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Electromagnetic Interference Shielding Properties of SiC Ceramic Matrix Composite Reinforced by Three-dimensional Silicon Carbide Nanowire Network

RUAN Jing[1,2,3], YANG Jinshan[1,2], YAN Jingyi[1,2,4], YOU Xiao[1,2,4], WANG Mengmeng[1,2,4], HU Jianbao[1,2], ZHANG Xiangyu[1,2], DING Yusheng[1,2], DONG Shaoming[1,2,5]

(1. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 2. Structural Ceramics and Composites Engineering Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China; 3. School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China; 4. University of Chinese Academy of Sciences, Beijing 100039, China; 5. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: Silicon carbide nanowires (SiCNWs) possess excellent electromagnetic absorption performance and a three-dimensional (3D) network structure is beneficial to the multiple reflection and absorption of electromagnetic waves (EMWs). The 3D staggered SiCNWs network preforms with a volume fraction of 20% was realized by vacuum filtration method. And then the PyC interphase and SiC matrix were prepared through chemical vapor infiltration (CVI) process, and the densified SiCNWs/SiC ceramic matrix composites were obtained through CVI and precursor impregnation pyrolysis (PIP) process. Methane (CH_4) and trichloromethylsilane (MTS) were selected as gaseous precursor of the PyC and SiC, respectively. With increase of deposited PyC from 0 to 29.5%, the electromagnetic interference (EMI) shielding efficiency (SE) of the porous SiCNWs increases from 9.2 dB to 64.1 dB in 8–12 GHz (X-band). The densified SiCNWs/SiC ceramic matrix composites with a mass gain of about 13% of PyC interphase present an average EMI SE of 37.8 dB in X-band. The achieved EMI shielding properties suggested that the potential application of the SiCNWs/SiC ceramic matrix composites may be a promising new-generation EMI shielding material.

Key words: SiC nanowire; electromagnetic interference shielding; ceramic matrix composite; PyC deposition; SiC matrix

Due to the intensive growing application of electronic devices, the harm of EMWs emitted from electronic devices to human health cannot be ignored[1-4]. Also, electromagnetic interference (EMI) can make electronic devices difficult for normal operation. To reduce the damage of EMI to the human body and electronic devices, materials are designed to shield or weaken EMI[5]. The shielding material can cut down the EMWs emitted by electronic equipments and prevent the EMWs from scattering, which can ensure a relatively independent working environment and prevent the information from leaking by the EMWs. Currently, metal is an optional EMWs absorption material, and the movable electrons can induce current in electromagnetic fields to consume EMWs[6-7]. EMWs are converted and consumed, which results in a considerable EMI SE. However, the properties of high density, easy to be oxidized and corroded significantly limit the application of metal in electromagnetic shielding material.

In recent years, one-dimensional nanomaterials with unique properties have attracted the attention of researchers. Especially, SiCNWs possess many unpaired chemical bonds on the surface than SiC_f, which can be polarized in electromagnetic fields to consume the EMWs[8-12]. So SiCNWs with the unique one-dimensional structure own excellent electromagnetic absorption performance, and the construction of a 3D spatial network is expected to further enhance the EMI SE[13-16]. The introduction of SiCNWs into composites can effectively improve the EMI shielding performance of the composites[10,17-19].

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Biography: RUAN Jing (1993–), male, PhD candidate. E-mail: ruanjing@shanghaitech.edu.cn
阮 景(1993–), 男, 博士研究生. E-mail: ruanjing@shanghaitech.edu.cn
Corresponding author: YANG Jinshan, professor. E-mail: jyang@mail.sic.ac.cn; DONG Shaoming, professor. E-mail: smdong@mail.sic.ac.cn
杨金山，研究员. E-mail: jyang@mail.sic.ac.cn; 董绍明，研究员. E-mail: smdong@mail.sic.ac.cn

Moreover, the twins SiCNWs possess higher energy and better electromagnetic absorption performance[20-23]. Compared with the traditional ferromagnetic materials, the one-dimensional structure makes SiCNWs easier to construct a 3D network structure, which can further expand the path of dissipation current and increase electromagnetic absorption loss[24]. For the application of SiCNWs on EMI shielding performance, the main method is the *in-situ* growth of SiCNWs inside the composite. The purity and mass of SiCNWs cannot be controlled, which makes it difficult to establish a relationship between introducing parameters of the SiCNWs and the improving performance of the composites. Another way for adding SiCNWs into the composite is to introduce the purified SiCNWs, which can avoid the problems of purity and uncertain parameters. However, the agglomeration makes SiCNWs difficult to construct a uniform network, which could result in performance deviation and weakening of enhancement effect.

The shielding efficiency of electromagnetic shielding materials can be expressed by the following formula[25]:

$$SE_T = SE_R + SE_A \tag{1}$$

Among them, SE_T represents the total shielding loss, SE_R and SE_A represent the reflection loss and absorption loss, respectively. SE_R relates to the structure of the material, and the increase of the specific surface area increases the reflection loss[26-28]. SE_A depends on the intrinsic properties of the components and different materials possess different absorption loss[29-31]. To enhance the EMI shielding performance, improving the reflection and absorption loss are the main ways.

In this work, 3D network preforms with 20% volume fraction of SiCNWs were prepared by vacuum filtration method, and the densified SiCNWs/SiC ceramic matrix composites with PyC interphase were obtained by CVI and PIP process. The PyC has a positive effect on the EMI shielding performance, the SE_T of the SiCNWs network preforms with PyC mass gain of 21.3% and 29.5% are 45.0 and 64.1 dB at 8 GHz, respectively. The SiCNWs/SiC ceramic matrix composite with PyC interphase shows a SE_T of 37.8 dB in X-band. The introduction of the PyC interphase makes EMWs strongly reflect and absorb at the interface of PyC, SiC and air, and the EMWs are repeatedly reflected and absorbed in the 3D network.

1 Experimental

1.1 Construction of a 3D SiCNWs network preform

The uniform SiCNWs suspension was firstly obtained by the ultrasonication of the mixture of commercial SiCNWs (Changsha Sinet Advanced Materials Co., Ltd., China) with the dispersant PVP. The mass ratio of SiCNWs and PVP is controlled at 6:1 and the ultrasonic power is set at 300 W. As for the vacuum filtration method, uniform suspension of SiCNWs with PVP dispersed was poured into vacuum filtration bottle and SiCNWs network preform with a volume fraction of 20% was prepared by vacuum filtration. The size of the preform is about 40 mm in diameter and 0.67 mm in thickness.

1.2 Preparation of PyC interphase and SiC matrix

The PyC interphase and SiC matrix were prepared by the CVI process. CH_4 was set at a flow rate of 50 sccm at 1100 ℃ and the PyC interphase was *in-situ* grown on the preforms through the pyrolysis of CH_4. During the preparation of the SiC matrix, hydrogen was selected as both carrier gas and diluent gas. The pyrolysis temperature of MTS is controlled at 1030 ℃ and the flow rate of carrier hydrogen and dilute hydrogen is controlled at 200 and 60 sccm, respectively. The whole reaction is set at 3 kPa for several hours. The PIP process was used for further densification of the porous SiCNWs/SiC ceramic matrix composite for that single CVI process leading to a huge densification difference between surface and internal. The introduction of the PIP process requires the sample high mechanical strength and open pores on the surface, so the further densification of the PIP process was performed after 40 h SiC matrix deposition, and a densified SiCNWs/SiC ceramic matrix composite was obtained after several PIP cycles.

1.3 Characterization

The microstructures of samples were characterized by scanning electron microscope (SEM; Hitachi SU8220, Japan). The pore parameters were tested by the mercury porosimeter (Micromeritics Instrument Co, Ltd, America). The EMI shielding performance was tested by the vector network instrument (Vector network analyer; ROHDE& SCHWARZ ZVB20; Germany).

2 Results and discussion

Fig. 1 is the surface and fracture morphologies of the SiCNWs network preforms prepared by the vacuum filtration method. Fig. 1(a-b) are the surface morphologies of the preforms which show a uniform pore size and SiCNWs restrict each other to keep a stable structure. Fig. 1(c-d) are the fracture morphologies of the preforms and SiCNWs almost perpendicular to the fracture which shows a relatively stable structure of the internal. The morphologies of the surface and fracture surface indicate that a 3D network structure with uniform pore size is prepared by vacuum filtration.

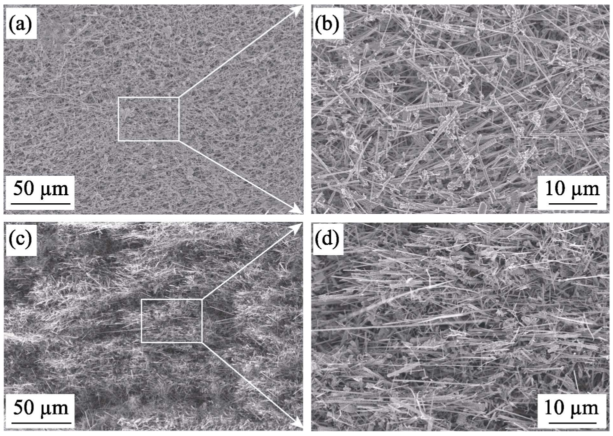

Fig. 1　SEM images of the SiCNWs network preforms prepared by vacuum filtration
(a-b) Surface; (c-d) Section

To solve the problem that the EMI SE of the sample decreases with the increase of frequency, PyC was introduced to cover SiCNWs. The layered structure of PyC owns many free electrons, and the conductivity increases with increasing free electrons. The influence of PyC on EMI shielding performance can be calculated by the following formula[32-35]:

$$SE_R = 39.5 + \lg\left(\frac{\sigma}{2\pi f \mu}\right) \tag{2}$$

$$SE_A = 8.7d\sqrt{\pi f \mu \sigma} \tag{3}$$

where f is the frequency of electromagnetic waves, μ is the permeability, d is the thickness of the SiCNWs network preform, and σ is the conductivity. SE_A and SE_R increase with the increase of the conductivity. SE_A increases, and SE_R decrease with the increase of frequency, while the frequency has a greater impact on SE_A than SE_R in X-band. So the deposition of PyC is expected to alleviate the decreasing tendency of EMI SE with the frequency increasing and improve the EMI SE of the preform.

The SiCNWs network preforms with a different amount of PyC were tested to carry out the influence of PyC on EMI shielding performance. As shown in Fig. 2, the SiCNWs preform without PyC deposition shows a higher SE_R and lower SE_A, which indicates that the reflection performance reduces and absorption performance increases after depositing PyC. For the SiCNWs preforms with PyC deposition, SE_A shows a monotonously increasing tendency with increasing mass of PyC. Compared to the preform without PyC deposition, SE_A of the preforms with 21.3% and 29.5% weight gain of deposited PyC significantly increase from 4.6 dB to 43.5 dB and 63.3 dB in X-band, which results in SE_T increasing from 9.2 dB to 45.0 dB and 64.1 dB in X-band. SE_A and SE_T are effectively enhanced by the incorporation of PyC.

The shielding efficiency can be calculated by the following formula, and the value of R and A represents

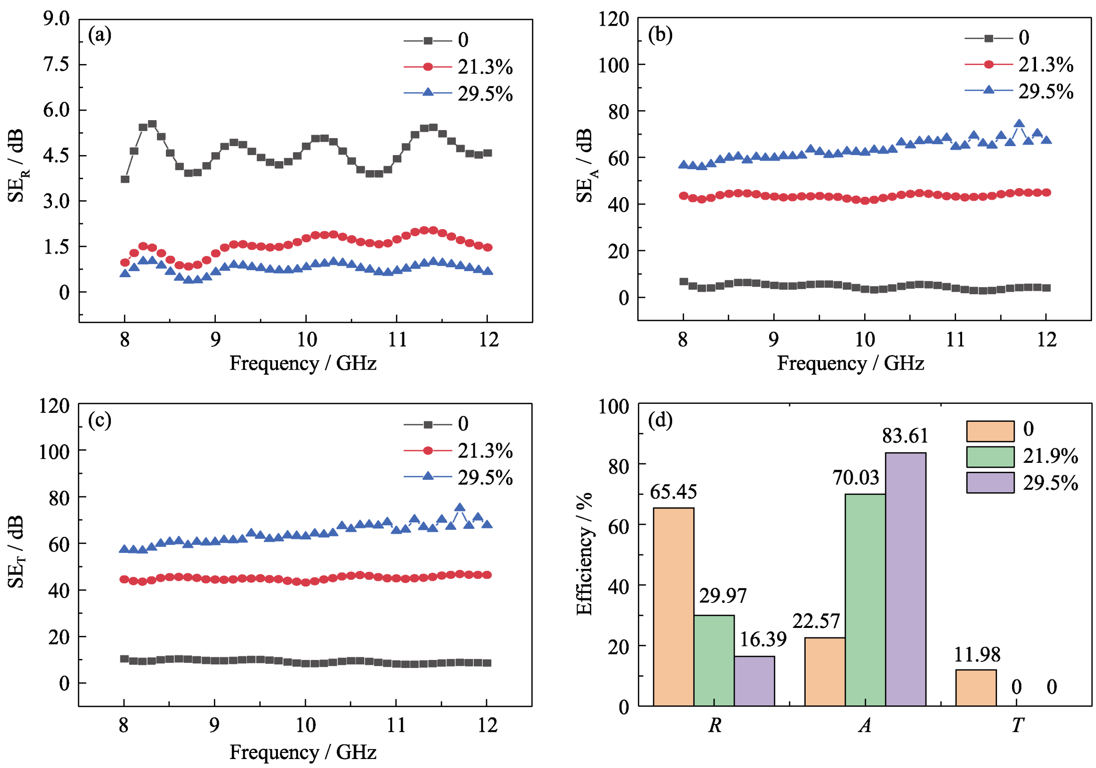

Fig. 2　Influence of the different amount of PyC on the EMI shielding performance of the SiCNWs network
(a) SE_R; (b) SE_A; (c) SE_T; (d) Shielding efficiency

the different shielding mechanism:

$$R = 1 - 10^{\left(-\frac{SE_R}{10}\right)} \quad (4)$$

$$T = 10^{\left(-\frac{SE_T}{10}\right)} \quad (5)$$

$$A = 1 - R - T \quad (6)$$

Fig. 2(d) is the shielding efficiency of the preform. The preform without PyC deposition takes reflection loss as the main shielding mechanism. After deposition PyC, the shielding mechanism converts to absorption loss and the value of A increases with the increasing amount of PyC.

The densification of the preform is achieved by CVI and PIP process, and the densified sample with a small size pore possesses a large surface area, which presents a high strength and increases the reflection of EMWs at the interface, so that EMWs are reflected and absorbed multiple times in the 3D space constructed by SiCNWs. The SiCNWs/SiC ceramic matrix composite shows a high density after CVI and PIP process, and the pore parameters are shown in Fig. 3. The pores of the SiCNWs/SiC ceramic matrix composites mainly distribute in small pores with size less than 3 μm, and the proportion of the small pores reaches almost 82%. Small pores account for a larger proportion of the total pore volume, so the composite has a high pore-specific surface area.

The EMI shielding performance of the densified SiCNWs/SiC ceramic matrix composite is shown in Fig. 4. The EMI shielding performance of the two samples decreases with increasing frequency. The reason is that the insufficient introduction of PyC interphase makes little balance for offsetting the frequency dependence. The large specific surface area of the small pores allows a considerable SE_R. The SiCNWs/SiC

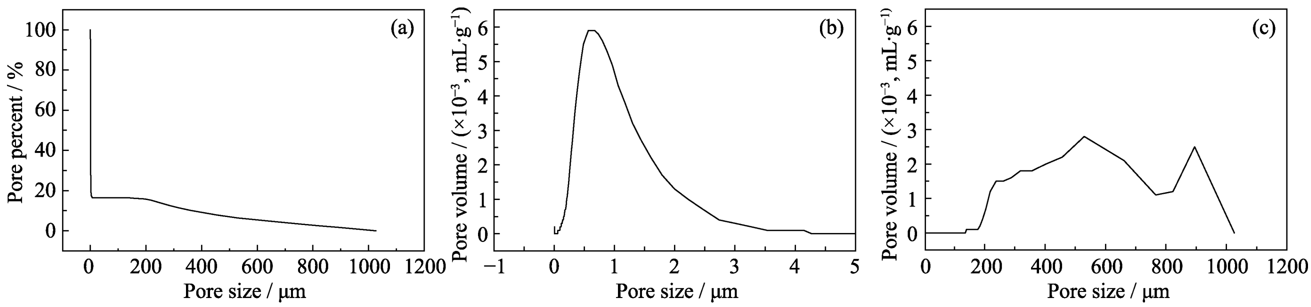

Fig. 3 Pore percentage (a) of different pore sizes, and pore volume of (b) 0–5 μm and (c) 5–1200 μm

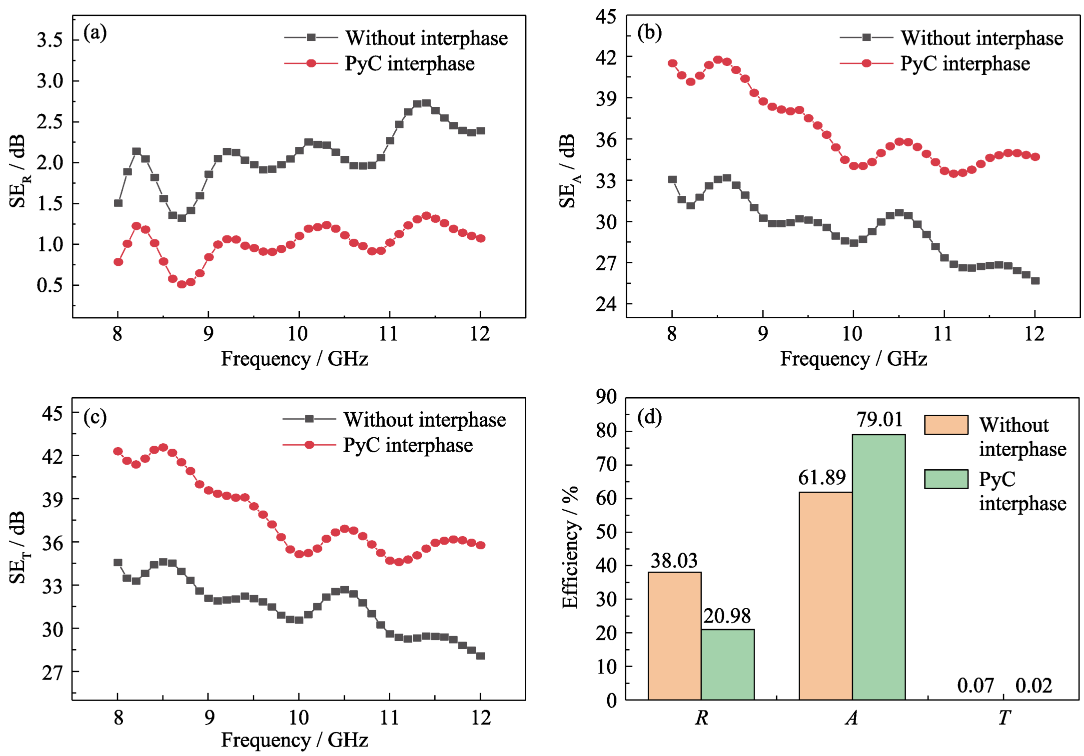

Fig. 4 EMI shielding performance of the SiCNWs/SiC ceramic matrix composite after treatment by CVI and PIP process
(a) SE_R; (b) SE_A; (c) SE_T; (d) Shielding efficiency

ceramic matrix composite without PyC interphase possesses higher SE_R than that with PyC interphase in X-band, while the SE_A is much lower than the sample with PyC interphase, which results in higher SE_T of the sample with PyC interphase than the one without interphase. The SE_T of the SiCNWs/SiC ceramic matrix composite without interphase is 31.5 dB in X-band, and the composite with PyC interphase reaches 37.8 dB. EMWs are reflected at the interface of air, SiC and PyC, which leads to multiple reflection and absorption of EMWs inside the composite. Both of two samples take absorption loss as the main shielding mechanism, and the value of the sample with PyC interphase equals 79%, which shows that EMWs are heavily absorbed. SE_T over 30 dB indicates that 99.9% of the incident power is blocked or only 0.1% incident power is transmitted, so the SiCNWs/SiC ceramic matrix composite with PyC interphase shows SE_T higher than 30 dB in X-band, and the composite is a potential military EMI shielding material.

3 Conclusion

3D SiCNWs network preforms with volume fraction of 20% were prepared by vacuum filtration method. PyC interphase and SiC matrix were used to modify the SiC network preforms. As the amount of PyC and SiC increases, the EMI shielding performance of the preforms is enhanced. The amount of the deposited PyC increases from 21.3% to 29.5 %, which makes SE_T of the SiCNWs network preform increases from 43.5 dB to 63.3 dB in X-band. Compared with the sample without PyC, the SE_T of the SiCNWs/SiC ceramic matrix composite with PyC interphase increased by 20% in X-band. The densified SiCNWs/SiC ceramic matrix composites with PyC interphase possess a higher SE_T than 30 dB in X-band, which shows an excellent EMI shielding performance.

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三维碳化硅纳米线增强碳化硅陶瓷基复合材料的电磁屏蔽性能

阮 景[1,2,3], 杨金山[1,2], 闫静怡[1,2,4], 游 潇[1,2,4], 王萌萌[1,2,4], 胡建宝[1,2], 张翔宇[1,2], 丁玉生[1,2], 董绍明[1,2,5]

(1. 中国科学院 上海硅酸盐研究所, 高性能陶瓷和超微结构国家重点实验室, 上海 200050; 2. 中国科学院 上海硅酸盐研究所, 结构陶瓷及复合材料工程研究中心, 上海 201899; 3. 上海科技大学 物质科学与技术学院, 上海 201210; 4. 中国科学院大学, 北京 100039; 5. 中国科学院大学 材料科学与光电工程中心, 北京 100049)

摘 要: 碳化硅纳米线具有优异的电磁吸收性能, 三维网络结构可以更好地使电磁波在空间内被多次反射和吸收。通过抽滤的方法制备得到体积分数 20%交错排列的碳化硅纳米线网络预制体。然后采用化学气相渗透工艺制备热解炭界面和碳化硅基体, 并通过化学气相渗透和前驱体浸渍热解工艺得到致密的 SiCNWs/SiC 陶瓷基复合材料。甲烷和三氯甲基硅烷分别是热解炭和碳化硅的前驱体, 随着热解碳质量分数从 21.3%增加到 29.5%, 多孔 SiCNWs 预制体电磁屏蔽效率均值在 8~12 GHz (X)波段从 9.2 dB 增加到 64.1 dB。质量增重 13%的热解碳界面修饰的 SiCNWs/SiC 陶瓷基复合材料在 X 波段平均电磁屏蔽效率达到 37.8 dB 电磁屏蔽性能。结果显示, SiCNWs/SiC 陶瓷基复合材料在新一代军事电磁屏蔽材料中具有潜在应用前景。

关 键 词: 碳化硅纳米线; 电磁屏蔽; 陶瓷基复合材料; 热解碳; SiC 基体

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