基于低温化学气相沉积法的碳化硅纤维表面氮化硼涂层制备及表征

王驰, 孙妮娟*, 张娟, 张大海

航天材料及工艺研究所, 先进功能复合材料技术国防科技重点实验室, 北京 100076

* 联系人, E-mail: sunnijuan@pku.org.cn

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摘要 以硼氨烷络合物为前驱体, 采用低温化学气相沉积(CVD)工艺, 在碳化硅纤维表面制备了氮化硼(BN)涂层. 采用扫描电子显微镜(SEM)、俄歇电子能谱(AES)、傅里叶变换红外光谱(FTIR)和掠入射X射线衍射(GIAXRD)对涂层进行了表征, 采用单纤维电子强力仪测试了碳化硅纤维沉积BN涂层前后的拉伸强度. 结果表明BN涂层无孔洞裂纹等缺陷, 且表面均一致密, B、N元素比例接近为1:1, 纤维与涂层之间相互渗透, 结合良好. 在较低的沉积温度下可以得到成分单一的BN涂层, 涂层微观结构随温度升高更加理想. 综合考虑结晶性与纤维强度保留率的情况下, 800~1000℃可作为碳化硅纤维BN涂层的最佳沉积温度. 在沉积温度为900℃时, 随涂层厚度的增加至0.28, 0.51和0.82 μm, 纤维强度保留率分别为92.7%, 83.6%, 77.7%.

关键词 硼氨烷络合物, 化学气相沉积, 碳化硅纤维, BN涂层

氮化硼(BN)以其优异的性能, 如高热稳定性、化学稳定性、热传导率、抗热震性和低介电常数被认为是非常有希望的陶瓷材料之一. 氮化硼纤维、薄膜、块体可以广泛地应用在电子设备、微波器件、透波材料、摩擦材料和航空航天领域^[1~5].

六方氮化硼(*h*-BN)有着类石墨的层状堆积结构, 每一层面内由硼和氮交替强共价键连接形成六边形结构, 层间由范德华力作用^[6,7]. 在陶瓷基复合材料中, 六方氮化硼因其更好的抗氧化性能(氮化硼在空气中的起始氧化温度为800℃, 而热解碳为450℃), 可以替代热解碳作为陶瓷基复合材料纤维和基体之间的界面涂层. 另外, 氮化硼氧化后形成的B₂O₃可以愈合微裂纹, 阻止氧化性气氛的扩散^[8~10].

化学气相沉积法(CVD)是目前国内外制备氮化硼涂层最常用的方法^[11]. 化学气相沉积法设备简单,

维护方便, 灵活性强, 可通过对反应室尺寸和反应气体驻留时间的调节在纳米到微米级别来控制涂层厚度, 并且涂层致密、均匀, 同时也可以较好地控制涂层的密度、纯度和晶粒度. 通常, 根据硼和氮来源的不同, 化学气相沉积可以分为双组元和单组元两种体系. 其中, 硼源和氮源为不同物质时为双组元体系, 如最常用的BCl₃-NH₃-Ar-H₂, BF₃-NH₃-Ar-H₂体系^[12,13], 其中BCl₃, BF₃为硼源, NH₃为氮源, Ar, H₂作为载气和稀释气体. 然而, 双组元体系中生成的副产物如HCl, HF等气体具有腐蚀性, 且不易形成化学计量比的BN涂层, 生成的NH₄Cl也会造成管路的堵塞. 此外, 双组元前驱体制备BN时沉积温度大都集中在1000℃以上, 制备过程对纤维的强度损伤较大. 另一种为单组元前驱体, 前驱体同时含有硼源和氮源, 如硼吡嗪(B₃N₃H₆)^[14]、三氯硼吡嗪(B₃N₃H₃Cl₃)^[15]等, 硼与氮的

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比例为1:1,易于形成化学计量比的氮化硼。但硼吡嗪化学性能不稳定,而且三氯硼吡嗪作为前驱体时会产生腐蚀性气体。

单组元前驱体硼氨烷络合物(BH_3NH_3)同时含有B、N两种元素,无毒无污染、不易燃、不易爆,室温下为固体,适当温度下升华^[16~19],是化学气相沉积法制备氮化硼优秀的备选前驱体之一,制备的BN可以作为陶瓷基复合材料的界面涂层。而碳化硅纤维增强陶瓷基复合材料,特别是SiC/SiC复合材料在航空航天、新能源等方面有广阔的应用前景。碳化硅纤维与基体之间的BN界面涂层可以起到传递载荷、偏折裂纹、使纤维拔出等作用增强复合材料韧性。相比于双组元前驱体,以硼氨烷络合物为前驱体制备的BN涂层在较低温度下具有良好的结晶性能,可最大限度地减少制备过程中高温对碳化硅纤维力学性能的影响。本文通过低温化学气相沉积,以硼氨烷络合物为单组元前驱体,在碳化硅纤维表面制备了氮化硼涂层,对涂层的形貌、元素组成、微观结构进行了表征,并研究了以此方法制备的氮化硼涂层对碳化硅纤维力学性能的影响。

1 实验

(i) 原料。硼氨烷络合物(BH_3NH_3 , 98.2%)来自北京伊诺凯科技有限公司;碳化硅纤维为江苏赛力菲公司生产的SLF-SiC-NF-10纤维,拉伸强度 2.2 ± 0.4 GPa,直径 14 ± 2 μm ,1000根/束。

(ii) 实验过程。本实验采用热壁化学气相沉积管式炉进行氮化硼纤维涂层的制备。碳化硅纤维在丙酮中超声浸渍30 min,除去表面保护膜,然后放入烘箱中,温度100℃,2 h烘干。除胶后的碳化硅纤维放置在管式炉的石英管反应区中,反应装置如图1所示。前驱体硼氨烷络合物(BH_3NH_3)放置在反应室左侧石英管内的石英舟上,与反应室形成一个封闭体系。反应期间,加热带加热至110~130℃使前驱体升华,由Ar气作为载气运送升华后的前驱体至反应区沉积,载气流量100~300 sccm。由于前驱体的升华是一个快速的过程,普通的一次性加热不能保证长时间的沉积。为了使沉积能持续的进行,本实验将前驱体按一定长度均匀平铺在石英舟上,在反应进行的过程中,加热带以0.167 cm/min的速率向右运动,使前驱体能够持续供应。同时,Si/SiO₂片也作为沉积的基底,可以用来测试傅里叶变换红外光谱(FTIR,

图1 低温CVD制备BN涂层反应装置示意图

Figure 1 Schematic diagram for preparation of BN coatings by CVD

V70FTIR, Bruker)和掠入射X射线衍射(GIAXRD, D/Max 2500v, Rigaku)。

(iii) 性能测试。扫描电子显微镜(SEM, SU-8010, Hitachi)用来表征纤维涂层表面和横截面形貌。俄歇电子能谱(AES, PHI-700, ULVAC-PHI),扫描型Ar⁺枪深度溅射,溅射速率49 nm/min。测试元素组成以及在深度方向上各元素的相对百分含量。用FTIR来测试涂层的化学成分,测试范围4000~600 cm⁻¹。GIAXRD用来测试涂层的相组成和结晶性能,入射角为1°,扫描速度3°/min。GIAXRD入射角较小,如本实验固定为1°,信号探测器做2θ角转动。相比于普通XRD入射X射线和信号探测器同时做θ角转动,GIAXRD的固定角只入射至材料表面,没有深入材料内部,对材料表面和界面结构信息敏感,可以测量较薄的涂层,消除基底的影响;所以在Si/SiO₂片上沉积BN涂层,进行FTIR和GIAXRD的表征。纤维强度由单纤维电子强力仪(YG001,太仓纺织厂)表征,加载速率1.5 mm/s。

2 结果与讨论

2.1 碳化硅纤维表面涂层微观形貌分析

图2为900℃下碳化硅纤维沉积BN涂层前后的横截面与SEM形貌图。图2(a)和(b)分别为空白碳化硅纤维和沉积有BN涂层的碳化硅纤维横截面形貌,可以看出,BN涂层连续紧密地包裹在碳化硅纤维外层,涂层厚度为~0.51 μm ,没有出现孔洞和裂纹等缺陷,与纤维的结合良好。图2(c)~(f)为空白纤维和沉积BN涂层后的表面形貌,其中图2(c)和(e)为空白碳化硅纤维的表面形貌,空白碳化硅纤维表面光滑均匀,无沟道等缺陷。图2(d)和(f)为900℃下碳化硅纤维沉积BN涂层后的表面形貌,涂层均一致密,无颗粒聚集、裂

图2 沉积温度为900℃时得到的沉积BN涂层前后的碳化硅纤维横截面和表面SEM对比形貌图。空白(a)和沉积(b)BN涂层后的碳化硅纤维横截面; (c), (e) 空白碳化硅纤维表面; (d), (f) 沉积BN涂层后的碳化硅纤维表面

Figure 2 Cross-section and surface morphology of BN coated silicon carbide fibers deposited at 900℃ and bare silicon carbide fibers by SEM. Cross-section morphology SEM images of bare fiber (a) and BN coated fiber at 900℃ (b). (c), (e) Surface morphology of bare fiber; (d), (f) surface morphology of BN coated fiber at 900℃

纹等缺陷, 涂层连续地包覆在碳化硅纤维上, 晶粒细小, 平均粒径在10~25 nm之间。结果表明, 此方法可以在碳化硅纤维表面制备均匀连续致密、可获得应用的涂层。涂层的厚度与沉积温度、时间有关, 而在一定温度下, 可通过调节沉积时间实现对涂层厚度的精细化控制。

2.2 碳化硅纤维表面涂层成分分析

采用俄歇电子能谱表征涂层沿厚度方向的元素组成, 对涂层的化学成分进行确认。图3为900℃下碳化硅纤维表面涂层的AES图谱, 对B, N, C, O, Si 5种元素进行深度溅射分析。从俄歇电子能谱可以看出, 涂层的主要元素为B, N, 且比例接近1:1, Si, C, O的含量极少, 说明碳化硅纤维表面涂层的主要成分为BN。从图3中也可以看出N元素含量相比于B元素略低, 这是由于 Ar^+ 离子轰击BN时, N元素会被优先溅射所导致^[4]。随着溅射深度的增加, B, N两种元素仍保持近似为1:1的比例, 说明在该沉积过程中能够获得组分较为单一的BN涂层。溅射深度超过0.28 μm后,

图3 碳化硅纤维表面BN涂层深度剖析俄歇电子能谱

Figure 3 AES depth profile of CVD BN-coated silicon carbide fibers

Si, C, O含量逐渐上升, B, N含量逐渐下降至接近于零, 说明纤维/涂层之间相互渗透, 涂层与纤维结合良好。

AES的表征结果表明在碳化硅纤维表面成功地沉积制备了BN涂层, 并且在纤维/涂层界面处二者相互渗透, 结合良好。在陶瓷基复合材料中, 涂层与纤维良好的结合可以保证作为界面的涂层使产生于基体的裂纹在界面涂层之间偏转, 增强复合材料韧性。

2.3 碳化硅纤维表面涂层微观结构表征

为了获得不同温度下在Si/SiO₂片上沉积得到的BN涂层的微观结构, 采用FTIR法对涂层进行表征。图4为不同沉积温度下BN涂层的FTIR图谱, 沉积温度分别为800, 900和1000℃, 同时对硼氨烷络合物进行了FTIR对比分析。

图4 800~1000℃沉积的BN涂层和硼氨烷络合物的FTIR光谱图

Figure 4 FTIR spectra of the coatings deposited at 800~1000℃ respectively, compared with ammonia borane

硼氨烷络合物的典型吸收谱可以在4000~600 cm^{-1} 很宽的范围内检测到. 其中, 波数在3305, 3248 3195 cm^{-1} 处的吸收峰由N-H的的伸缩振动引起, 而波数在1597, 1369, 1053 cm^{-1} 处的吸收峰为N-H的面内弯曲振动. B-H的伸缩振动峰在2277, 2214, 2115 cm^{-1} 波数处, 面内弯曲振动峰在1153, 723 cm^{-1} 两处可检测到. 779 cm^{-1} 处的吸收峰为B-N的伸缩振动. 这些检测结果与文献[20,21]报道的结果相符合. 前驱体硼氨烷络合物同时存在着B-N, B-H, N-H 3种化学键的吸收峰.

对于上述温度下沉积的涂层, 在1371和795 cm^{-1} 都出现了两处明显的吸收峰, 其中1371 cm^{-1} 处为B-N键的伸缩振动, 波数为795 cm^{-1} 的吸收峰是B-N键的面内弯曲振动^[22]. 在800~1000℃的温度范围内, 沉积得到了BN涂层, 且并未观察到B-H, N-H的伸缩和弯曲振动所引起的吸收峰, 说明沉积过程中前驱体分解得较完全.

为进一步证明碳化硅纤维表面BN涂层的微观结构, 对不同温度下在Si/SiO₂片上沉积的BN涂层进行GIAXRD表征, 获得了涂层的精细结构和晶型的详细信息. 图5给出了沉积温度在800~1000℃范围内所制备BN涂层的GIAXRD图谱. 从图中可以看出, 在上述温度下, 涂层均有两个主要的衍射峰, 分别在24°和42°左右, 24°左右的衍射峰对应六方氮化硼(002)面的衍射, 而42°左右的衍射峰为(100)和(101)两个晶面衍射的叠加. 结合(002)面比较宽的衍射峰($d_{(002)}$ 间距较大)和FTIR图谱, 可以看出涂层为涡轮层状氮化硼(*t*-BN)^[23]. *t*-BN为*h*-BN的三维无序结构, 其中B₃N₃六圆环面内二维有序排列, B₃N₃六圆环之间大

致平行, 可沿*c*轴旋转和位移^[24]. 随着沉积温度的上升, (002)衍射峰收窄并且向右移动, 并且42°处的峰也随之明显、收窄, 说明所制备BN涂层的结晶性随着沉积温度升高而趋于显著.

通过FTIR和GIAXRD表征的结果, 可以看到在较低的沉积温度(800~1000℃)下, 以硼氨烷络合物为前驱体, 能够在纤维表面获得成分单一的BN, 而所获得的BN涂层具有较适于作为界面的结构, 即介于非晶和*h*-BN之间的*t*-BN. 相比于文献[25]所报道的以硼吡啶为前驱体在800℃气相沉积会出现N-H吸收峰, 以及硼酸尿素法1000℃以下会有大量的O-H键^[26], 本实验所采用的方法有效降低了化学气相沉积温度, 且在较低温度下能够获得组分相对单一的BN涂层; 随着温度的升高, B-N的微观结构更加理想. 鉴于本方法的目的在于获得复合材料的理想界面层, 因此降低化学气相沉积的温度对提高纤维的强度保留率具有十分重要的意义. 与目前通用的以化学气相沉积制备BN涂层的方法相比^[27], 本方法将气相沉积反应的温度降低了至少100℃; 与之前报道的某些方法相比^[4,28], 反应温度甚至降低了500℃. 对于陶瓷纤维包括石英纤维而言, 这将会有效地降低沉积过程中长时间高温反应所带来的力学性能大幅度下降的问题, 提高复合材料的力学性能.

2.4 涂层对碳化硅纤维力学性能的影响

为了考察涂层厚度对纤维力学性能的影响, 本文对有无沉积BN涂层的碳化硅纤维进行了单丝拉伸强度的测试和分析. 图6给出了900℃下进行气相沉积所得到的不同BN涂层厚度的碳化硅纤维的拉伸强度对比结果, 以空白碳化硅纤维的拉伸强度作为对比. 从图中可以看出, 未沉积BN涂层的空白碳化硅纤维的强度为1.842 GPa, 而沉积了厚度为0.28 μm BN涂层的碳化硅纤维强度保留率92.7%(1.707 GPa). 在该温度下, 随着沉积时间的延长, 涂层沉积厚度增加, 涂层厚度为0.51和0.82 μm 的碳化硅纤维所对应的拉伸强度分别为1.539和1.432 GPa, 保留率分别为83.6%和77.7%.

上述分析中碳化硅纤维的强度随涂层厚度的增加而有一定程度的下降, 可能是由以下两个原因造成: (1) 所采用的碳化硅纤维含氧量较高, 主要由SiC微晶和无定型SiC_xO_y组成, 热稳定性较差, 高温下其拉伸强度随时间的延长会有所下降; (2) 由于BN涂

图5 800~1000℃沉积的BN涂层GIAXRD谱图

Figure 5 GIAXRD spectra of the coatings deposited at 800~1000℃

图6 无BN涂层及不同涂层厚度的碳化硅纤维单丝拉伸强度对比
Figure 6 Tensile strength of silicon carbide fibers without or with different thickness of BN coating

层和碳化硅纤维之间热膨胀系数不匹配,在降温过程中BN涂层产生的热应力对纤维造成一定损伤,导致其强度下降,而随涂层厚度增加其热失配现象越显著,这和文献报道的现象一致。比如, Liu和Tian^[26]在1000℃用硼酸-尿素法在碳化硅纤维表面制备BN

涂层,纤维强度随厚度增加而下降,涂层厚度为0.4 μm时,碳化硅纤维强度保留率为~60%。

本方法制备的BN界面涂层厚度在不超过0.8 μm时,其强度保留率达到80%以上,可满足陶瓷基复合材料的制备对纤维力学性能的要求。而若想获得力学性能优异的复合材料,建议BN涂层厚度范围控制在0.3~0.5 μm范围内^[29]。

3 结论

本文以硼氨烷络合物为前驱体,采用低温化学气相沉积法成功地制备了氮化硼涂层,并在碳化硅纤维上得到了应用。沉积温度在800℃以上时,可获得成分单一的BN,且B、N比例接近1:1。随沉积温度的升高其微观结构更加理想,并且BN涂层均一致密,晶粒细小,无孔洞裂纹等缺陷。涂层厚度为0.28, 0.51和0.82 μm时碳化硅纤维强度保留率分别为92.7%, 83.6%和77.7%。该方法可以在较低温度下制备陶瓷纤维的BN涂层,有效地降低长时间高温反应带来的力学性能的下降,进而提高其相应的复合材料的力学性能。

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Preparation and characterization of boron nitride coating on silicon carbide fibers based on low-temperature chemical vapor deposition

WANG Chi, SUN NiJuan, ZHANG Juan & ZHANG DaHai

Science and Technology of Advanced Functional Composite Laboratory, Aerospace Research Institute of Materials and Processing Technology, Beijing 100076, China

Boron nitride (BN) has been considered as promising material owing to its unique properties, such as high thermal stability, high chemical stability, high thermal conductivity and thermal shock resistance. Chemical vapor deposition (CVD) is the most popular method for the preparation of BN. However, the side-products (like HF, HCl and HBr) are corrosive and the crystallinity of BN is poor if the deposition temperature is 1300°C. Herein we reported a new method for preparing BN by low-temperature CVD using ammonia borane as precursor on silicon carbide fibers. Ammonia borane was sublimated at 110–130°C using a heating belt, and the sublimated gaseous substance was transported to the deposition region where the silicon carbide fibers were placed at the deposition temperature of 900°C. During the sublimation, a certain quantity of ammonia borane was uniformly distributed in the quartz boat with a certain length, and the heating belt moved along the quartz tube with a fixed speed to the end of the boat. Thus the sublimation gas substances could be supplied continually and steadily. Scanning electronic microscopy (SEM), auger electron spectroscopy (AES), Fourier translation infrared spectroscopy (FTIR), and grazing incidence angle X-ray diffraction (GIXRD) were used to characterize the properties of the coatings, and single fiber electron tensile machine was used to test the tensile strength of silicon carbide fibers without and with different thickness of coatings. The results illustrated that BN coating enwrapped well with the fibers with no defects like voids or cleavages. Meanwhile, the surface of the coating was uniform and dense. And the ratio of B and N was approximate 1: 1. Pure BN coating could be acquired at a relatively low deposition temperature, and microstructure of the BN coating was more ideal with the increasing of deposition temperature. Considering the balance between the coating crystallinity and strength retention of the fiber, 800–1000°C was the optimum deposition temperature range of BN coating on silicon carbide fibers. Compared with previous reports, this method reduced the preparation temperature effectively and could acquire pure BN on relatively low temperature. In this work, we aimed at preparing the ideal interphase of ceramic composite, and reducing the deposition temperature to elevate the fiber strength retention. This work could reduce the deposition temperature by at least 100°C and even 500°C compared with some cases. It would solve the reduction of mechanical properties during long time and high temperature deposition. At 900°C, the strength retention of the fibers retained 92.7%, 83.6% and 77.7%, as the coating thickness was 0.28, 0.51 and 0.82 μm , respectively. The strength retention of the silicon carbide fiber can meet the requirement of ceramic composite.

ammonia borane, chemical vapor deposition, silicon carbide fibers, BN coating

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