly focused on the microstructure and effect on mechanical properties. Results about the effect of PyC on dielectric and microwave absorbing properties of ceramic fiber or ceramic matrix composites are rare.

In the present investigation, the PyC was coated on Al_2O_3 fiber fabrics using the method of chemical vapor deposition (CVD). And the microstructure of the PyC coatings was characterized by Raman spectroscopy. Then the influence of PyC deposition time on the complex permittivity of Al_2O_3 fiber fabrics at X band was studied.

2 Experimental

2.1 Materials

The Nextel 440 Al_2O_3 fibers were provided by 3M. The fabrics were braided by Nanjing Glass Fiber Institute (China). Table 1 shows the parameters of Nextel 440 fibers. The fabrics structure is 2.5D shallow bending joint shown in Fig. 1. The fiber volume fraction of fabrics was about 40%.

2.2 CVD PyC coatings on fabrics

The PyC coatings were deposited in a hot-wall low-pressure CVD reactor from the C_3H_6 and H_2 gas systems. The C_3H_6 was the gas precursor, and H_2 was the diluent gas. The thickness of PyC coatings was controlled

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Table 1 Parameters of Nextel 440 fiber

Diameter/ μm	Density/ (g·cm^{-3})	Tension strength/ MPa	Elastic modulus/ GPa	Mass fraction/%		
				Al_2O_3	SiO_2	B_2O_3
10−12	3.05	2000	190	70	28	2

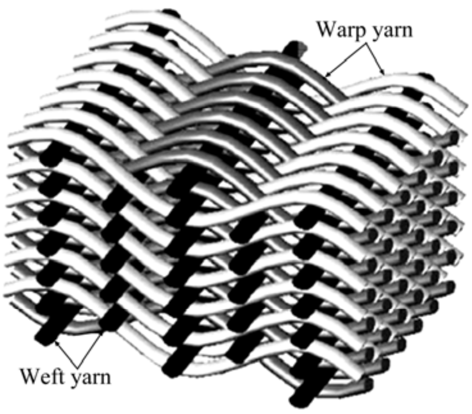

Fig. 1 Schematic showing fabrics structure

by deposition time. It can be confirmed that the thickness of CVD coatings increases linearly with elongation of deposition time. The temperature and pressure of CVD were 800 °C and 7 kPa, respectively. And the flow rates of C_3H_6 and H_2 were 900 and 600 m^3/min, respectively.

2.3 Electric conductivity measurement

The DC conductivity (σ_d) of Nextel 440 filaments was calculated as the following equation:

$$\sigma_d = 1/\rho = \frac{L}{RS} \tag{1}$$

where ρ is the special conductivity; R is the resistance; S is the cross-section area of filament; L is the length of filament. The electrical resistance of Al_2O_3 filaments at room temperature was measured by two-probe direct current method [16]. The filaments were tin−lead bonded on alumina substrate. The length of filaments was 1 cm. The average diameter of filaments was considered 11 μm.

2.4 Complex permittivity measurement

The ε' and ε'' of complex permittivity correlate polarization and loss; the real part (μ') of complex permeability represents the mount of energy stored in the magnetic material from AC magnetic field, while the imaginary part (μ'') is the energy loss to the magnetic field. The complex permittivity and permeability of fabrics were measured by the method of waveguide using vector network analyzer (E8362B). Because of the low complex permittivity of paraffin wax, the fabrics/ paraffin wax composites were fabricated in order to avoid dispersing of fiber bundles. The dimensions of measured samples were 22.86 mm×10.16 mm×2.0 mm. The wax was insulator, whose ε' and ε'' were 2.26 and 0 at X band. So, the complex permittivity of the fabric/wax composites was determinated mostly by the fabrics.

Giving the convenience of discussion later, the influence of wax on the complex permittivity was ignored. Based on the measured complex permittivity and permeability, we evaluated the microwave absorbing properties by the following equations with MATLAB [11]:

$$L_R = 20\lg\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right| \tag{2}$$

where L_R denotes the reflection loss in dB unit; Z_0 is the characteristic impedance of free space; Z_{in} is the input characteristic impedance at the absorber/free space interface, which can be expressed as:

$$Z_{in} = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left(j\left(\frac{2\pi ft}{c}\right)\sqrt{\mu_r\varepsilon_r}\right) \tag{3}$$

where c is the velocity of light; t is the thickness of an absorber; in this paper, t values are in mm unit; the ε_r is the measured relative complex permittivity; μ_r is permeability, whose u' and u'' are considered 1 and 0, respectively, because the Al_2O_3 fibers and PyC coatings both are none-magnetic substance.

3 Results and discussion

3.1 Microstructure characterization

SEM images of as-received and PyC coated fibers are shown in Fig. 2. It was observed that there are microflaws on the surface of as-received fiber and the PyC coating is smooth.

Many previous studies showed that Raman spectroscopy can be used successfully to determine information about the microstructure of various carbon materials [17, 18]. It has been confirmed that the PyC consists of disorder carbon and micro-crystallite graphite embedded in disorder carbon [14]. As previous studied, the D (disordered) and G (graphitic) peaks at about 1600 and 1330 cm^{-1} assigned to sp^3 and sp^2 bonded carbons [9,10]. In the present study, the G peak (1587 cm^{-1}) is obvious in Raman spectroscopy of fibers with PyC coatings, whereas there are only broad peaks in the range of 250−500 cm^{-1} in Raman spectroscopy of as-received fibers shown in Fig. 3. Generally, the band area ratio (I_D/I_G) was used to obtain information about the degree of disorder in carbon materials. The relationship between I_D/I_G and L_a (graphite crystallite size) is [17−19]

$$C'(\lambda)L_a = \frac{I_D}{I_G} \tag{4}$$

where $C'(\lambda)$ is a wavelength-dependent pre-factor, and its value is 4.362.

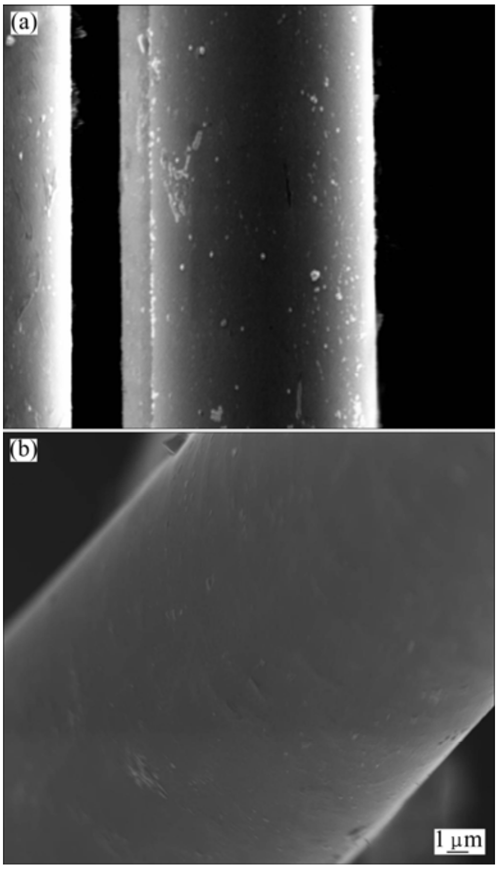

Fig. 2 SEM images of as-received (a) and PyC coated (b) Al_2O_3 fibers

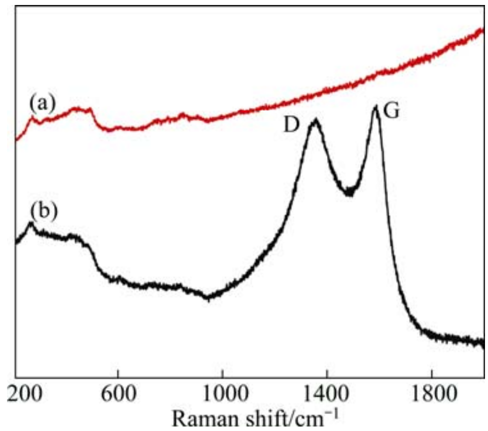

Fig. 3 Raman spectra of Al_2O_3 fiber fabrics without (a) and with (b) PyC coatings

Based on equation (4), we calculated the value of L_a, which is 17.96 nm. One can conclude that there is sp^2 bonded carbons in PyC coatings.

3.2 Electrical conductivity of Al_2O_3 fibers

The as-received Al_2O_3 fibers are typical insulator, whereas the PyC has a significantly higher conductivity because of the existing of π-bonding in PyC. Table 2 shows that the electrical conductivity of fiber with PyC coating increases with the increase of coating time. The value increased from 5 to 334 S/cm. The electrical conductivity of Al_2O_3 fiber increased sharply when the time of PyC coating was 90 min. We suggest that the conductance mechanism of Al_2O_3 fiber with PyC coatings is migrating conductance in the graphite plane and hopping conductance among graphite planes based on the discussion on conductance of carbon fibers supposed by CAO et al [19, 20]. In other words, there are free electrons in the graphite plane and weak bond electrons among graphite planes in PyC coatings.

Table 2 σ_d of Al_2O_3 fiber as function of deposition time of PyC coatings

Sample	Time of Pyc coating/min	Electrical conductivity/(S·cm^{-1})
a	0 (As-received)	5
b	30	6
c	60	5
d	90	44
e	120	334

3.3 Complex permittivity of fabrics

Figures 4 and 5 show the ε′ and ε″ of complex permittivity of the Al_2O_3 fiber fabrics with various PyC deposition time at X band, respectively. Overall, it can be noted that the values of ε′ and ε″ increase with increasing the thickness of PyC coatings. The ε′ and ε″ of as-received Al_2O_3 fiber fabrics are 2.8−3.6 and from −0.1 to 0.2, respectively, which is one typical microwave transmitting material. As to ε′, the value increases from about 3 of sample a to about 9 of Sample e with 120 min coating time. When the time is below 60 min, the ε′ shows insignificant increase. For the Sample d, when the time is 60 min, the ε′ increases obviously to 3.5−5.4. The

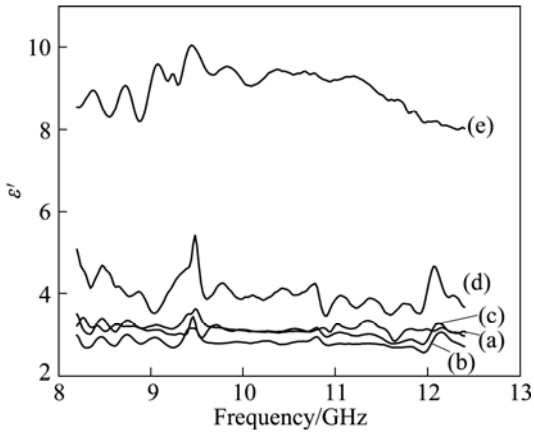

Fig. 4 ε′ as function of frequency in range of 8.2−12.4 GHz for Al_2O_3 fiber fabrics with various PyC deposition time: (a) As-received; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min

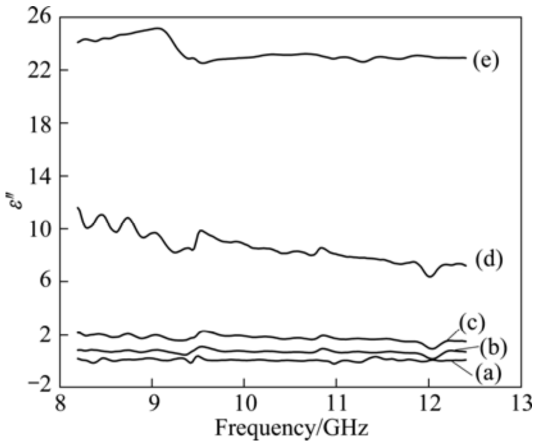

Fig. 5 ε'' as function of frequency in range of 8.2−12.4 GHz for Al_2O_3 fiber fabrics with various PyC deposition time: (a) As-received; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min

ε' increases sharply to 8.2−10.0 in the case of Sample d. The increase of ε'' keeps the same trend as for ε' described above, and the value increases to 22.5−25.2 for the Sample e. Besides, the ε' and ε'' spectra for samples (a)−(d), show two obvious resonance peaks at about 9.5 and 12.2 GHz. It is worthwhile to mention that the ε'' increases more rapidly than ε'.

In dielectric materials, the loss (ε'') consists of dielectric loss and conductance loss, which are induced by dielectric polarization and free electrons, respectively. At X band, the possible mechanism is electronic relaxation polarization. The loss due to ion displacement polarization is very weak. The weak bound electron in dielectric materials can induce electron relaxation polarization, which is an energy consumption process. This polarization can increase the ε' and ε'' of complex permittivity, which can be expressed as follows:

$$\varepsilon'_e = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+(\omega\tau)^2} \tag{5}$$

$$\varepsilon''_e = \frac{\varepsilon_s - \varepsilon_\infty}{1+(\omega\tau)^2}\omega\tau \tag{6}$$

where ε_e' and ε_e'' are the increased parts of ε' and ε'' induced by electron relaxation polarization; ε_s is the static permittivity; ε_∞ is the relative dielectric permittivity at the high frequency limit; ω is the angular frequency; τ is the relaxation polarization time [19,20]. For the conductance loss, there is

$$\varepsilon''_c = \frac{\sigma}{\omega\varepsilon_0} \tag{7}$$

where ε''_c and ε_0 are increased by conductance loss and dielectric constance in vacuum. So, we obtain the following relation:

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{1+(\omega\tau)^2}\omega\tau + \frac{\sigma}{\omega\varepsilon_0} \tag{8}$$

Based on the discussion on structure of PyC coatings above, the increase of ε' may be attributed to the electron relaxation polarization induced by hopping electrons among graphite layers, and the increase of ε'' may be mainly induced by conductance loss. The electron relaxation polarization contributed to the increase of ε'' to some extent. As samples (a)−(c), the ε' values are similar and the ε'' increases slightly. The reason may be that the graphite planes are too few to establish conductive network. When the PyC coating is enough thick, for samples (d) and (e), the graphite planes are enough to establish conductive network. So, the ε' and ε'' increase obviously.

3.4 Microwave absorbing properties

To evaluate the microwave absorbing potential, the reflection loss (RL) in dB unit can be tested or calculated. If the RL values of an absorber are less than −10 dB (90% absorption), then we can say that the absorber works very well. And, the microwave absorbing frequency band (AFB) is defined as the frequency range, in which the RL values are less than −10 dB. The microwave absorbing properties of as-received fiber fabrics are poor due to the low complex permittivity which cannot dissipate electromagnetic energy effectively. Figure 6 shows the calculated reflection loss of samples (b)−(e) at different thicknesses. It was observed that the microwave absorbing potential of Al_2O_3 fiber fabrics can be improved by PyC coatings. The best results were obtained for Sample c with the time of 60 min. It shows a minimum RL of about −40.4 dB at about 9.5 GHz, and its AFB is about 4 GHz. The matched thickness is 4.5 mm. The reason for smooth absorption curve for Sample b shown in Fig. 6(a) is similar to that of as-received sample. However, when the deposition time is too long (the PyC coating is too thick) for samples (d) and (e), the microwave absorbing properties of fabrics deteriorate. The reason is that the complex permittivity is too high, which cannot match the characteristic impedance of free space.

4 Conclusions

1) The PyC coatings were fabricated on Al_2O_3 fiber fabrics by the method of CVD. The deposition time of PyC coatings plays an important role in complex permittivity and microwave absorbing properties of Al_2O_3 fiber fabrics. The values of ε' and ε'' increase with increase of coating time of PyC, especially when the time is above 90 min. The increase of ε' and ε'' is mainly attributed to electron relaxation polarization and

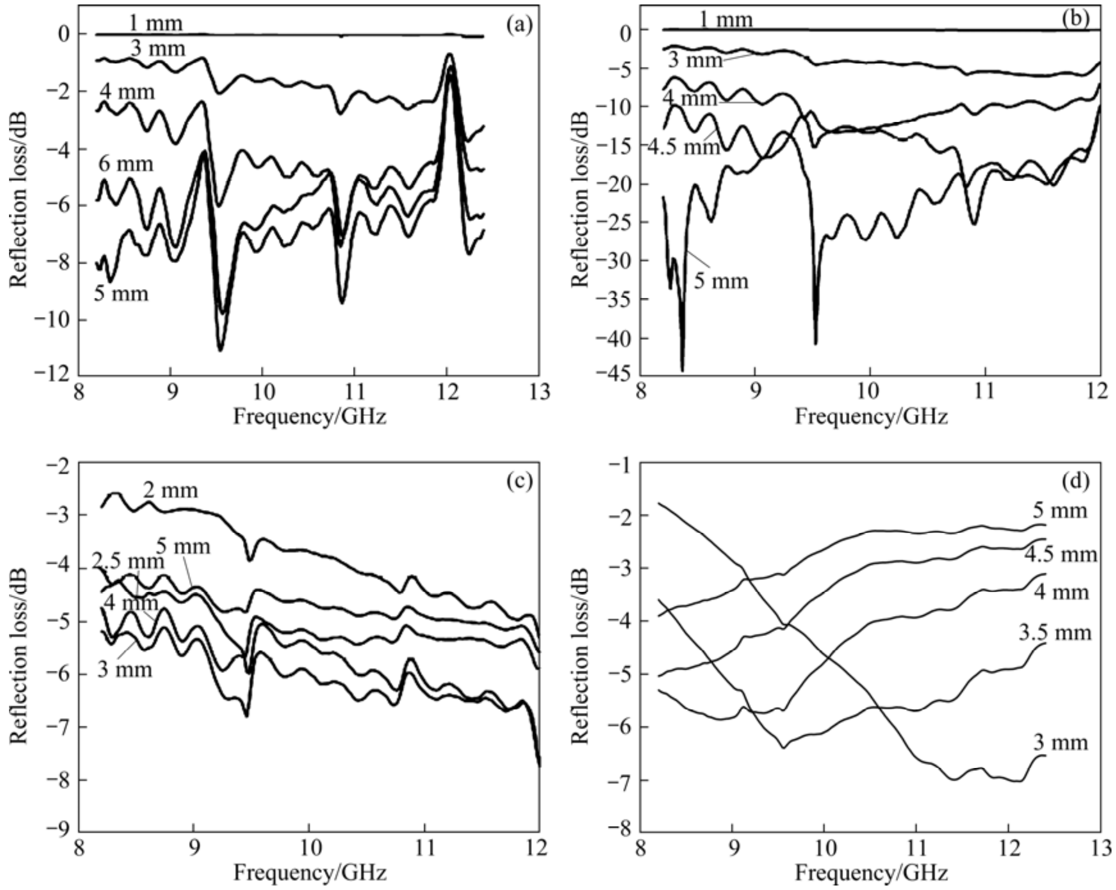

Fig. 6 Microwave absorbing properties of Al_2O_3 fiber fabrics with different sample thicknesses: (a) 30 min; (b) 60 min; (c) 90 min; (d) 120 min

conductance loss.

3) The microwave absorbing potential of Al_2O_3 fiber fabrics can be improved by PyC coatings. The best results were obtained for Sample c, whose deposition time was 60 min. It shows a minimum RL of about −40.4 dB at about 9.5 GHz, and its AFB is about 4 GHz.

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热解碳涂层对 Al_2O_3 纤维编织体介电及吸波性能的影响

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摘 要：采用化学气相沉积法在 Al_2O_3 纤维编织体上沉积热解碳涂层，利用 SEM 及激光拉曼光谱表征沉积与未沉积热解碳界面层的纤维编织体，并研究热解碳沉积时间对纤维电导率及编织体 X 波段介电吸波性能的影响。结果表明：纤维电导率及编织体复介电常数随着热解碳沉积时间的延长而增大。电子松弛极化引起复介电常数实部的增大，电导损耗引起虚部的增大。热解碳涂层可以改善 Al_2O_3 纤维编织体的吸波性能，对于沉积 60 min 热解碳涂层的编织体，反射率在 9.5 GHz 附近达到−40.4 dB，吸波频带接近 4 GHz.

关键词：介电性能；热解碳涂层；Al_2O_3 纤维

(Edited by LI Xiang-qun)