CHIN. PHYS. LETT. Vol. 34, No. 10 (2017) 105201

Enhancement of Heat-Resistance of Carbonyl Iron Particles by Coating with Silica and Consequent Changes in Electromagnetic Properties

Zhao-Wen Ren(任朝闻)[1], Hui Xie(谢辉)[2**], Ying-Ying Zhou(周影影)[2,3]

[1]*School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an 710021*
[2]*School of Materials Engineering, Xi'an Aeronautical University, Xi'an 710077*
[3]*State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072*

(Received 12 May 2017)

Silica-coated carbonyl iron particles (CIPs) are fabricated with the Stober method to improve their heat-resistance and wave-absorption properties. The morphology, heat-resistance, electromagnetic properties and microwave absorption of raw-CIPs and silica-coated CIPs are investigated using a scanning electron microscope, an energy dispersive spectrometer, a thermal-gravimetric analyzer, and a network analyzer. The results show that the heat-resistance of silica-coated CIPs is better than that of raw CIPs. The reflection losses exceeding −10 dB of silica-coated CIPs are obtained in the frequency range 9.3–12.4 GHz for the absorber thickness of 2.3 mm, and the same reflection losses of uncoated CIPs reach the data in the lower frequency range for the same thickness. The enhanced microwave absorption of silica-coated CIPs can be ascribed to the combination of proper electromagnetic impedance match and the decrease of dielectric permittivity.

PACS: 52.70.Gw, 52.70.Ds DOI: 10.1088/0256-307X/34/10/105201

With the rapid development of the optical technology and wireless communication, the optical absorption and microwave absorbing materials are becoming significant in both military and civil application.[1−7] As conventional microwave absorbing materials, carbonyl iron particles (CIPs) with the merit of high saturation magnetization, high Curie temperature and large magnetic permeability can break Sneok's limit in GHz.[8] Although CIPs have a high Curie temperature of approximately 770℃,[9] the CIPs without anti-oxidation treatment can be oxidized over 250℃ and the oxidation of CIPs will decrease the property of microwave absorption due to the worse magnetic properties.[10,11] Therefore, it is a good way to protect CIPs from oxidation using surface coating technology to form silica-coated CIPs.

Li *et al.*[12] prepared silica-coated CIPs using the tetraethyl orthosilicate (TEOS) as silica source and aminopropyltriethoxysilane (APTES) as surface modifier. Qing *et al.*[13] fabricated silica-coated flake CIPs by the Stober method and studied the silica-coated CIPs after thermal treatment. Yan *et al.*[14] also coated the nanoshell silica layer on the surface of nanoflake Fe by the Stober method and attributed the good wave absorbing performance to the coated nanoflake Fe which can reduce the permittivity and can improve the electromagnetic impedance match. In brief, the wave absorption properties of silica-coated CIPs are better than that of raw CIPs.

Researchers commonly fabricate silica coating layers by the Stober method.[12−16] However, these references are lacking in heat-resistance analysis about the raw CIPs and silica-coated CIPs. In this work, silica-coated CIPs were prepared by hydrolysis of TEOS in the alkaline environment. Furthermore, the silica-coated CIPs improved the heat-resistance of raw CIPs so that the microwave absorption materials of CIPs can be used in higher temperature. At the same time, the microwave absorption properties of the raw CIPs are also improved by the silica coating layer. The morphology, heat-resistance, electromagnetic properties and microwave absorption of raw-CIPs and silica-coated CIPs were investigated in detail.

The CIPs were used as the raw material. Its average diameter was 5 μm and purchased from Xinghua Chemical Co. Ltd., Shaanxi Province, China. The silica coating was fabricated as follows: CIPs (8 g) were dispersed in TEOS (100 ml) and were vibrated by ultrasonic cleaning machine for 30 min. The ammonia solution (200 ml deionized water and 7 ml ammonia) was added to the mixture to adjust PH of the solution to 10. Coating was carried out by stirring the CIPs (250 r/min) for 5 h in a constant temperature water bath at 80℃. The silica-coated CIP samples were obtained after drying and washing.

For permittivity and permeability test, the powder samples were mixed with melted paraffin (7:3 in mass) and then poured into the mold ($22.86 \times 10.16 \times 2.5$ mm).

The sample morphologies were observed using a scanning electron microscope (SEM; Model JSM-6360, JEOL, Tokyo, Japan) and the composition of the raw CIPs and silica-coated particles were examined by an energy dispersive spectrometer (EDS). The heat-resistance property was tested by thermal gravimetric analysis (TGA) on the SDT Q600V8.3 Build 101. The electromagnetic parameters of the samples were measured by a vector network analyzer (Agilent Technologies E8362B). In addition, the effective permittivity and permeability are derived using the Newton method by comparing the measured S-parameter with the theoretical S-parameter of the equivalent

**Corresponding author. Email: xiehui@xaau.edu.cn
© 2017 Chinese Physical Society and IOP Publishing Ltd

circuit.[17]

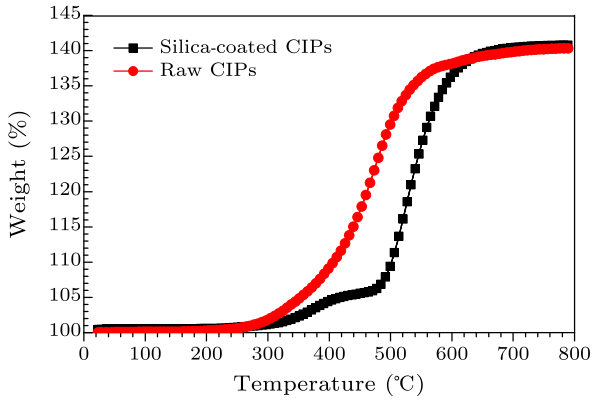

Fig. 1. TGA curves of the silica-coated CIPs and raw CIPs.

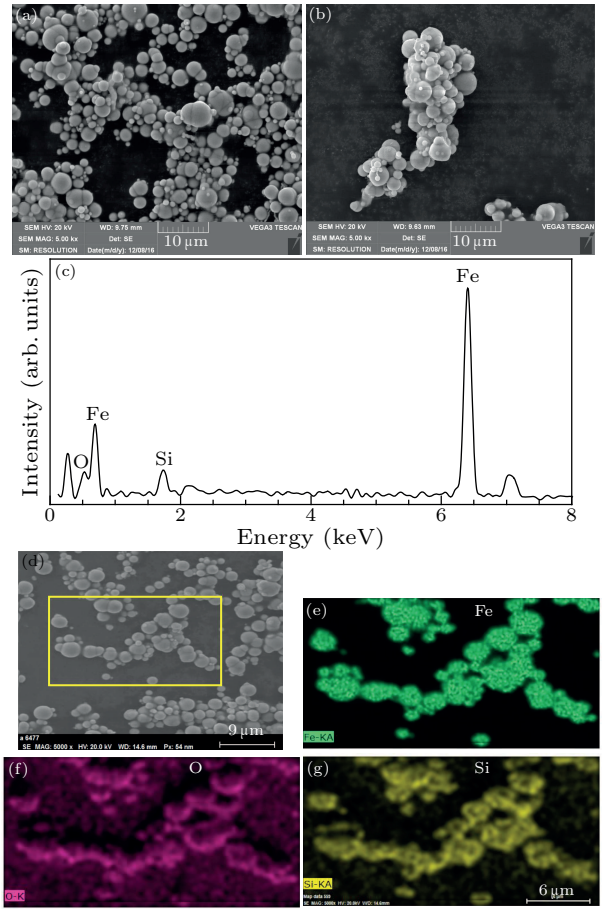

Fig. 2. SEM images of raw CIPs (a) and silica-coated CIPs (b), the EDS spectra of silica-coated CIPs (c), and elemental mapping of Fe (e), O (f) and Si (g) corresponding to the SEM image (d) of a representative zone.

Figure 1 shows the thermal stability of the raw and silica-coated CIPs samples. The samples were heated from room temperature to 800℃ in air with a heating rate of 10℃/min. As seen from Fig. 1, the mass of the samples increases with the temperature owing to the fact that the samples were oxidized by oxygen. The raw CIPs have a stable weight until 250℃. However, the weight of silica-coated CIPs starts rising from approximately 330℃. The silica-coated CIPs exhibit better heat-resistance than the raw CIPs. It can be attributed to the uniform and homogeneous silica shell on the surface of raw CIPs, which is a barrier that limits access of oxygen. These results show that the silica shell can prevent CIPs from being oxidized at high temperature.[18]

Figure 2 shows the SEM images and EDS spectra of the raw and silica-coated CIPs samples. As shown in Figs. 2(a) and 2(b), the size and surface morphology of raw CIPs and silica-coated CIPs can be observed clearly. It could be found that the surface of spherical CIPs is smooth while the silica-coated CIPs' surface is rough.

As shown in Fig. 2(c), the existence of Si and O elements in the silica-coated CIPs can be confirmed by EDS. Figure 2(d) shows the representative zone of silica-coated CIPs, and Figs. 2(e)–2(g) are elemental mappings of Fe, O and Si, respectively. It is significant that they not only appear on the surface of raw CIPs, but also are uniformly and homogeneously coated on the raw CIPs. Fe, O and Si labeled in the images indicate that Si and O elements are uniformly coated on the raw CIPs.

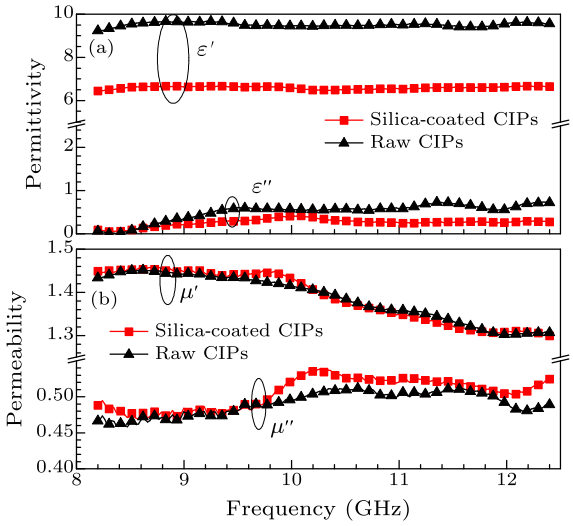

Fig. 3. Real and imaginary parts of the permittivity (a) and permeability (b) of raw CIPs and silica-coated CIPs.

Figure 3 shows the complex permittivity ε_r ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability μ_r ($\mu_r = \mu' - j\mu''$) of raw CIPs and silica-coated CIPs measured using a vector network analyzer in the frequency range 8.2–12.4 GHz.

The real permittivity (ε') of raw CIPs and silica-coated CIPs almost keeps constant in the measured range, in which the values are about 9.5 and 6.5, respectively. The raw CIPs' imaginary part of permittivity (ε'') gradually increases from 0.05 to 0.60 in the frequency range 8.2–9.5 GHz, and the silica-coated CIPs imaginary part of permittivity gradually increases from 0.05 to 0.27 in the frequency range 8.2–10 GHz. Then they keep constant at 0.60 and 0.27 in the frequency range 10–12.4 GHz, respectively.

The two factors mainly determine the complex

permittivity: (i) orientation polarization of electric dipole, and (ii) interfacial polarization between the silica-coated layer and raw CIPs. Compared with raw CIPs, it is reasonable that the lower permittivity of silica-coated CIPs is mainly attributed to the increase of resistivity and the decrease of space charge polarization after coating with the silica layer.[19]

Figure 3(b) shows the real (μ') and imaginary (μ'') part of the complex permeability of silica-coated CIPs and raw CIPs versus frequency. The μ' curves of both silica-coated CIPs and raw CIPs decrease from 1.45 to 1.3 in the frequency range 8.2–12.4 GHz. The values of μ'' of silica-coated CIPs and raw CIPs gradually increase from 0.49 and 0.47 to approximately 0.52 and 0.50 in the frequency range 8.2–12.4 GHz, respectively.

Generally, the microwave magnetic loss of magnetic particles originates from hysteresis. This can be determined by eddy current effect, domain-wall resonance and natural resonance.[19] The domain-wall resonance was below the gigahertz range. The eddy current effect can be excluded after coating the silica layer.[20] As stated above, the complex permeabilities of silica-coated CIPs and raw CIPs are mainly determined by the natural resonance.[21] It can be seen that there is slight difference permeability between the silica-coated CIPs and raw CIPs. This can be attributed to fact that the proper thickness of silica coated layer has slight effect on the permeability of CIPs. In addition, the perfect microwave absorption materials aim at zero reflection. Furthermore, the absorber reflection coefficient can be expressed as[22]

$$\Gamma = \frac{Z - Z_0}{Z + Z_0}, \tag{1}$$

where Z is the dielectric wave impedance

$$Z = E/H = \sqrt{\mu_r \mu_0 / \varepsilon_r \varepsilon_0}, \tag{2}$$

and Z_0 is free space wave impedance

$$Z_0 = \sqrt{\mu_0/\varepsilon_0}. \tag{3}$$

Thus the perfect microwave absorption requires impedance match that the real and imaginary parts of permittivity and permeability are equal, respectively ($\varepsilon_r = \mu_r$). For the CIPs, it has relatively high permittivity and low permeability. The silica-coated CIPs have smaller permittivity that can offer better impedance match. Furthermore, the low permittivity of silica-coated CIPs can reach proper impedance match, which means that most of the incident microwave can transmit into the silica-coated CIPs and can obtain more reflection loss.

According to the transmission line theory, the reflection loss (RL) of samples can be calculated by complex permittivity, complex permeability and thickness of microwave absorbing materials. The RL of single-layer coated can be calculated by

$$\mathrm{RL} = 20 \log |\Gamma| = 20 \log \left| \frac{Z_{\mathrm{in}} - Z_0}{Z_{\mathrm{in}} + Z_0} \right|, \tag{4}$$

where Γ is the reflection coefficient, Z_{in} is the input impedance of the absorber, and Z_0 is the impedance of the free space. The expressions of Z_0 and Z_{in} are

$$Z_0 = \sqrt{\mu_0/\varepsilon_0}, \tag{5}$$

$$Z_{\mathrm{in}} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left[j \frac{2\pi f d}{c} \sqrt{\mu_r \varepsilon_r} \right], \tag{6}$$

where μ_0 and ε_0 are the dielectric constant and permeability of free space, μ_r and ε_r are the relative permeability and permittivity of absorber, respectively. In addition, f is the frequency of the incident wave, d is the thickness of the absorber, and c is the velocity of light in free space (3×10^8 m/s).[23–25]

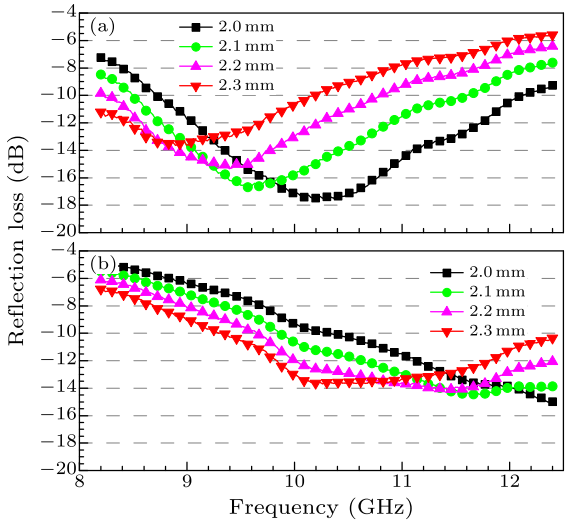

Fig. 4. The RL curves of raw CIPs (a) and silica-coated CIPs (b).

As shown in Fig. 4, the RL of raw CIPs and silica-coated CIPs samples with different thicknesses can be observed. For raw CIPs, the minimum reflection loss increases from −17.5 dB to −13.6 dB with the thickness ranging from 2.0 mm to 2.3 mm, and the minimum reflection loss values move toward a low frequency band. The RL values exceeding −10 dB are reached in the frequency range 8.2–10.1 GHz for the absorber thickness of 2.3 mm. In addition, the RL of the sample can reach −10 dB, which means 90% microwave absorption in the same thickness range.

After coating a silica layer, the CIPs shows good absorbing properties compared with the raw CIPs. The minimum RL values can reach below −14 dB for the absorber thickness of 2 mm, and the bandwidth below −10 dB can exceed 3.1 GHz for the sample with 2.3 mm.

The thicker absorber corresponding to the low RL can be due to the geometric effect. As shown in Fig. 5, an electromagnetic wave is normally incident to an absorber backed by a metal shell, which will be partially reflected at the surface of absorber and the other part enters the absorber. When the wave enters the absorber, one part will be lost by hysteresis and eddy current loss. The other part of transmittance microwave reaches the surface of metal shell, and it will

be reflected and emerged from the surface of absorber. The two waves cancel at surface of absorber when they are out of phase by 180°.

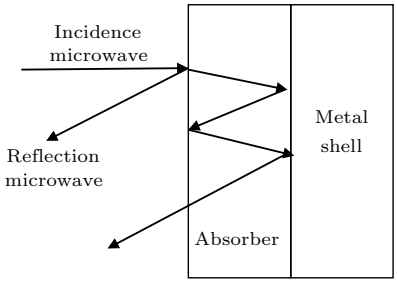

Fig. 5. The sketch map of an electromagnetic wave incident to an absorber with metal shell.

Therefore, the thickness of the absorber is satisfied under the quarter-wavelength condition,

$$t_{\rm m} = \frac{nc}{4f_{\rm m}\sqrt{\varepsilon_{\rm r}\mu_{\rm r}}}, \quad n = 1, 3, 5\ldots, \tag{7}$$

where $t_{\rm m}$ and $f_{\rm m}$ are the matching thickness and the matching frequency, respectively. The RL peak comes from the quarter-wavelength cancelation of the two waves reflected at the surface of absorber and at the interface of absorber and metal shell. In this case, at 2.0 mm, the two reflected waves are nearly satisfied under the quarter-wavelength condition at 10.2 GHz. For the other thicknesses, the two waves reflected from the surface of absorber and metal cannot cancel completely.[26] Thus the thicker absorber corresponding to more RL is not accurate enough. Furthermore, $f_{\rm m}$ increases with the decreasing thickness. Therefore, the match frequency will move to low frequency with thicker microwave absorption materials.

Generally, the appropriate electromagnetic impedance match and the effectively attenuate microwave are two keys to achieve more RL values.[14]

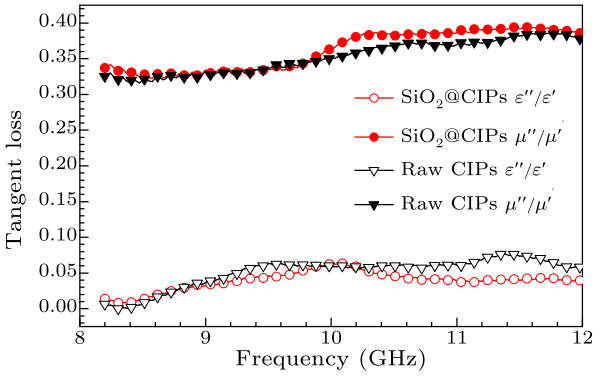

Fig. 6. Dielectric factor loss ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) and the magnetic factor loss ($\tan\delta_\mu = \mu''/\mu'$) of silica-coated and raw CIPs.

Figure 6 shows the dielectric factor loss ($\tan\delta_\varepsilon = \varepsilon''/\varepsilon'$) and the magnetic factor loss ($\tan\delta_\mu = \mu''/\mu'$) of silica-coated CIPs and raw CIPs, respectively. The silica-coated CIPs and raw CIPs all have large magnetic loss and very low dielectric in the frequency range 8.2–12.4 GHz. The large magnetic loss indicates that microwaves in silica-coated CIPs can be intensively attenuated, which is due to the strong and broadband natural resonance. As mentioned above, the broad absorption bandwidth and good microwave absorption properties of silica-coated CIPs can result from the appropriate electromagnetic impedance match and the large magnetic loss.

In summary, a silica layer has been successfully prepared on the surface of spherical CIPs. EDS result indicates that the Si and O elements are coated on the surface of CIPs. TGA curves show that the silica-coated layer can prevent CIPs from being oxidized at higher temperature. The permittivity of silica-coated CIPs decreases dramatically, while permeability changes slightly. The RL exceeding −10 dB of silica-coated CIPs are obtained in the frequency range 9.6–12.0 GHz for the thicknesses of 2.3 mm. The silica-coated layer possesses enhanced microwave absorption that can be attributed to the proper electromagnetic impedance match and large magnetic loss. Therefore, the silica-coated layer is significant to improve the ability of heat resistance, high frequency absorption and broadband absorption of CIPs.

References

[1] Dong W, Qiu Y, Yang J et al 2016 *J. Phys. Chem.* C **120** 12713
[2] Cao T, Wei C, Simpson R E et al 2014 *Sci. Rep.* **4** 3955
[3] Cao T, Wei C, Simpson R E et al 2013 *Opt. Mater. Express* **3** 1101
[4] Cao T, Zhang L, Simpson R E et al 2013 *J. Opt. Soc. Am.* B **30** 1580
[5] Zhao L, Jiang W, Jin Y et al 2009 *IFMBE Proc.* **25** 172
[6] Li D Y, Wang K, Wang X et al 2013 *IFMBE Proc.* **39** 1624
[7] Kong L B, Li Z W, Liu L et al 2013 *Int. Mater. Rev.* **58** 203
[8] Zhao F, Duan H, Wang W et al 2012 *Physica* B **407** 2495
[9] Woo C H 2009 *Philos. Mag.* **89** 2921
[10] Yin C, Fan J, Bai L et al 2013 *J. Magn. Magn. Mater.* **340** 65
[11] Abshinova M A, Kazantseva N E, Sáha P et al 2008 *Polym. Degrad. Stab.* **93** 1826
[12] Li J, Feng W J, Wang J S et al 2015 *J. Magn. Magn. Mater.* **393** 82
[13] Qing Y C, Zhou W C, Shu J et al 2011 *Physica* B **406** 777
[14] Yan L, Wang J, Han X et al 2010 *Nanotechnology* **21** 095708
[15] Stöber W, Fink A and Bohn E 1968 *J. Colloid Interface Sci.* **26** 62
[16] Zhu J, Wei S, Lee I et al 2012 *RSC Adv.* **2** 1136
[17] Ebara H, Inoue T and Hashimoto O 2006 *Sci. Technol. Adv. Mater.* **7** 77
[18] Małecki P, Królewicz M, Hiptmair F et al 2016 *Smart Mater. Struct.* **25** 105030
[19] Ma J, Li J, Ni X et al 2009 *Appl. Phys. Lett.* **95** 102505
[20] Wang H, Zhu D, Zhou W et al 2015 *J. Magn. Magn. Mater.* **375** 111
[21] Liu L, Duan Y, Liu S et al 2010 *J. Magn. Magn. Mater.* **322** 1736
[22] Chen L, Duan Y, Liu L et al 2011 *Mater. Des.* **32** 570
[23] Zhou Y, Zhou W, Wang H et al 2015 *J. Polym. Res.* **22** 1
[24] Gao B, Qiao L, Wang J et al 1970 *J. Appl. Phys.* **41** 3850
[25] Jin H B, Li D, Cao M S et al 2011 *Chin. Phys. Lett.* **28** 037701
[26] Wang T, Han R, Tan G et al 2012 *J. Appl. Phys.* **112** 104903