Rare Metal Materials and Engineering
Volume 49, Issue 9, September 2020
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2020, 49(9): 3030-3034.

ARTICLE

Novel Method for in situ Growth of Carbonyl Iron on the Surface of Hollow Cenospheres and Determination of Its Microwave Absorption Properties

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Abstract: This study develops an effective, simple, and low-cost method of metal organic chemical vapor deposition for manufacturing carbonyl iron (CI)-coated hollow cenospheres (Ce) as new composites for microwave absorption. Structure and morphology analyses demonstrate that the composites have a complete core/shell structure with Ce as the core and CI layers as the shell. Compared with Ce, the composites have higher complex permeability and permittivity, indicating their improved absorption capacity. The measured electromagnetic parameters are used to analog and calculate the reflectance curves of Ce and Ce@CI coating under the condition of thickness d=2 mm. The absorption peak of the Ce@CI sample shifts to the high frequency, and the minimum reflection peak decreases to -26.2 dB. The frequency at less than -10 dB bandwidth increases to 6 GHz, which covers the entire Ku band.

Key words: carbonyl iron; hollow cenospheres; microwave absorption

Cenospheres (Ce) are one of the most valuable added fractions of coal fly ash. Ce has a hollow spherical structure and can be applied in microwave absorption due to its superior properties, such as light mass, good fluidity, and stable chemical performance, and low cost[1]. At present, researchers use electroless plating or electroplating to coat the surface of hollow Ce[2-4]. Kim et al[2] fabricated conductive and magnetic microspheres through electroless plating of Co, Co-10% Fe, Ni, and Ni-15% Fe films on hollow Ce and investigated their high-frequency electromagnetic and microwave absorption properties. However, electroless plating or electroplating generally needs complex sensitization, activation, and other treatments with high cost, slow plating speed, long time, and easy introduction of other impurities (such as phosphorus); as such, obtaining a pure coating is difficult[5,6].

Metal-organic chemical vapor deposition (MOCVD) is a new technology that uses organometallic compounds and has the following remarkable characteristics: low deposition temperature, fast deposition speed, strong deposition flexibility, and controllable composition of synthetic materials. The thickness, composition, and deposition of shell growth can be precisely controlled by regulating these process parameters [7, 8].

Carbonyl iron (CI) is widely used in microwave absorbing materials because of its simple preparation process, low cost, and large magnetic loss [9]. CI has good dielectric properties at high frequency, and the composite dielectric constant can be effectively adjusted based on the CI content of the composite [10]. In the present study, a light and cheap microwave absorption material is obtained using light weight and fly ash hollow microspheres and $Fe(CO)_5$ as the material source through chemical vapor deposition method to grow CI in situ on the surface of hollow Ce. The micromorphology and electromagnetic properties of the samples are determined before and after surface modification. The microwave absorption properties of the modified hollow Ce, as a new light and cheap microwave absorption material, are also investigated.

1 Experiment

The experimental device is divided into three parts: metal

Received date: February 13, 2020
Foundation item: Chongqing Basic Science and Cutting Edge Technology Research Grant (cstc2017jcyjax0078)
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organic supply system, fluidization reaction system, and tail gas treatment system. The structural principle of the entire device is shown in Fig.1.

The experimental procedures are as follows:

(1) A total of 10 g of hollow cenospheres were added into the reactor. The gas valve (carrier gas cylinder) of nitrogen cylinder was opened. Valves A and B were also opened. The closure of valves C, D, E and F was ensured. The flow of nitrogen with flowmeter 1 was adjusted, and the air tightness of the device was checked. Ventilation was conducted for 30 min to discharge air in the reactor and confirm the intact air tightness of the device.

(2) The evaporator and reactor were heated. When the evaporator temperature and the reactor temperature reached 80 and 180 °C, respectively, 30 mL of $Fe(CO)_5$ was injected into the evaporator. Valve B was closed, and the nitrogen cylinder gas valve (fluidizing cylinder) was opened. Valves C, D, and E were also opened, and the carrier gas flow was adjusted to 30 mL/min with flowmeter 1. The gas flow with flowmeter 2 was also adjusted to obtain sufficient fluidization. The deposition time was controlled to 30 min. The reactor pipes were all covered with a layer of heat preservation sleeve to prevent gaseous $Fe(CO)_5$ from condensing at low temperatures, resulting in the blocked pipes.

(3) After reaching the preset deposition time, the evaporator was heated and the fluidized bed was stopped. Nitrogen was continuously injected. Valve D was closed, and valve F was opened to control effectively the deposition time and prevent the reaction from reaching beyond the preset time ($Fe(CO)_5$ still evaporated during cooling). Other experimental conditions would remain unchanged until the temperature of the evaporator and the fluidized bed decreased to room temperature. The nitrogen flow was stopped, and valves A, C, E, and F were opened. The reactor was opened, and the reaction products were collected into operation seal after grinding.

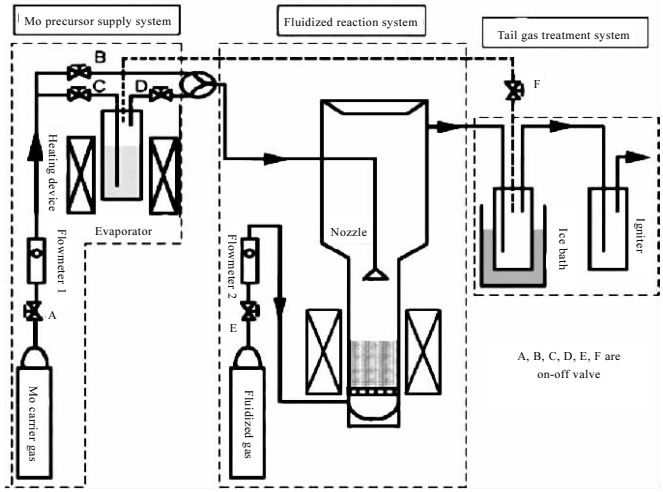

Fig.1 Principle diagram of MOCVD device

The phase structure of the powder was identified by X-ray diffraction (XRD; D/max-IIB, Japan). VEGA II XMU INCA scanning electron microscopy (SEM) was employed for morphological analysis. INCA 7718 energy-dispersive X-ray spectroscopy (EDS) was used to analyze the element distribution in the sample. Complex permeability and permittivity were measured using a vector network analyzer (HP-8720ES) within the frequency range of 2~18 GHz. The samples used for EM parameter measurements were prepared by dispersing powders into paraffin wax at a mass fraction of 40% and then pressing the mixtures into a compact toroidal shape with outer and inner diameters of 7.0 and 3.0 mm, respectively.

2 Results and Discussion

2.1 XRD analysis

Fig.2 shows the satisfactory XRD patterns of Ce and Ce@CI. Ce anastomosis was very good, and no peaks corresponding to impurities were found. Sharp XRD peaks were found in the crystal plane. After the CI was coated on the surface of Ce, the diffraction peaks of Ce and α-Fe phase (JCPDS 06-0696) were observed in the sample, indicating that no other impurity phase was generated except for Ce and α-Fe phase. In addition, the Ce@CI composites had similar diffraction peaks to those of Ce and CI, but the intensity of the peaks of the composites decreased (Fig.1). Moreover, a peak at approximately 2θ=44.6° was observed, indicating that the shell layer was composed of CI.

2.2 SEM analysis

The SEM image of the Ce and Ce@CI samples are shown in Fig.3. Based on the SEM images, Ce powder has regular sphere-like crystals with smooth surfaces and the average particle size is 30 μm (Fig.3a). Particles stacked on top of each other were uniformly coated with CI (spherical particle distribution on the surface of Ce, Fig.3b), and the average particle size is 30.5 μm. Fig.3c is a part of Fig.3b with four times magnification. CI particles (little spherical particles) were found on the Ce particle surface. Moreover,

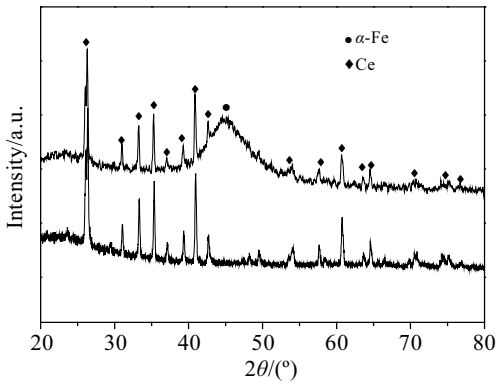

Fig.2 XRD patterns of Ce and Ce@CI core-shell powder

EDS analysis shows that the major components of the Ce@CI samples are O, Si, C, Al, and Fe (Fig.3d).

2.3 Complex permittivity and permeability

The complex permittivity and permeability of Ce powder and Ce@CI composites are shown in Fig.4. In Fig.4a and Fig.4b, the real and imaginary complex permittivity (ε', ε'') of Ce and Ce@CI exhibited significant variation with frequency. In addition, the values (ε', ε'') of Ce@CI composites were higher than those of Ce within the range of 2~18 GHz. The CI shell could greatly increase the conductivity of the samples and contribute to the improvement of permittivity. According to Fig.4a and Fig.4b, the reason of Ce@CI dielectric enhancement mainly comes from the dielectric relaxation of heterogeneous interface[11]. Secondly, polar groups (hydroxyl, carbonyl, etc.) can reduce the band gap, which leads to the increase of the conductivity and contributes to the enhancement of the dielectric constant[12]. Fig.4c shows the real and imaginary complex permeability(μ', μ'') of Ce@CI as a function of frequency within 2–18 GHz. The data of Ce are not shown in Fig.4c due to its μ' and μ'' values that were almost 1 and 0, respectively. The μ' and μ'' values of Ce@CI gradually changed with increasing frequency within 1.3~1.89 and 0.58~1.39, respectively.

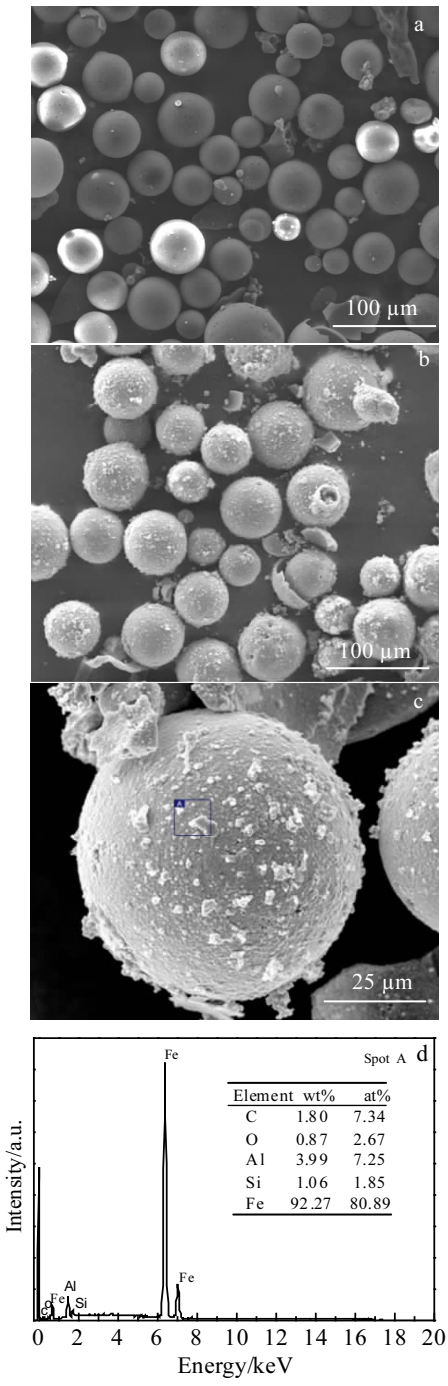

Fig.3 SEM images of Ce powders (a), Ce@CI powders (b, c), and EDS analyses of Ce@CI (d)

A general loss of microwave magnetic material could be primarily due to eddy current losses, magnetization vector rotation, natural resonance, and magnetic domain wall resonance[13]. Magnetization vector rotation only occurs in a strong magnetic field. Moreover, the magnetic domain wall resonance contribution at the microwave frequency was very small and thus could be neglected[14]. Therefore, the magnetic loss of Ce@CI was primarily caused by eddy current losses or natural resonance. If Ce@CI magnetic loss was only from the eddy current loss, then $f^{-1}(\mu')^{-2}\mu''$ should be constant[14]. The values of $f^{-1}(\mu')^{-2}\mu''$ versus the frequency of Ce@CI are shown in Fig.4d. The value showed a constant value trend as the frequency increased. Hence, the natural resonance loss could be ruled out. Furthermore, Ce@CI magnetic loss was primarily dominated by eddy current. From Fig.3, we can see the CI layer is formed by the aggregation of carbonyl iron particles. Conductivity of CI layer varies with carbonyl iron density, the higher the density, the higher the conductivity[15]. Therefore, eddy current loss is the main loss mechanism.

2.4 Microwave absorption properties

Microwave reflection loss (R_L) was calculated by transmission line theory[16, 17]:

$$R_L = 20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right| \quad (1)$$

$$Z_{in} = Z_0\left(\frac{\mu_r}{\varepsilon_r}\right)^{\frac{1}{2}}\tanh\left(\frac{j2\pi df\sqrt{\varepsilon_r\mu_r}}{c}\right) \quad (2)$$

where Z_{in} is the normalized input impedance of a metal-backed microwave absorption layer, Z_0= 377 Ω is the intrinsic impedance of free space, ε_r and μ_r are the relative complex permittivity and permeability, respectively, f is the frequency of the EMW, d is the thickness of absorber, and c is the velocity of light in a vacuum.

The microwave reflection loss of Ce@CI composites and Ce powders under the condition of thickness d=2 mm are shown in Fig.5. CI coating on Ce could effectively

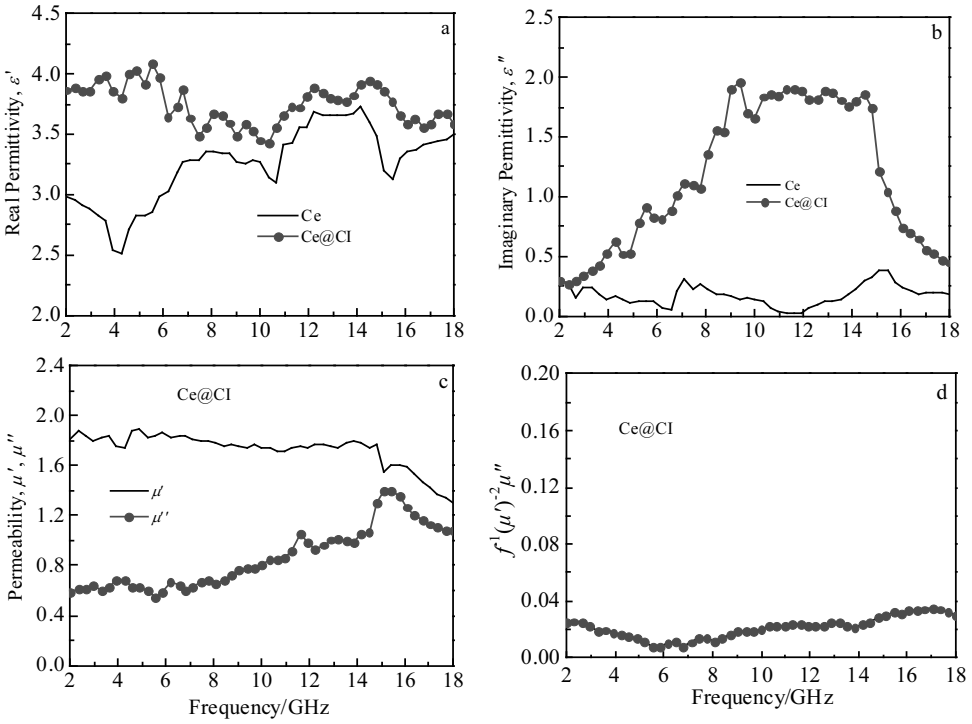

Fig.4 Real permittivity (a), imaginary permittivity (b), complex permeability (c), and $f^{-1}(\mu')^{-2}\mu''$ values versus frequency of Ce@CI (d)

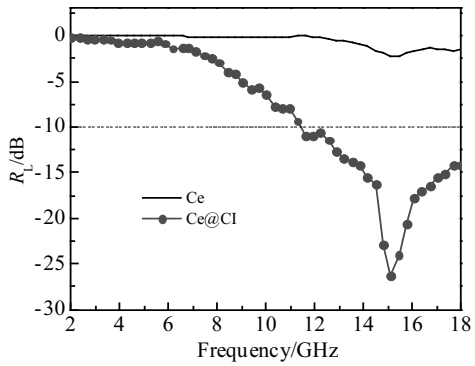

Fig.5 Microwave reflection loss of Ce@CI composites and Ce powders

improve the absorbing properties of Ce, particularly at high frequencies (12~18 GHz). After surface modification of Ce, the minimum reflection peak reduced to –26.2 dB, and less than –10 dB bandwidth increased to 6 GHz, which covered the entire Ku band.

3 Conclusions

1) CI coating on Ce can effectively improve the absorbing properties of Ce, particularly at high frequencies (12~18 GHz).

2) After surface modification of Ce, the minimum reflection peak reduced to −26.2 dB, and less than −10 dB bandwidth increased to 6 GHz under the condition of thickness d=2 mm.

3) Compared with other methods used to modify Ce, the current research develops a unique, simple, and low-cost method to obtain Ce@CI with good absorption properties in engineering.

References

1 Ranjbar N, Kuenzel C. *Fuel*[J], 2017, 207: 1

2 Kim Sun Tae, Kim Sung Soo. *Journal of Applied Physics*[J], 2014, 115(17): 17A528

3 Zhan J, Zhang H, Zhu G. *Ceramics International*[J], 2014, 40(6): 8547

4 Li Menghao, Wang Deren, Xue Jianchao *et al*. *Ceramics International*[J], 2019, 45(18Part A): 24 919

5 Fu Dao, Zhang Lei, Sun Wanchang *et al*. *Material & Heat Treatment*[J], 2012, 41(16): 158

6 Jin G P, Wang X L, Fu Y *et al*. *Chemical Engineering Journal*[J], 2012, 203: 440

7 Wang R, Wan Y Z, He F *et al*. *Applied Surface Science*[J], 2012, 258(7): 3007

8 Manasevit H M. *Applied Physics Letters*[J], 1968, 12(4): 156

9 Liu Yuan, Shi Jingfeng, Jia Ying *et al*. *Rare Metal Materials and Engineering*[J], 2019, 48(12): 3997 (in Chinese)

10 Cheng Y L, Dai J M, Wu D J *et al*. *Journal of Magnetism and Magnetic Materials*[J], 2010, 322(1): 97

11 Yang Huijing, Cao Maosheng, Li Yong *et al*. *Advanced Op-*

tical Materials[J], 2014, 2: 214
12 Jia Yahui, Gong Pei, Li Shulong *et al*. *Physics Letters A*[J], 2019, 384: 126 106
13 Jian Z, Bo C. *Journal of Materials Science: Materials in Electronics*[J], 2017, 28(104): 1
14 Iqbal N, Wang X, Babar A A *et al*. *Scientific Reports*[J], 2017, 7(1): 15 153
15 Li Yanjing, Li Shulong, Gong Pei *et al*. *Physica E: Low-dimensional Systems and Nanostructures*[J], 2018, 104: 247
16 Naito Y, Suetake K. *IEEE Trans Microwave Theory Technique*[J], 1971, 19: 65
17 Meshram M R, Nawal K Agrawal, Bharoti Sinha *et al*. *Journal of Magnetism and Magnetic Materials*[J], 2004, 271: 207

空心微球表面原位生长羰基铁的新方法及其微波吸收性能

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摘 要：本研究开发了一种有效、简单、低成本的金属有机化学气相沉积法制备羰基铁(CI)包覆中空微球(Ce)作为新型微波吸收复合材料的方法。结构和形貌分析表明，复合材料具有完整的核/壳结构，其中 Ce 为核层，CI 为壳层。与 Ce 相比，复合材料具有更高的复合导磁率和介电常数，说明复合材料的吸收能力有所提高。利用实测电磁参数模拟计算了厚度 *d*=2 mm 条件下 Ce 和 Ce@CI 涂层的反射率曲线。Ce@CI 样品的吸收峰移至高频，最小反射峰减小至–26.2 dB，小于–10 dB 带宽的频率增加到 6 GHz，覆盖了整个 Ku 频段。

关键词：羰基铁；中空微球；吸波性能

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