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钴酸镍/亲水碳布微波吸收复合材料及其热裂解特性研究

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摘要: 随着智能电子设备的普及,电磁辐射污染问题愈发严峻,开发新型高性能微波吸收材料已成为当下新材料领域的一大研究热点。由于微波吸收材料的吸波性能在高温条件下会出现不同程度的衰减,因此,针对高温环境下微波吸收材料的吸波性能变化及热裂解特性展开研究。采用简易水热法与高温煅烧相结合的工艺,将钴酸镍(Nickel cobalt oxide,$NiCo_2O_4$)成功负载于亲水碳布(Hydrophilic carbon cloth,HCC),获得具有优异热稳定性和微波吸收性能的$NiCo_2O_4$/HCC复合材料。通过SEM、XRD和XPS对$NiCo_2O_4$/HCC复合材料进行了微观结构与材料成分分析,通过VNA和TGA-IR对$NiCo_2O_4$/HCC复合材料进行了吸波性能和热裂解特性测试。结果表明,针状$NiCo_2O_4$均匀地负载于HCC表面,这为$NiCo_2O_4$/HCC复合材料引入了磁损耗。与纯HCC基体相比,针状$NiCo_2O_4$与HCC形成的异质界面结构使$NiCo_2O_4$/HCC复合材料的微波吸收能力得到显著提升。XRD和XPS分析结果表明,$NiCo_2O_4$/HCC复合材料中的$NiCo_2O_4$为尖晶石结构。当填充的$NiCo_2O_4$质量分数为25%及厚度为4.98 mm时,$NiCo_2O_4$/HCC复合材料的反射损耗(RL)高达−50.00 dB。TGA-IR分析结果表明,$NiCo_2O_4$/HCC复合材料在25—800 ℃范围的质量损失率主要源于HCC上功能基团和$NiCo_2O_4$的分解。经25—800 ℃的高温热裂解后,$NiCo_2O_4$/HCC复合材料的RL为−48.67 dB,较热裂解前的RL强度损失率小于5%,表明该复合材料在高温环境下依然保持着良好的微波吸收性能。制备的$NiCo_2O_4$/HCC复合材料有望成为高温微波吸收材料的潜在选择之一,为指导该材料在高温场景中的实际应用提供一定的理论支撑。**(专精特新·电磁波吸收与屏蔽用新型材料的研究进展专辑十二之八)**

关键词: 钴酸镍;亲水碳布;微波吸收;复合材料;水热法;反射损耗;有效吸收带宽;热裂解

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TIAN Konghu, YANG Hang, GAO Kaipeng, et al. Research on Nickel Cobalt Oxide / Hydrophilic Carbon Cloth Microwave Absorption Composites and their Thermal Cracking Characteristics[J]. Materials Research and Application, 2025, 19(1): 91-97.

0　引言

随着通讯技术的迅猛发展,电磁辐射污染问题愈发严峻,开发高性能的微波吸收材料成为当前研究的热点之一[1-4]。当微波吸收材料应用于航空航天、核能以及电子工业等领域的特殊零部件制造时,不仅要求其在室温环境下具备优异的微波吸收性能,还要求其微波吸收性能在经历高温环境后依然能够保持良好的稳定性。因此,针对高性能微波吸收材料及其在高温环境条件下的热裂解特性开展研究,具有重要的理论探究价值。

$NiCo_2O_4$作为一种具有独特结构的功能材料,其高磁导率等特性使其在微波吸收领域具有巨大的应用潜力[5]。HCC具有良好的热稳定性和机械性能[6-7],其可作为耐高温微波吸收材料的碳材料基体。Cao等[8]在制备的聚乳酸(PLA)中添加碳纤维(CF)来提高PLA的热稳定性和力学性能。Li等[9]通过化学气相渗透方法在CF上包覆SiC涂层,增强其高温机械性能及其韧性。通过将$NiCo_2O_4$与HCC有效复合,有望制备出热稳定性能优异的微波吸收复合材料。

本研究通过简易的水热法和高温煅烧成功制备了$NiCo_2O_4$/HCC复合材料,并对其微波吸收性能和

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热裂解过程进行探究，为开发适用于高温环境条件下的高性能微波吸收复合材料提供理论依据和实验支持。

1　实验部分

1.1　$NiCo_2O_4$/HCC 复合材料的制备

$NiCo_2O_4$/HCC 复合材料的制备流程如图 1 所示。取 HCC（2 cm×2 cm）进行酸化处理。在去离子水（75 mL）中加入 $Ni(NO_3)_2·6H_2O$（1 mmol）、$Co(NO_3)_2·6H_2O$（2 mmol）、NH_4F（3 mmol）和尿素（9 mmol），对混合溶液进行超声处理和磁力搅拌 30min 后放入酸化后的 HCC，继续超声处理和磁力搅拌 6 h。将含有酸化 HCC 的混合溶液转移至反应釜，在 120 ℃下水热处理 14 h。取出反应后的产物，用水和乙醇清洗各三次，在 60 ℃下真空干燥 24 h，400 ℃、N_2 气氛下煅烧 3 h，得到 $NiCo_2O_4$/HCC 复合材料。

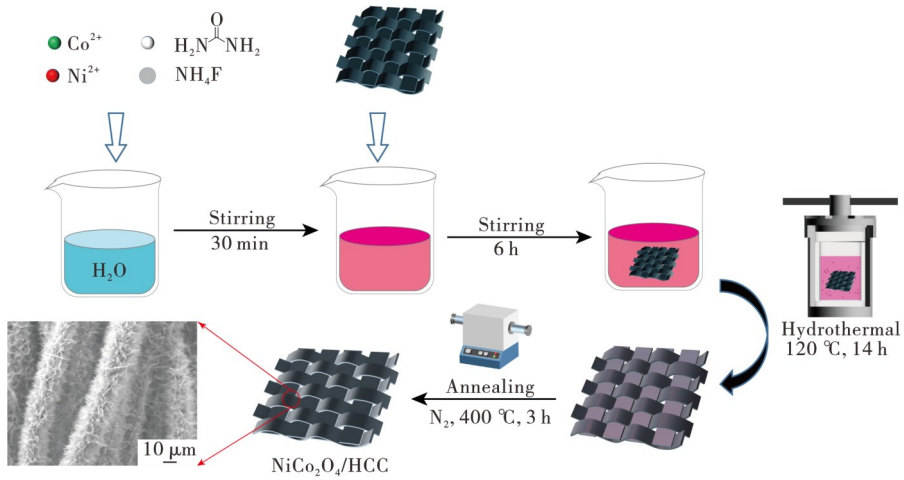


图 1　$NiCo_2O_4$/HCC 复合材料的制备工艺流程图

Figure 1　$NiCo_2O_4$/HCC composites preparation process flow chart

1.2　测试表征

采用扫描电子显微镜（SEM，FlexSEM1000）观察样品的微观形貌；采用 X 射线衍射分析仪（XRD，Smartlab SE，Cu-Kα 辐射）分析样品的晶体结构；采用 X 射线光电子能谱（XPS，ESCALAB Xi+）研究样品的元素组成和化学状态；采用热重红外联用分析仪（TGA-IR，TGA/DSC3-1337、Nicoletis50）分析样品的热裂解过程。将所得样品按质量分数 25% 和石蜡混合，压制成外径为 7.00 mm，内径为 3.04 mm 的圆环，采用矢量网络分析仪（VNA，Keysight E5080B）测量 $NiCo_2O_4$/HCC 复合材料的微波吸收特性。

2　结果与讨论

2.1　微波吸收性能分析

图 2 为室温环境下 $NiCo_2O_4$/HCC 复合材料的反射损耗（RL）图。从图 2 可见，当 $NiCo_2O_4$/HCC 复合材料厚度为 4.98 mm 时，其 RL 高达 −50.00 dB；其厚度为 4.81 mm 时，有效吸收带宽（EAB）为 2.00 GHz。结果表明，该复合材料在室温环境下具有优异的微波吸收性能。

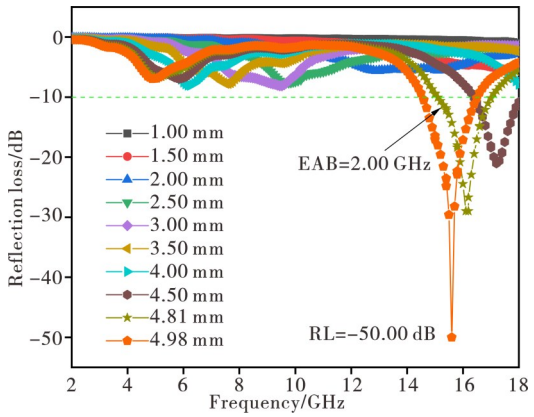


图 2　$NiCo_2O_4$/HCC 复合材料的 RL 图

Figure 2　RL diagram of $NiCo_2O_4$/HCC composites

2.2　形貌和结构分析

图 3 为 $NiCo_2O_4$/HCC 复合材料的 SEM 图。从图 3 可见，针状 $NiCo_2O_4$ 被均匀地负载于 HCC。与纯 HCC 基体相比，制得的复合材料增加了异质界面

结构,且引入了更多的磁损耗机制,从而使得其微波吸收能力得到显著增强[10]。均匀负载的针状$NiCo_2O_4$为复合材料提供了更多的活性位点,有助于该复合材料与入射电磁波相互作用,进一步提升了其微波吸收性能。

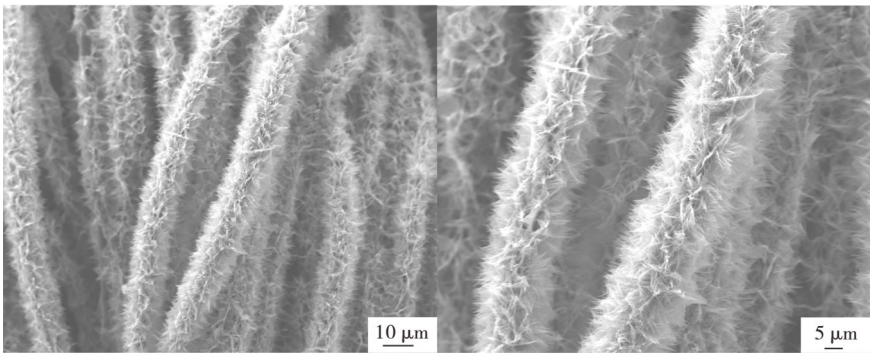


图3 $NiCo_2O_4$/HCC复合材料的SEM图

Figure 3 SEM image of $NiCo_2O_4$/HCC composites

采用XRD对$NiCo_2O_4$/HCC复合材料的物相组成进行了测试,结果如图4所示。从图4可见,$NiCo_2O_4$/HCC在26.0°左右处存在一个较宽的衍射峰,对应于HCC的石墨化碳物相。2θ=18.9°、31.1°、36.7°、44.6°、59.1°、65.0°处的衍射峰,分别对应$NiCo_2O_4$物相(JCPDS NO:20-0781)的(111)、(220)、(311)、(400)、(511)、(440)晶面。在经过25到800℃的热裂解过程后,复合材料XRD图谱中的$NiCo_2O_4$物相特征衍射峰消失,而出现了CoO和NiO物相的特征衍射峰,说明$NiCo_2O_4$在热裂解过程中被分解成CoO和NiO(JCPDS NO:78-0431和JCPDS NO:71-1179)。

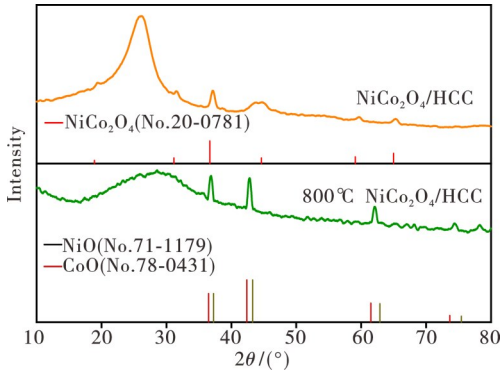


图4 $NiCo_2O_4$/HCC复合材料的XRD图

Figure 4 XRD pattern of $NiCo_2O_4$/HCC composites

D峰(1 345 cm^{-1}左右)是由HCC的结构缺陷或杂质引起的。G峰(1 586 cm^{-1}左右)是由HCC中sp^2杂化碳原子的C—C键的伸缩振动引起的[11]。复合材料中碳的无序程度可以用D带与G带的比值(I_D/I_G)来表征,无序程度越高,则I_D/I_G的比值越大。图5为所得样品的Raman图,可以看到,I_D/I_G比值排序为HCC<$NiCo_2O_4$/HCC<800 ℃ $NiCo_2O_4$/HCC,D带在逐渐增强,可以推断,均匀负载$NiCo_2O_4$和高温热裂解过程都会增加HCC中碳的无序度或有利于表面缺陷的产生[12]。

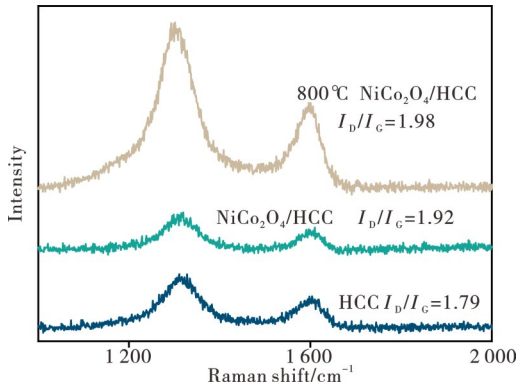
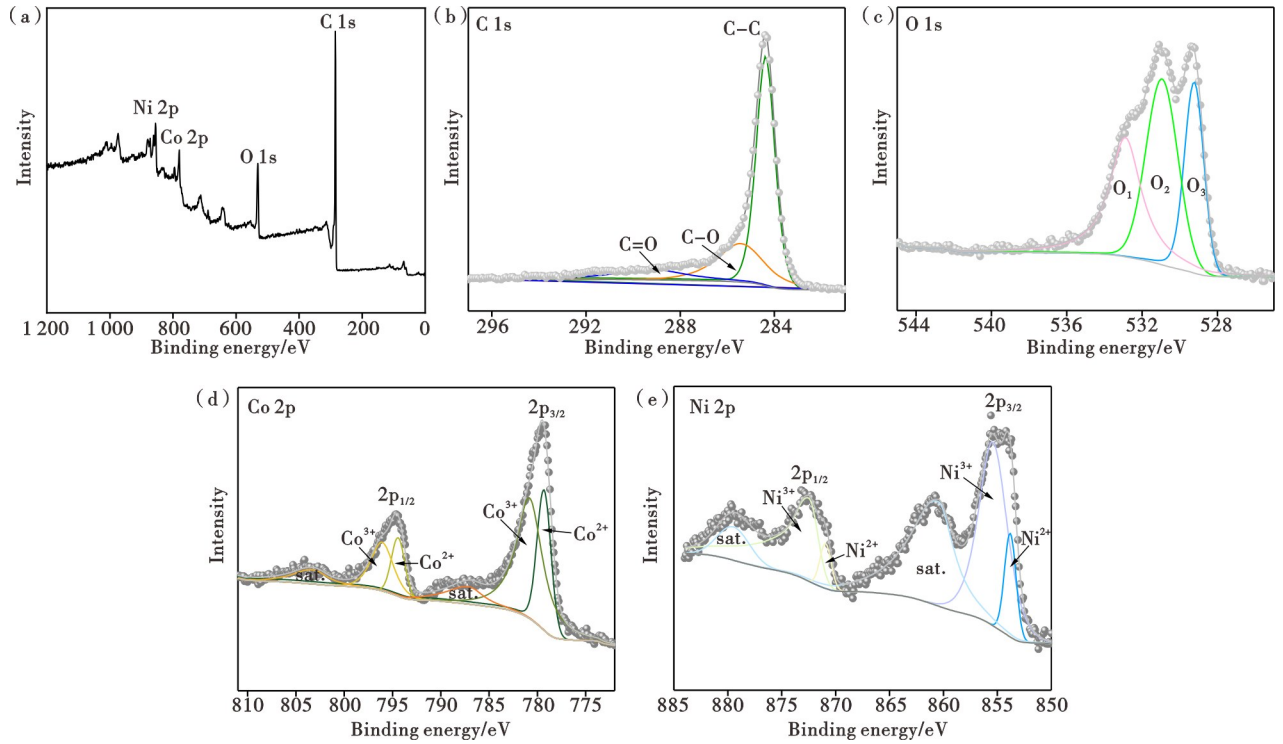


图5 HCC和$NiCo_2O_4$/HCC复合材料的Raman图

Figure 5 Raman diagram of HCC and $NiCo_2O_4$/HCC composites

图6为$NiCo_2O_4$/HCC复合材料的XPS全谱图和精细谱图。从其全谱图中可见,$NiCo_2O_4$/HCC复合材料只有C、O、Co和Ni四种元素。从图6(b)可见,结合能在284.8、286.1和288.4 eV的三个特征峰分别对应C—C、C—O和C=O,且碳元素主要以C—C的形式存在。从图6(c)可见,结合能在529.2、531.2和533.0 eV处的特征峰分别对应Ni—O/Co—O、C—O和C=O[13]。图6(d)为Co 2p轨道拟合出的四个主峰,分别对应于Co $2p_{3/2}$峰处结合能为779.5 eV(Co^{2+})和781.1 eV(Co^{3+}),在Co $2p_{1/2}$峰处结合能为794.5 eV(Co^{2+})和796.1 eV(Co^{3+}),以及两个卫星振动峰(787.9和803.6 eV)。

图 6(e)为 Ni 2p 轨道拟合出四个主峰，在 Ni $2p_{3/2}$ 峰处分别对应结合能为 853.8 eV(Ni^{2+})和 855.5 eV(Ni^{3+})，在 Ni $2p_{1/2}$ 峰处结合能为 872.3 eV(Ni^{2+})和 875.6 eV(Ni^{3+})，以及两个卫星振动峰(861.1 和 880.1 eV)。XPS 分析结果表明，复合材料中的 $NiCo_2O_4$ 为尖晶石型结构[14]。这一结果与 XRD 分析结果相吻合。



(a)—全谱图；(b)—C 1s；(c)—O 1s；(d)—Co 2p；(e)—Ni 2p。

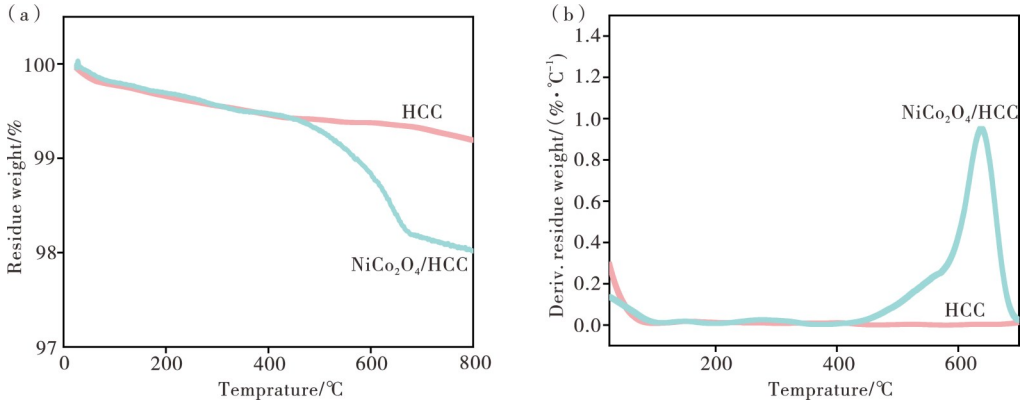
(a)—full spectrum; (b)—C 1s; (c)—O 1s; (d)—Co 2p; (e)—Ni 2p.

图 6 $NiCo_2O_4$/HCC 复合材料的 XPS 全谱图和精细谱图

Figure 6 XPS full spectrum and XPS fine spectrum of $NiCo_2O_4$/HCC composites

2.3 热裂解特性分析

TGA 和 DTG 分析在 25—800 ℃的温度范围和 N_2 气氛条件下进行。图 7 为 HCC 和 $NiCo_2O_4$/HCC 的 TGA 和 DTG 曲线。从图 7(a)可见，在 300 ℃之前发生的失重，主要来自所得样品中的物理吸附水[15]；加热到 800 ℃时，有较小的质量损失，主要归因于 HCC 上含氧基团、酰胺基团和氨基基团的分解[16]。HCC 与 $NiCo_2O_4$/HCC 的 TGA 曲线对比发



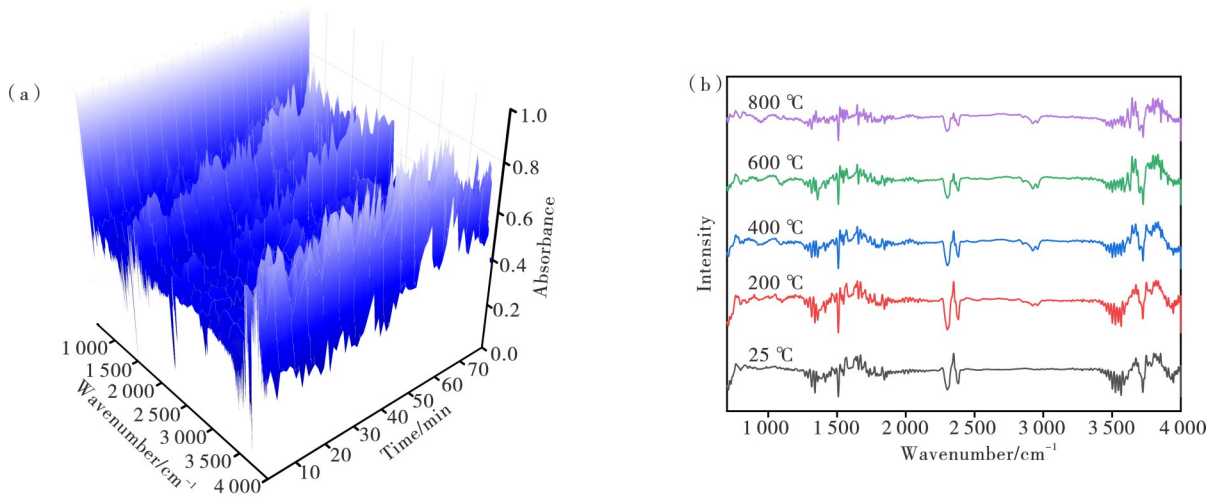
(a)—TGA；(b)—DTG。

图 7 HCC 和 $NiCo_2O_4$/HCC 复合材料的 TGA 曲线和 DTG 曲线

Figure 7 The TGA curves and DTG curves of HCC and $NiCo_2O_4$/HCC composites

现,HCC 在 25—800 ℃热裂解过程质量损失仅有 1%。而 $NiCo_2O_4$/HCC 复合材料在 450—650 ℃之间失重主要是由于 $NiCo_2O_4$ 发生高温热裂解,结合 XRD 分析可推知 $NiCo_2O_4$ 的分解产物为 CoO 和 NiO。从图 7(b)可见,对于 HCC 在 N_2 气氛下质量损失速率基本稳定在水平位置,而 $NiCo_2O_4$/HCC 在 N_2 气氛下的最大分解温度在 636.5 ℃,对应的质量损失速率小于 1 %·℃$^{-1}$,表明在 N_2 气氛下 HCC 和 $NiCo_2O_4$/HCC 的残炭量较高。

$NiCo_2O_4$/HCC 复合材料的 TGA-IR 分析结果如图 8(a)所示,展示了该复合材料的热裂解产物与时间的关系。图 8(b)为热裂解过程中温度为 25、200、400、600 和 800 ℃时,$NiCo_2O_4$/HCC 复合材料所对应的同步 IR 图。从图中可见,CO_2(2 270—2 390 cm^{-1})、H_2O(3 725 cm^{-1} 左右)和 C—H(2 962cm^{-1} 左右)[17-21]的特征吸收峰均与 $NiCo_2O_4$/HCC 复合材料的热裂解相关。



(a)—3D;(b)—2D。

图 8 $NiCo_2O_4$/HCC 复合材料红外光谱

Figure 8 Infrared spectrum of $NiCo_2O_4$/HCC composites

经过热裂解后的 $NiCo_2O_4$/HCC 复合材料的微波吸收性能如图 9 所示。厚度为 4.39 mm 时,热裂解后的 $NiCo_2O_4$/HCC 复合材料的 RL_{min} 达到 −48.67 dB,EAB=1.76 GHz。通过对比 $NiCo_2O_4$/HCC 复合材料热裂解过程前后的 RL 图可知,经过热裂解后 $NiCo_2O_4$/HCC 复合材料的微波吸收性能整体保持较为良好,仅有轻微的损失。由此可见,该复合材料不仅具有优异的微波吸收能力,而且在热裂解过程中表现出良好的稳定性,其有望在高温环境下的微波吸收材料领域具有潜在应用价值。

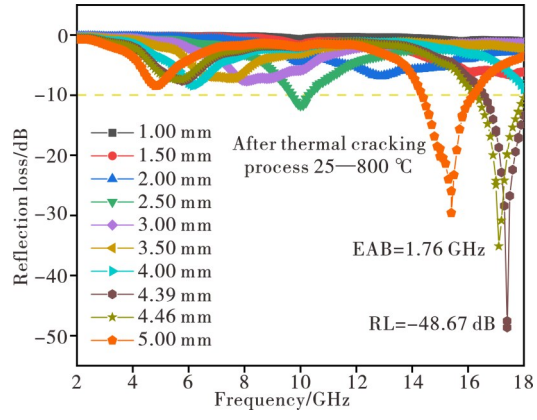


图 9 热裂解过程后 $NiCo_2O_4$/HCC 复合材料的 RL 图

Figure 9 RL diagram of $NiCo_2O_4$/HCC composites after thermal cracking process

3 结论

采用水热法与高温煅烧相结合的方式成功制备出 $NiCo_2O_4$/HCC 复合材料。通过微观结构和成分分析,针状结构的 $NiCo_2O_4$ 均匀负载于 HCC,$NiCo_2O_4$/HCC 复合材料的最佳反射损耗高达 −50.00 dB。通过 TGA-IR 对 $NiCo_2O_4$/HCC 复合材料进行热裂解过程研究,结果表明,该复合材料在 N_2 气氛下,25—800 ℃的热裂解过程后仍具有高达 −48.67 dB 的 RL,说明该复合材料在 800 ℃以下具有优异的热稳定性。$NiCo_2O_4$/HCC 复合材料在高温环境下的微波吸收材料领域具有潜在应用价值。

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Research on Nickel Cobalt Oxide / Hydrophilic Carbon Cloth Microwave Absorption Composites and Their Thermal Cracking Characteristics

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Abstract: With the increasing popularity of smart electronic devices, the problem of electromagnetic radiation pollution caused by them is becoming increasingly severe. Developing new high-performance microwave absorbing materials has become one of the research hotspots in the field of new materials. One of the critical issues in the application of microwave absorbing materials is that their absorption performance often decreases to varying degrees at high-temperature. Therefore, research on the changes in microwave absorbing performance and thermal cracking characteristics of microwave absorbing materials under high-temperature environment can provide a theoretical basis for guiding their practical applications in high-temperature environment. In this paper, nickel cobalt oxide ($NiCo_2O_4$) was successfully loaded onto hydrophilic carbon cloth (HCC) by combining a facile hydrothermal method with high-temperature calcination, which fully utilizing the advantages of both components to obtain $NiCo_2O_4$/HCC composites with excellent thermal stability and microwave absorption properties. The SEM, XRD, and XPS were used to analyze the microstructure and material composition of $NiCo_2O_4$/HCC composites. The VNA and TGA-IR were used to test the microwave absorbing performance and thermal cracking characteristics of $NiCo_2O_4$/HCC composites. The results indicate that needle-shaped $NiCo_2O_4$ is uniformly loaded onto HCC, which can introduce magnetic losses into $NiCo_2O_4$/HCC composites; Compared with single HCC material, needle-shaped $NiCo_2O_4$ and its heterogeneous interface structure significantly enhance the microwave absorbing performance of $NiCo_2O_4$/HCC composites. The XRD and XPS analysis results indicate that $NiCo_2O_4$ in the $NiCo_2O_4$/HCC composites has a spinel structure. When the filling ratio is 25 wt% and the thickness is 4.98 mm, the reflection loss (RL) of $NiCo_2O_4$/HCC composites is as high as −50.00 dB. The TGA-IR analysis results of $NiCo_2O_4$/HCC composites in the range of 25—800 ℃ indicate that the mass loss rate may be mainly attributed to the decomposition of functional groups on HCC and $NiCo_2O_4$. After high-temperature thermal cracking at 25—800 ℃, the RL of $NiCo_2O_4$/HCC composites is −48.67 dB, with a strength loss rate of less than 5% compared to before high-temperature thermal cracking, indicating that the composites still maintain good microwave absorbing performance in high-temperature environment. Therefore, the prepared $NiCo_2O_4$/HCC composites is expected to become one of the potential choices for high-temperature microwave absorbing materials.

Keywords: nickel cobalt oxide; hydrophilic carbon cloth; microwave absorption; composites; hydrothermal method; reflection loss; effectively absorb bandwidth; thermal cracking

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