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Electromagnetic and microwave absorption properties of surface modified Fe–Si–Al flakes with nylon

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ABSTRACT

The surface modified Fe–Si–Al alloy flakes with nylon 6 were prepared by a simple melt compounding method, and the electromagnetic and microwave absorption properties were presented. After surface modification, the complex permittivity of the flakes decreases dramatically with increasing amount of nylon 6, while the complex permeability remains nearly intact. The calculated microwave reflectivities show that surface modification is able to improve the microwave absorption performance of Fe–Si–Al flakes and that the composite containing modified flakes with an appropriate amount of nylon 6 is a promising candidate for a thin microwave absorbing material in S-band (2–4 GHz).

1. Introduction

Due to the rapid development of wireless communications and high frequency circuit devices in GHz range, electromagnetic interference and electromagnetic radiation pollution have grown to a critical issue to be addressed. Therefore, microwave absorbing materials have attracted considerable attention because of their abilities to reduce and eliminate the electromagnetic radiation and interference [1–5]. Among the candidates for microwave absorbers, flake-shaped soft magnetic metallic powders are particularly interesting for their high permeability and high magnetic loss in GHz range originating from high saturation magnetization and large shape anisotropy [6–13]. High permeability and high magnetic loss are favorable for improving the microwave absorption properties in a low frequency band and for which the thickness of absorbing material can remain thin simultaneously [13–17]. Therefore, flake-shaped soft magnetic metallic powders are expected to achieve an effective microwave absorbing materials with thin layer thickness in GHz range. In recent years, flake-shaped Sendust (Fe–Si–Al) alloy powders have been extensively studied for microwave absorbing materials due to the high electrical resistivity, good machinability, excellent soft magnetic property and low cost [9,18–21]. However, a high permeability is generally accompanied with a high permittivity in flake-filled composites [9,18,22], which degrades the impedance matching and limits the absorption property to some extent [23]. Since surface modification is an effective way to suppress the permittivity [16], it is believed that the modification of Fe–Si–Al flakes is of great significance to improve the microwave absorption property in GHz range.

Until now, numerous studies have been performed for surface-modified magnetic metallic flakes to improve microwave absorption properties, such as SiO_2 coated Fe [24,25], ZnO coated Fe [26], Ce_2O_3 coated Fe–Co [12], SiO_2 coated Fe–Ni–Mo [27], Fe–Ni coated with its oxide [16], Fe–Cu–Nb–Si–B coated with its oxide [28], and Fe–Co–Zr coated with polystyrene [29], and so on. However, most of these reports focused on inorganic oxides as the surface coating, and little attention has been paid to organics for surface modification of Fe–Si–Al alloy flakes. Nylon 6, one of the most common organics, can be a potential candidate for surface coating because of its high adhesion and excellent insulation properties. Moreover, a better dispersion of inorganic powders in organic polymers can be achieved via surface treatment with nylon 6 [30], which improve the mechanical property of composite. Hence, it is supposed that the surface modified Fe–Si–Al alloy flakes with nylon 6 could be promising candidates for application of microwave absorbing materials.

In this work, we reported an effective method to fabricate Fe–Si–Al flakes coated with nylon 6 and investigated the electromagnetic and microwave absorption properties after surface modification with different amounts of nylon 6.

2. Experimental details

The Fe–Si–Al alloy flakes were prepared by the conventional mechanical milling process. Spherical Fe–Si–Al alloy powders with a composition of 9.5 wt%Si–5.5 wt%Al–bal. Fe (purchased from Advanced Technology & Materials Co.,

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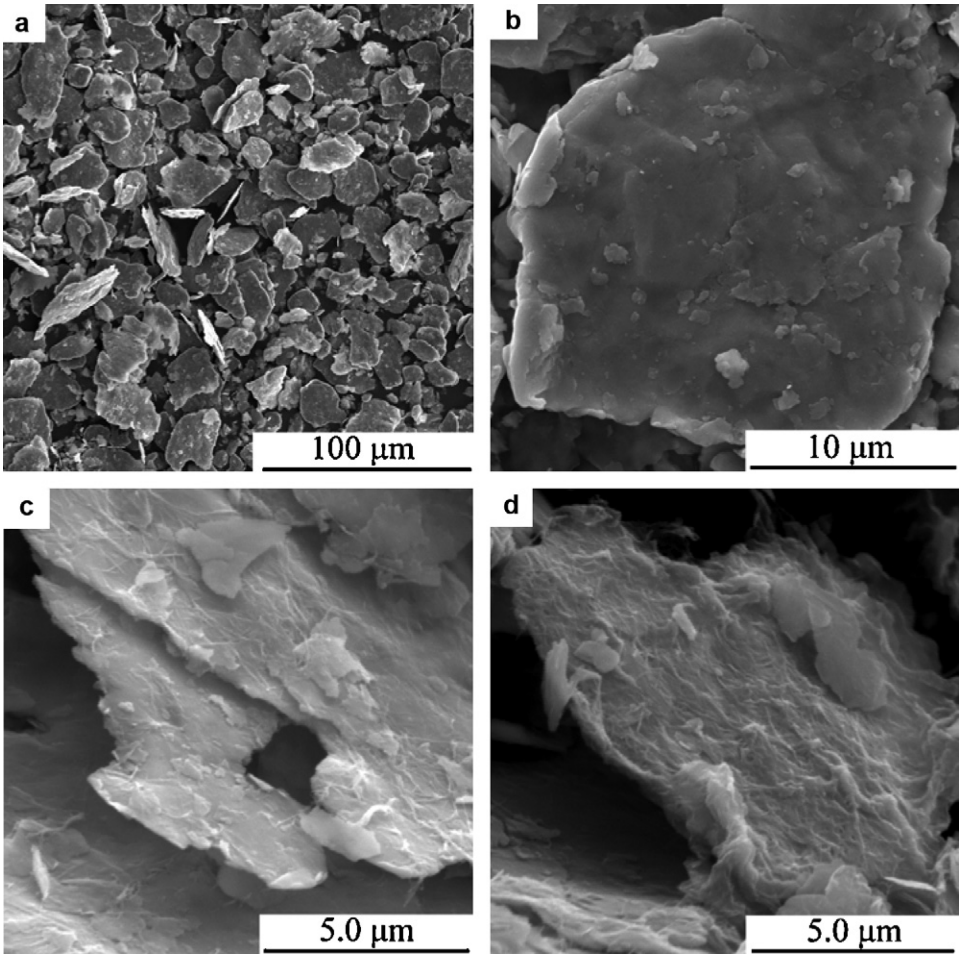

Fig. 1. The SEM micrographs of Fe–Si–Al particles: (a) and (b) as-milled (S0); (c) after surface modification with 2% nylon 6 (S1); and (d) after surface modification with 4% nylon 6 (S2).

Ltd., China) were mechanically milled for 14 h on a planetary mill at a rotation speed of 250 rpm, where anhydrous ethanol was added as the process control agent. The ball-to-powder weight ratio was 20:1.

Surface modification of Fe–Si–Al flakes with nylon 6 was performed by a melt compounding process. Firstly, the nylon 6 (purchased from Ube Industries, Ltd. Japan) was dried in vacuum at 80 °C for 24 h to eliminate the absorbed water. Then a certain amount of the as-milled Fe–Si–Al flakes and nylon 6 were added into anhydrous ethanol. The mixture was heated in a vacuum autoclave at 160 °C for 2 h with a constant stirring speed of 600 rpm. The initial heating rate was 5 °C/min, and the mixture cooled down naturally after compounding. At last, the product was washed twice with anhydrous ethanol and dried in a vacuum oven at 80 °C for 8 h. In this work, two kinds of surface modified samples were prepared with nylon 6 mass fraction of 2% and 4%, and denoted as S1 and S2, respectively. The sample of as-milled Fe–Si–Al flakes was named S0 for comparison.

The morphology of the samples was observed by a FEI Quanta 200 scanning electron microscope (SEM) and the phase was characterized by X-ray diffraction (XRD) (Philips X'Pert PRO; Cu Kα, λ = 0.1542 nm). For microwave measurement, the composite materials were homogeneously dispersed in paraffin wax with a mass fraction of 75%, and the mixture was formed into a toroidal specimen through a coaxial mould, with an inner and outer diameter of 3.04 and 7.00 mm, respectively. The relative complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) of the toroidal specimens were measured using a vector network analyzer (Agilent 8722ES) in the frequency range of 2–18 GHz.

According to the transmission line theory, the reflectivity (R, in decibels) of a single-layer metal-backed absorber for the normal incident electromagnetic (EM) wave can be calculated from the complex permittivity and permeability by the following equations [31]:

$$Z_{\text{in}} = Z_0 \left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2} \tanh\left[j\left(\frac{2\pi fd}{c}\right)(\mu_r\varepsilon_r)^{1/2}\right] \tag{1}$$

$$Z_0 = \left(\frac{\mu_0}{\varepsilon_0}\right)^{1/2} \tag{2}$$

$$R(dB) = 20\,lg\left|\frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0}\right| \quad (dB) \tag{3}$$

where Z_{in} is the input impedance of the absorber, f is the frequency of the incident EM wave, and d is the thickness of the absorber. ε_0, μ_0, c, and Z_0 are the dielectric constant, permeability, velocity of light, and impedance, respectively, all in free space.

3. Results and discussion

The SEM image of S0 is shown in Fig. 1a. It is obviously that all the as-milled Fe–Si–Al particles are in the form of flakes. The diameter of flakes is mostly in the range of 20–40 μm and the thickness is about 1 μm. The aspect ratio is as large as 20:1 at least. It clearly reveals that such large shape anisotropy is achieved for the as-milled Fe–Si–Al flakes. After surface modification, it is found that the particle surface for S1 is coated with a very thin layer of nylon (Fig. 1c). As the amount of nylon 6 reaches to 4%, a flocculent layer can be obviously observed on the particle surface for S2 (Fig. 1d), indicating that the surface coated Fe–Si–Al flakes with different amounts of nylon 6 were successfully prepared.

Fig. 2 displays the XRD patterns of S0 and S2. There are three prominent diffraction peaks in either S0 or S2, which are associated with the (1 1 0), (2 0 0) and (2 1 1) planes of α-Fe (Si, Al) solid-solution with a body-centred-cubic structure, respectively. Using the Scherrer formula and the full width at half maximum (FWHM) of the main peak, the average grain sizes for both samples are estimated to be around 13.5 nm. Under the limit of instrument sensitivity, no obvious difference is observed from the XRD patterns

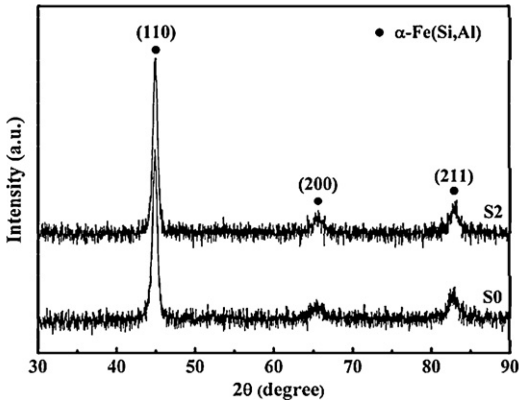

Fig. 2. The XRD patterns of the as-milled Fe–Si–Al flakes (S0) and surface modified flakes with 4% nylon 6 (S2).

for S0 and S2, indicating that there was no variation for microstructure of particles prepared by the melt compounding process and no other chemical reaction occurred in the compounding process.

The frequency dependence of the real part (ε') and imaginary part (ε'') of relative complex permittivity of S0, S1 and S2 is shown in Fig. 3. A high permittivity is observed in S0, where the values of ε' and ε'' are 55 and 32 at 2 GHz, respectively. As the frequency increases, both ε' and ε'' of S0 firstly steep decrease from 2 to 5 GHz, and then reduce slowly in the high frequency range. But for S1, ε' has the similar variation trend with S0, while ε'' is almost constant in the whole frequency range. It is worth noting that both ε' and ε'' of S1 obviously reduce in the frequency of 2–18 GHz comparing with S0, especially ε'' in the frequency of 2–5 GHz. For S2, the permittivity varies similarly to S1, only further decreases. These results demonstrate that surface modification with nylon 6 plays an important role in the reduction of permittivity.

Generally, there are several kinds of dielectric polarization mechanisms in materials, such as electronic, ionic, atomic, dipolar (orientational), and interfacial polarization (space charge polarization) [32]. For heterogeneous materials such as conductor-loaded composites, interfacial polarization is common and can result in high values of dielectric permittivity and loss which decrease rapidly with frequency [22,33]. Combined with the experimental results, it is believed that the interfacial polarization is dominant in S0 composite due to the large surface area and high electrical conductivity of the flake particles [22]. In contrast, the insulative nylon membrane as the surface modified shell in S1 and S2 composites immensely increases the resistivity of particles, thus significantly suppressing the permittivity [16,29,34]. Moreover, the as-milled Fe–Si–Al flakes can easily constitute local electric conducting networks in the matrix via Ohmic contact, resulting in an additional conduction loss in S0 composite. This is also contributed to the high ε'', especially in the lower frequency range (2–5 GHz) [32]. However, considering that the surface modification with insulative nylon membrane prevents the formation of electric conducting networks, the conduction loss severely weakens. Thus, the decrease of ε'' is more significant in the lower frequency range after surface modification. In addition, the resistivity of surface modified particles increases with increasing the amount of nylon 6 and the volume fraction of metal component decreases slightly, thus the permittivity of S2 is lower than that of S1.

Fig. 4 shows the frequency dependence of relative complex permeability of the three samples. The real part (μ') of complex permeability in S0, S1 and S2 decreases from 5.0, 4.7 and 3.7 to 1.0, 0.9 and 0.8 with increasing the frequency from 2 to 18 GHz, respectively. The imaginary part (μ'') in S0 decreases from 2.5 to 0.4 in a similar fashion, while the μ'' curves of both S1 and S2 present a peak at 2.4 GHz with maxima of 2.47 and at 3.5 GHz with maxima of 2.23, respectively. The permeability slightly decreases after surface modification, which can be ascribed to the reduction of the specific saturation magnetization of the particles after coating with nonmagnetic nylon [24]. Generally, for magnetic metal-loaded composite, the permeability spectra are mainly explained by eddy current effect and natural resonance in the GHz range. The skin depth, δ, is described by the equation $\delta = \sqrt{\rho/(\pi f \mu_0 \mu_i)}$, where μ_i and ρ are the intrinsic permeability and the electric resistivity, respectively. $\rho = 8.2 \times 10^{-7}\ \Omega\,\mathrm{m}$ for Fe–Si–Al alloy [35], and we can conclude that the skin depth of Fe–Si–Al alloy is more than 2 μm in the frequency range of 2–18 GHz [36]. Obviously, the skin depth is larger than the thickness of flakes (about 1 μm), resulting in suppression of eddy currents. Thus, the permeability spectra of the samples are mainly determined by natural resonance. Two factors, namely, the suppression of the eddy current and the reduction of the Fe–Si–Al flakes volume fraction, are mainly considered for the shift of the natural resonance frequency to a higher frequency range. It is known that eddy currents could result in low-frequency shift of the loss peak relatively to the natural resonance frequency [23]. However, the effect of the eddy current can be suppressed by decreasing electric conductivity after surface treatment [16], resulting in a high-frequency shift of the natural resonance frequency. On the other hand, as the Fe–Si–Al flakes volume fraction

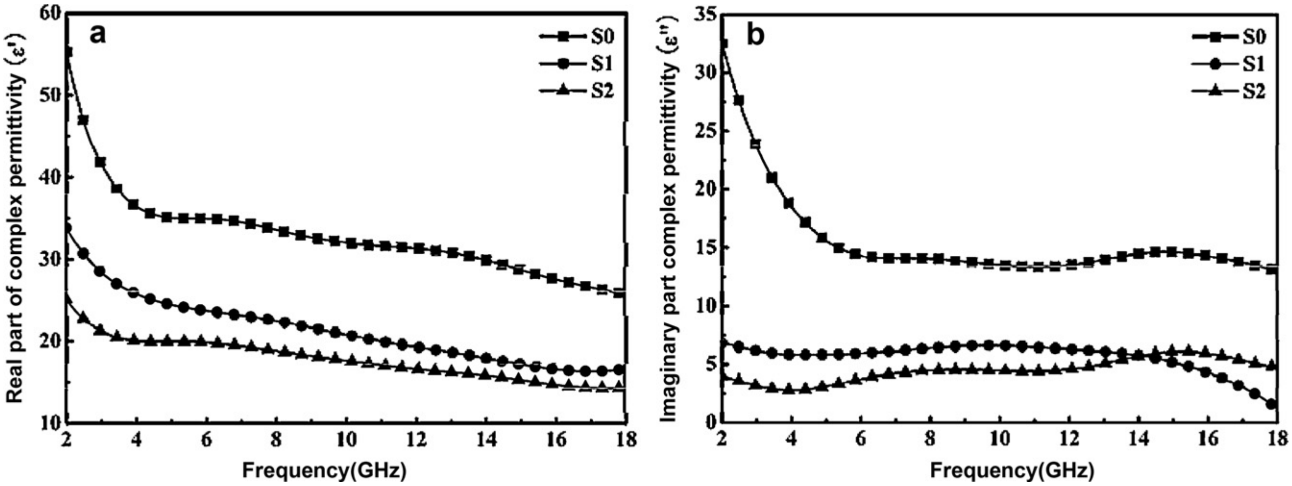

Fig. 3. The frequency dependence of relative complex permittivity of the samples: (a) the real part and (b) the imaginary part.

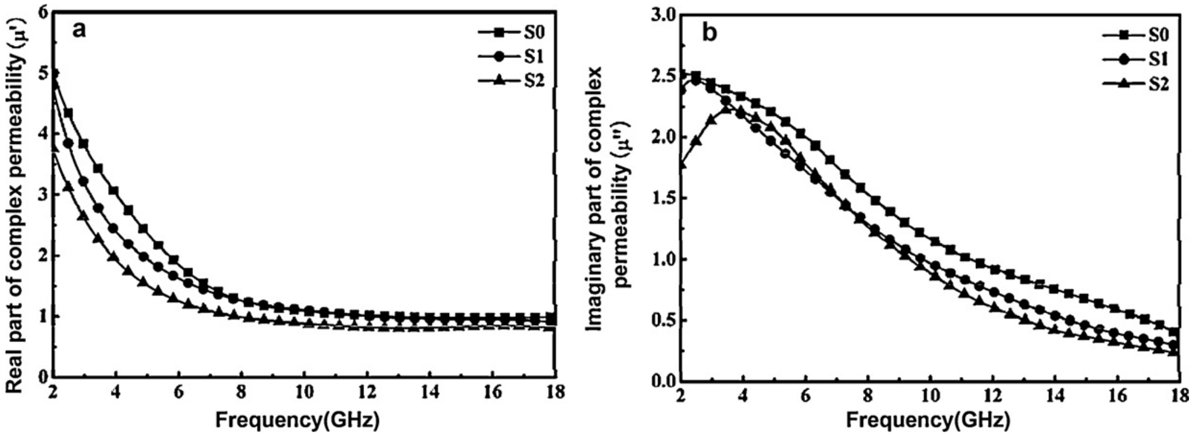

Fig. 4. The frequency dependence of relative complex permeability of the samples: (a) the real part and (b) the imaginary part.

reduces, the local demagnetizing fields add to the total anisotropy field and consequently increase the resonance frequency [37].

Fig. 5 shows the frequency dependence of calculated reflectivities (R) for the samples with different single-layer thicknesses. Apparently, all composites exhibit a low frequency band absorbing performance with the given thicknesses (more than 2 mm), and the surface modification extremely improves the absorbing performance. As shown in Fig. 5a, the minimum R is higher than −8.5 dB within the thickness range of 1.5–2.75 mm for the unmodified Fe–Si–Al flakes (S0), indicating relatively poor microwave absorption. Meanwhile, the minimum R reach to −10 dB for the modified samples (S1 and S2) as the thickness is more than 2 mm (Fig. 5b and c). It also reveals that both the minimum R and the corresponding frequency (peak frequency) decrease with increasing the given thicknesses. In addition, comparing with the absorption properties for the surface modified samples with different amounts of nylon, it is shown that both the minimum R and the peak frequency for S1 are lower than those for S2 with the same thickness. If the R value of −10 dB is considered as an adequate microwave absorption [38], and the corresponding frequency bandwidth ($R < -10$ dB) is also taken into account in the frequency range of 2–18 GHz, the optimalizing thicknesses are 2.25 mm and 2.75 mm for S1 and S2,

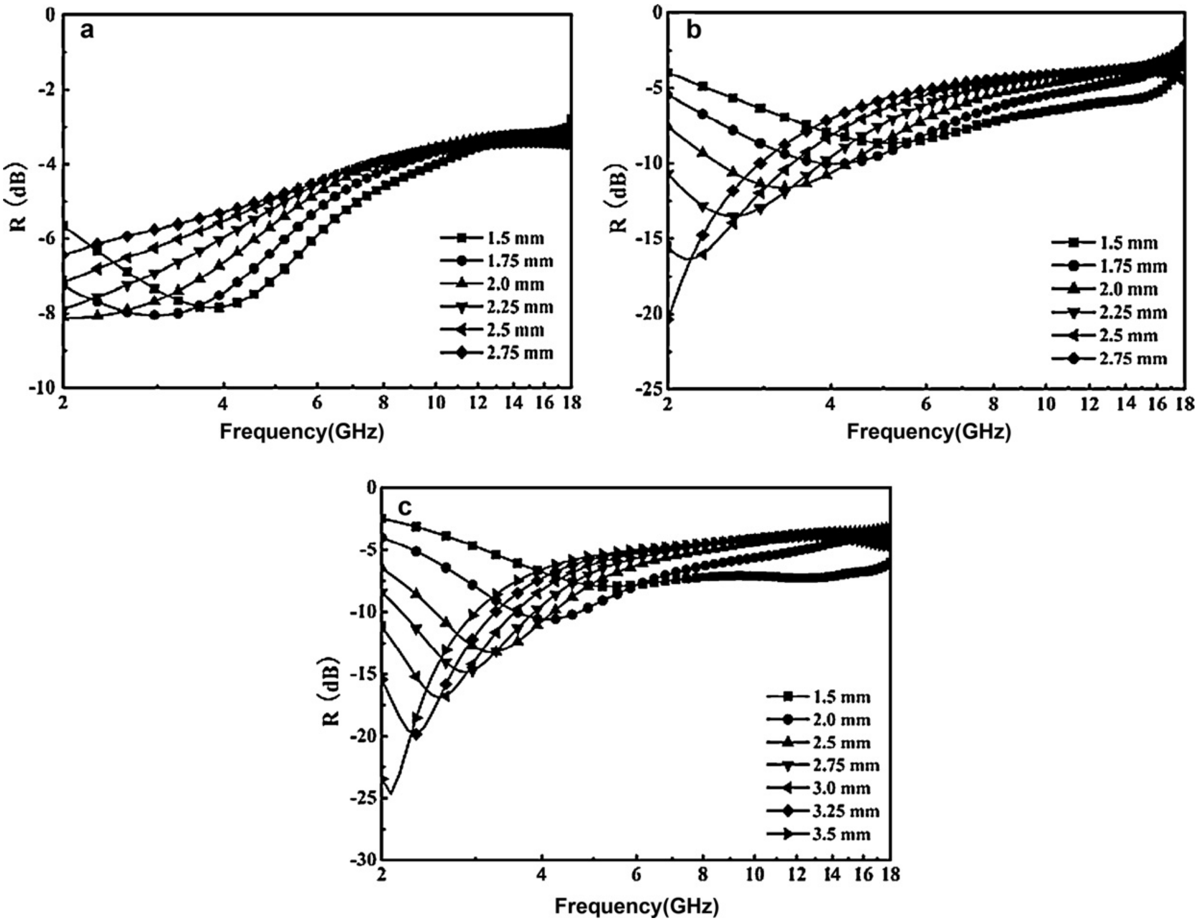

Fig. 5. The frequency dependence of calculated reflectivities (R) with different single-layer thicknesses for the samples: (a) S0, (b) S1 and (c) S2.

respectively. For S1 with the thickness of 2.25 mm, the minimum R reaches to −13.5 dB at 2.64 GHz and the frequency bandwidth ($R < -10$ dB) is 1.96 GHz (2–3.96 GHz, Fig. 5 b), while the minimum R reaches to −14.8 dB at 2.88 GHz and the frequency bandwidth is 1.60 GHz (2.24–3.84 GHz) for S2 with the thickness of 2.75 mm (Fig. 5c). Therefore, it is clear that both the modified samples exhibit good absorption properties in S-band (2–4 GHz) and that the absorption properties of S1 are better than those of other two samples in respect of the reflectivity, the bandwidth and the layer thickness.

For good absorbing performance, a magnetic composite is needed with high microwave permeability, high magnetic loss, a favorable form of frequency dependence of permeability, and a proper ratio between the permeability and permittivity [23]. It reveals that the impedance matching between the material and free space is essential for low reflectivity, which is also implied in Eq. (3). For the as-milled Fe–Si–Al flakes, the relative complex permittivity is overlarge compared with the relative complex permeability, which leads to considerable impedance mismatching and poor microwave absorption. In contrast, the microwave absorption properties are obviously improved via the surface modification, because the decrease of permittivity can give rise to the improvement of impedance matching. In addition, the composite containing Fe–Si–Al flakes as a Dallenbach layer utilizes a combination of loss and resonant cancellation for microwave absorption [39,40]. The thickness of the absorber is one of the crucial parameters to affect the minimum intensity of R and the peak frequency. For resonant cancellation of EM wave, the thickness of the absorber is required to equal to the quarter wavelength in the absorber [15,16], i.e.,

$$d_m = \frac{\lambda_m}{4} = \frac{c}{4f_m\sqrt{|\varepsilon_r\mu_r|}} \tag{4}$$

where $\lambda_m = c/(f_m\sqrt{|\varepsilon_r\mu_r|})$ is the wavelength in the absorber, d_m and f_m are the matching thickness and frequency, respectively. When the thickness of the absorber meets the condition expressed by Eq. (4), the minimum R appears at the given matching frequency. According to Eq. (4), it is reasonable that the peak frequency shifts towards a lower frequency range with increasing the thickness, and the peak frequency for S1 is lower than that for S2 with the same thickness because of the relatively higher ε_r and μ_r. Similarly, it is conjectured that the matching thickness is thinner for S1 comparing with S2 at the same matching frequency. Thus, S1 exhibits the better absorbing performance than S2 in S-band, suggesting that surface modification with the appropriate amount of nylon 6 is required, and it is concluded that the reduced permittivity and the enhanced permeability are essential for the composite containing magnetic metallic flakes used as the microwave absorbing material with thin thickness, broad bandwidth and strong absorption in GHz range.

4. Conclusions

We have successfully prepared surface modified Fe–Si–Al flakes with nylon 6 by a simple melt compounding method. The electromagnetic and microwave absorption properties for as-milled and surface modified samples were investigated in the frequency range of 2–18 GHz. The as-milled flakes exhibit a large permittivity. After surface modification, the permittivity of the flakes decreases dramatically with increasing the amount of nylon 6, while the permeability decreases not obviously. It is found that the microwave absorption performance can be significantly improved by surface modification owing to the improvement of impedance matching. The reflectivity exceeding −10 dB for surface modified composite with 2% nylon 6 is obtained in the frequency range of 2–3.96 GHz with a layer thickness of 2.25 mm, indicating that the composite containing modified Fe–Si–Al flakes with an appropriate amount of nylon 6 is an attractive candidate for a thin microwave absorbing material in S-band.

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