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Enhanced microwave absorption properties of the milled flake-shaped FeSiAl/graphite composites

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ABSTRACT

FeSiAl alloy powders in an irregular shape mixed with graphite were ball-milled for 24 h to achieve flake-shaped FeSiAl/graphite composites. The size of the milled composite particles is in the range of 5–40 μm with the average thickness less than 1 μm. The complex permittivity ($\varepsilon' - j\varepsilon''$) and permeability ($\mu' - j\mu''$) are measured by using the transmission/reflection method in the frequency range of 2–18 GHz. Compared to the raw irregular-shaped FeSiAl, the complex permittivity (ε' and ε'') of the milled composites are greatly enhanced as the weight ratio of graphite in the composite samples increases. For milled FeSiAl/graphite (weight ratio of 8:2) composites absorber with a coating layer thickness of 3 mm, the reflection loss reaches a minimum of −21.0 dB at 6.7 GHz with −10 dB bandwidth of 2.0 GHz. The microwave absorption is significantly enhanced as the weight ratio of graphite in the FeSiAl/graphite composite increases from 10% (9:1) to 20% (8:2). Moreover, the absorption bandwidth with reflection loss exceeding −10 dB can reach up to 2.4 GHz with the coating thickness only of 1.5 mm, and the absorption frequency range can be tuned easily by varying the coating thickness. The results indicate that the milled flake-shaped FeSiAl/graphite composites can be potential microwave absorbers in the higher GHz range compared with those of raw FeSiAl and milled FeSiAl absorbers.

1. Introduction

The use of gigahertz (GHz) electronic systems and telecommunications has been increasing due to the need of high speed data transmission by using ultra high frequency (UHF) in the range of 0.3–3 GHz and super high frequency (SHF) in the range of 3–30 GHz. This frequency increase, however, has resulted in a growing and intense interest in the development of GHz-electromagnetic (EM) wave absorbers to solve the induced EM interference (EMI) problem. A number of materials, such as iron, cobalt, nickel, metal alloys and ferrites, are used as electromagnetic absorbers. However, high specific gravity and high cost limit these conventional microwave absorption materials' application [1]. Microwave absorption materials with high absorption rate, wide absorption band, thin coating and light weight are hot-pursued.

FeSiAl alloy as a traditional soft magnetic material applied in EMI area, has attracted much interests due to its excellent magnetic properties, good temperature stability and low cost. However, these materials have some difficulties in increasing the permeability in GHz region due to their low Snoek's limit and can only be used as good microwave absorbers in the low GHz range [2,3]. Recently, several researchers suggest that the flake-shaped magnetic particles can have a higher resonance frequency above Snoek's limit in the gigahertz frequency range due to their low eddy current loss coming from the particle shape effects [4–7]. On the other hand, the light-weight carbon-based materials are outstanding microwave absorbents because of their dielectric properties and excellent cooperative effect when they were mixed with magnetic absorbents [8,9]. Specially, flake graphite has attracted extensive concerns as microwave absorption materials due to its low density, low cost, good electrical conductivity, high corrosion-resistance and high temperature-resistance [10,11]. To develop microwave absorbers in higher GHz range, FeSiAl alloy powder in an irregular shape mixed with light-weight graphite, was ball-milled for 24 h to achieve flake-shaped FeSiAl/graphite composites. The planar anisotropy produced by the material processing as well as combining FeSiAl as a magnetic material with graphite as a conductive material can lead to microwave absorbers with both high magnetic and dielectric losses which are tunable by adjusting the ratios of graphite in the composites. Thus, the electromagnetic properties of the raw FeSiAl alloy, usually used in the low frequency range, can exhibit greatly improved microwave absorption in the higher gigahertz frequency range by ball milling

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with graphite to obtain flake-shaped FeSiAl/graphite composite absorbers.

2. Experimental details

Commercially available FeSiAl alloy (Al 5%, Si 10%, and Fe 85%) was used in this study. The raw FeSiAl particles are of irregular shape and the average particle sizes are between 20 and 50 μm. The flake-shaped FeSiAl/graphite composites were obtained by ball milling the mixed powder of FeSiAl alloy and graphite for 24 h. The weight ratio of FeSiAl alloy to graphite varied from 9:1 to 8:2. As a control group, the milled flake-shaped FeSiAl powder was prepared by ball milling raw FeSiAl alloy for 24 h as well. The morphology and microstructure of the products were studied by employing scanning electron microscopy (SEM, Hitachi S-4800 and Oxford JSM-6700F) and X-ray diffractometer (XRD, Japan Rigaku D/MAX-cA) using a Cu*K*a radiation (λ = 1.5406 Å), respectively.

The raw FeSiAl, milled flake-shaped FeSiAl, and milled FeSiAl/graphite composite powder with a weight ratio of 40 wt.%, were added to a paraffin matrix and then mixed uniformly to prepare the microwave absorber coating layers. The as-prepared composite absorbers were made into toroidal-shaped specimens with 7.0 mm outer diameter and 3.04 mm inner diameter for transmission/reflection measurements. The specimen under test was tightly inserted between the inner and outer conductor of the Agilent coaxial transmission airline (850151-60010). Calibration based on the Agilent calibration kit (85050C) was performed before the experiments. The complex scattering parameters (S_{11} and S_{21}) for the TEM mode were measured by using an Agilent 8510C vector network analyzer in the frequency range from 2 to 18 GHz as shown in Fig. 1. The frequency-dependent complex permittivity and permeability (ε', ε'', μ', and μ'') for each sample were then obtained from Agilent 85071E material measurement software which is based on Nicolson–Ross's reflection/transmission formulation [7].

The reflection loss (RL) of electromagnetic waves of as-prepared samples backed by a perfect conductor can be calculated from the measured complex relative permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) and permeability ($\mu = \mu' - j\mu''$) for a given frequency and absorber coating layer thickness by using the following equations [12–14]:

$$Z_{in} = Z_0\sqrt{\mu/\varepsilon}\tanh[j(2\pi fd/c)\sqrt{\mu\varepsilon}] \quad (1)$$

$$RL = 20\ \log|(Z_{in} - Z_0)/(Z_{in} + Z_0)| \quad (2)$$

where Z_{in} is the input impedance when the electromagnetic wave incidence is normal to the absorber layer, f is the frequency of the electromagnetic wave, d is the thickness of the absorber layer, c is the velocity of light, and Z_0 is the impedance of free space. For impedance matching (zero reflected condition), the matching frequency (f_m) and matching thickness (d_m) can be determined by setting Z_{in} = 1 in Eq. (1).

The experimental RL data was also measured by the terminated one-port technique using a short S_{11} test fixture according to the literature [15]. The simulated data are compared to those from the experimental one-port technique.

3. Results and discussions

The morphologies of the raw FeSiAl, the milled flake-shaped FeSiAl and the milled FeSiAl/graphite composites are shown in Fig. 2. The raw FeSiAl powder in an irregular shape with particle size of 20–50 μm can be seen clearly in Fig. 2(a). After the milling process, the particles in the milled FeSiAl (Fig. 2(b)) and the milled FeSiAl/graphite composites (Fig. 2(c and d)) become flaky. The sizes of the milled products are in the range of 5–40 μm, which are a little bit smaller than those of the raw FeSiAl particles mainly caused by the effect of microforging and cold-welding during ball milling process. The thicknesses of all milled products are below 1 μm, which is propitious to decrease eddy current loss. Accordingly, the aspect ratios, i.e., length/thickness of the milled product, are much higher than that of the raw FeSiAl.

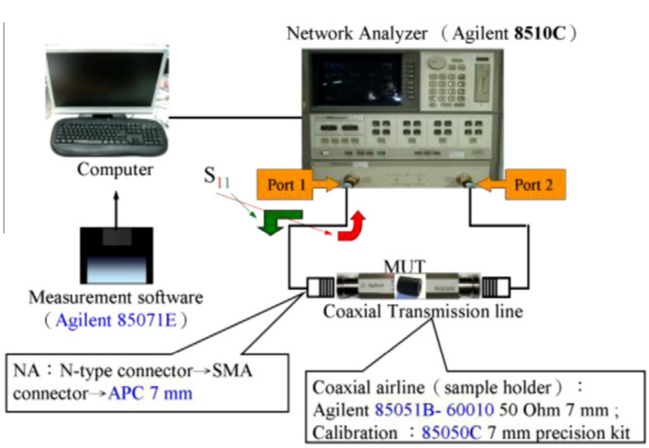

Fig. 1. Measurement system.

X-ray diffraction (XRD) patterns of the raw FeSiAl, the milled flake-shaped FeSiAl and the milled FeSiAl/graphite composites are shown in Fig. 3. The diffraction peaks (1 1 0), (2 0 0) of α-Fe crystalline phase are clearly displayed for the raw FeSiAl sample. After ball milling, the α-Fe diffraction peaks of both milled flake-shaped FeSiAl and milled FeSiAl/graphite composites are slightly broaden, suggesting a more disordered crystal structure, which is due to the reduction of grain size and the increase of internal strain during milling [4]. The XRD pattern of the milled FeSiAl/graphite composites shows two new diffraction peaks at 26° and 55°, which denote the typical reflections (0 0 2) and (0 0 4) of the graphite, respectively.

Fig. 4 shows the complex permittivity and permeability of the raw FeSiAl, the milled FeSiAl, and the milled flake-shaped FeSiAl/graphite composites embedded in paraffin matrix with the same weight fraction of 40%. As shown in Fig. 4(a), the real part of permittivity (ε') for the FeSiAl/paraffin absorber is almost constant (~4) over the whole 2–18 GHz frequency range. A significant improvement in the dielectric loss with the addition of graphite powders is noted. After ball milling, the ε' of the milled FeSiAl/paraffin absorber increased 25–37% (ε' = 5–5.5) compared to that of the raw FeSiAl/paraffin absorber. With 10 wt.% and 20 wt.% of the graphite powders were added into the milled flake-shaped FeSiAl/graphite composites, a substantial increase from 63% to 73% (ε' = 6.5–6.9) and 213–228% can be observed. More significantly, the corresponding imaginary part of permittivity (ε'') of the milled flake-shaped FeSiAl/graphite composites increased from 0.19–0.71 to 1.36–3.16 as the graphite/FeSiAl weight ratios increased from 1/9 (10 wt.%) to 2/8 (20 wt.%). The notable increase of complex permittivity for the milled flake-shaped FeSiAl/graphite composites can be mainly attributed to the electrical charge of flake powder can be more easily polarized, the space-charge polarization enhance with the increase of surface area, and the eddy current loss reduce with the particle shape change from particle to thin flake [16–18].

As shown in Fig. 4(c), it can be observed that the real part of complex permeability (μ') of the raw FeSiAl, the milled FeSiAl, and the milled flake-shaped FeSiAl/graphite absorbers all exhibit peaks at low frequency around 2.5 GHz and then decrease with increasing frequency in the range of 2.5–18 GHz. The real part of complex permeability of milled flake-shaped FeSiAl and the milled flake-shaped FeSiAl/graphite absorbers are slightly increased as compared to that of raw FeSiAl absorber, which may arise from the orientation of magnetic moments in FeSiAl particles. As the shape of FeSiAl alloy change from irregular to flaky, the orientation of magnetic moments tends to lie in the particle plane [19]. It can be seen from Fig. 4(d), the imaginary parts of complex permeability (μ'') of all milled samples have obviously increased when they are compared to the raw FeSiAl with irregular shapes. Therefore, the complex permeability (μ' and μ'') is strongly dependent on the shape of the FeSiAl particles. However, the effect of the added graphite in the FeSiAl/graphite composite on its complex permeability is not significant. This is consistent with the fact that graphite is nonmagnetic.

The experimental and simulated reflection losses data for raw FeSiAl, milled FeSiAl and milled FeSiAl/graphite composite powders in a paraffin matrix are compared in Fig. 5, which are in agreement with each other. All the composite absorbers were processed at 40% powder weight fraction with the coating thickness of 3 mm.

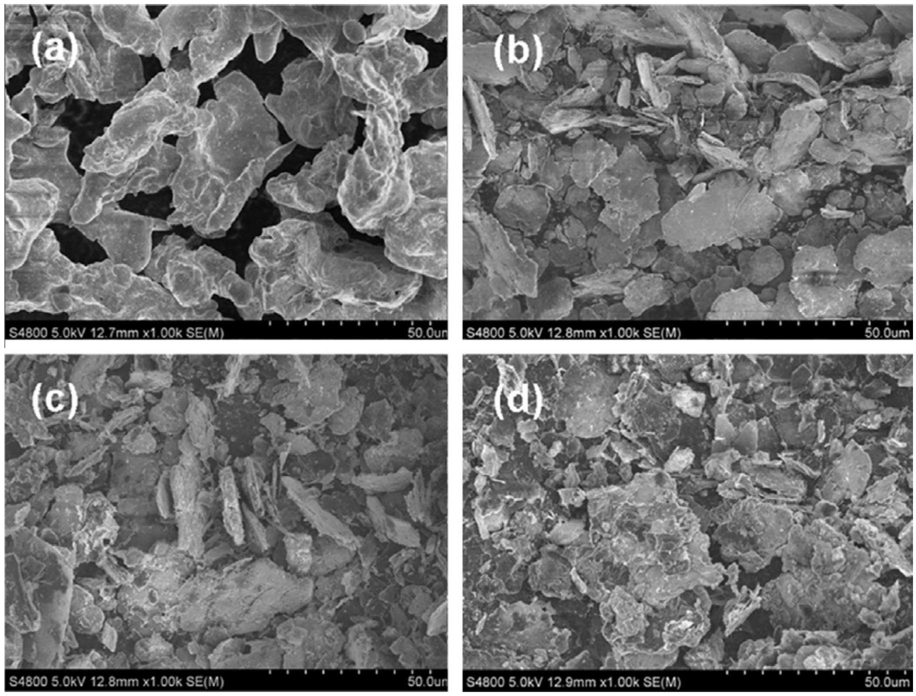

Fig. 2. SEM images of (a) raw FeSiAl, (b) milled flake-shaped FeSiAl, and FeSiAl/graphite composites with FeSiAl: graphite weight ratios of (c) 9:1 and (d) 8:2.

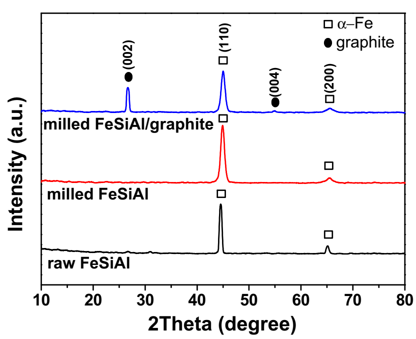

Fig. 3. XRD patterns of the raw FeSiAl, the milled flake-shaped FeSiAl and the milled FeSiAl/graphite composites.

The results of calculations show that the raw FeSiAl/paraffin coating exhibits a poor absorption of only −3.6 dB at 10.7 GHz. The absorption peak of the milled flake-shaped FeSiAl/paraffin has slightly increased to −5.1 dB at 10.3 GHz. It should be noted that the microwave reflection losses are remarkably enhanced when the graphite powders are added into the FeSiAl during the ball milling process. The minimum reflection loss of the milled flake-shaped FeSiAl/graphite composite with mass ratio of 9:1 achieves −12.0 dB at 9.6 GHz. The bandwidth less than −10 dB was 2.1 GHz which was just in the X-band frequencies. Moreover, the minimum reflection loss of the milled FeSiAl/graphite composite with weight ratio of 8:2 reaches −21.0 dB at 6.7 GHz and the −10 dB bandwidth keeps as wide as 2.0 GHz. Importantly, the as-prepared milled FeSiAl/graphite samples exhibit a wider band-width (2.1 and 2.0 GHz versus 1.96 and 1.6 GHz in Ref. [6]), stronger absorption (−21.0 dB at 6.7 GHz versus −6.2 dB at 3 GHz in Ref. [4], −9.74 dB at 1.23 GHz in Ref. [2], −14.8 dB at 2.88 GHz in Ref. [6]) and lighter weight (40% versus 85% in Ref. [4], 75% in Ref. [2], 75% in Ref. [6]) than that reported in the similar literature. Furthermore, the absorption frequencies have also been greatly increased (9.6 and 6.7 GHz versus 3 GHz in Ref. [4], 1.23 GHz in Ref. [2], 2.88 GHz in Ref. [6]).

For the milled flake-shaped FeSiAl/graphite composites, the intensity of reflection loss peaks are significantly enhanced with the increasing of the mass content of graphite, meanwhile, the absorption frequency shift to a lower frequency range. This can be attributed to the increase of the complex permittivity and permeability (Fig. 4). It is well known that the relationship between matching frequency and thickness can be expressed by [20]

$$f_m = \frac{c}{4d_m}\frac{1}{\sqrt{\varepsilon'\mu'}}\left(1 + \frac{1}{8}\tan^2\delta_\mu\right)^{-1} \tag{3}$$

where f_m and d_m are the matching frequency and thickness and δ_μ is the magnetic loss tangent. It is clear that the matching frequency decrease by $\sqrt{\varepsilon'\mu'}$ times at a given thickness. As shown in Fig. 4, the values of ε' and μ' are both obviously increased as the mass content of graphite in the FeSiAl/graphite composite increases from 10% (9:1) to 20% (8:2), hence, the reflection loss peaks shift to lower frequency region for the higher value of ε' and μ'. This study has demonstrated that the milled flake-shaped FeSiAl/graphite composites can be used as good microwave absorbers in the higher GHz range. The results indicated that the position and intensity of the reflection loss peak is quite sensitive to the mass content of graphite. That is, the maximum reflection loss increases and the matching frequency shifts to low frequency with the increasing mass content of graphite, which is also attributed to the increase of complex permittivity and permeability.

Fig. 6 shows the relationship between the simulated reflection loss and frequency for the composites with 40 wt.% as-prepared FeSiAl/graphite powders at different thickness. The minimum reflection losses were found moving toward the lower frequency region with thickness increasing. The microwave absorption properties of all as-prepared FeSiAl/graphite (weight ratio of 8:2) are better than that of FeSiAl/graphite (weight ratio of 9:1) with the same thickness. It is worth noting that the value of reflection loss exceeding −10 dB can be obtained in the range of 3.2–16.9 GHz for the milled FeSiAl/graphite (weight ratio of 8:2) composite with a variation in thickness from 1 to 5 mm. These results are of

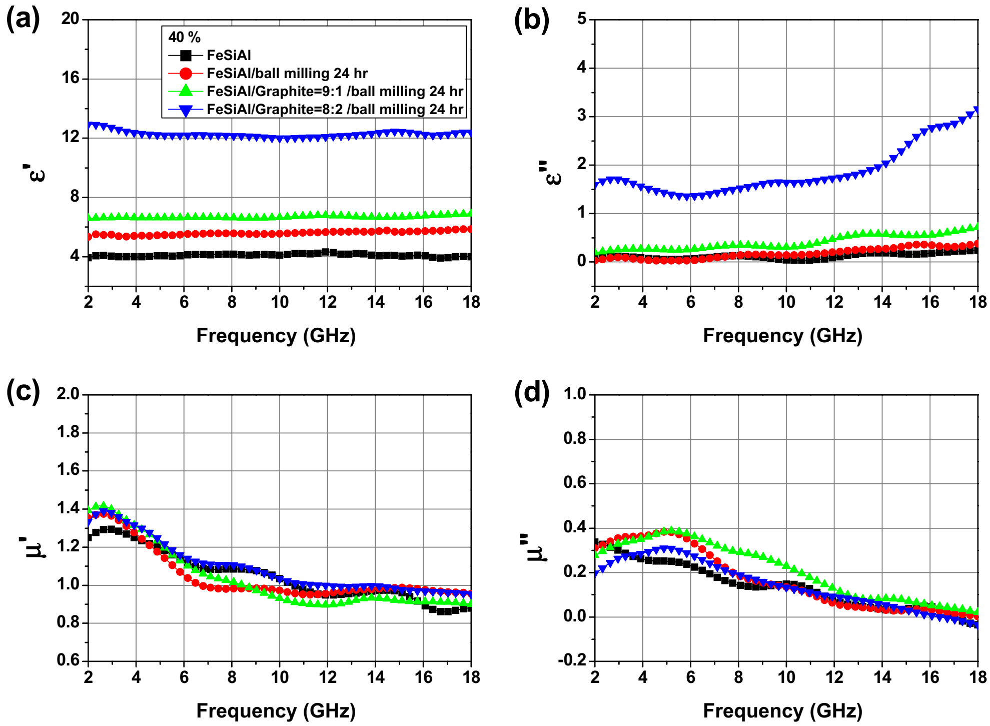

Fig. 4. (a) Real part and (b) imaginary part of complex permittivity, (c) real part and (d) imaginary part of complex permeability of raw FeSiAl, milled FeSiAl, and the milled flake-shaped FeSiAl/graphite composites.

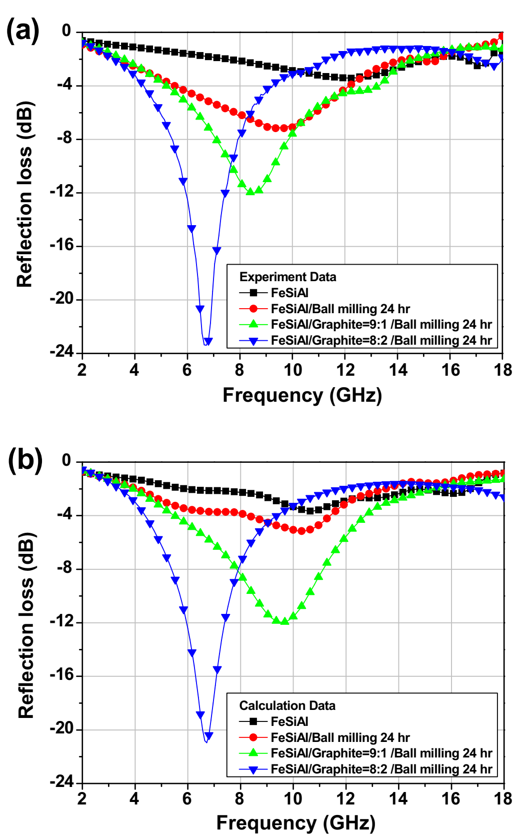

Fig. 5. (a) The experimental and (b) simulated reflection losses of raw FeSiAl, milled FeSiAl, and the milled flake-shaped FeSiAl/graphite composites in paraffin matrix with a coating layer thickness of 3 mm, respectively.

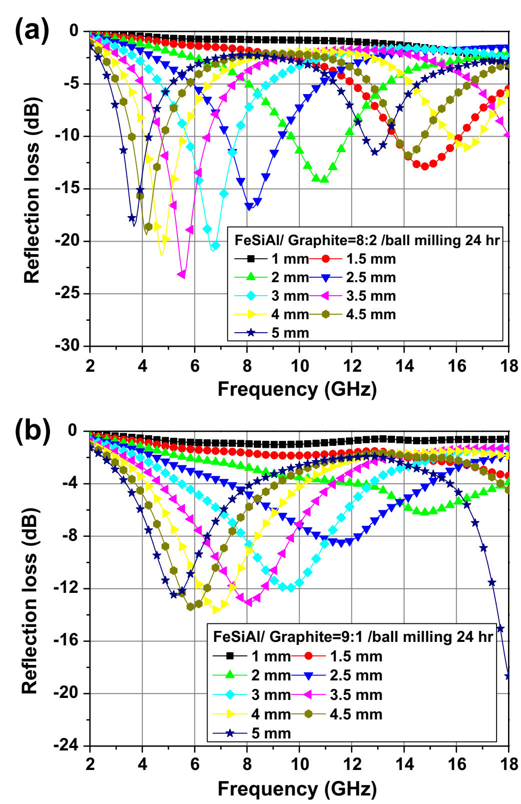

Fig. 6. The simulated reflection losses for the milled flake-shaped FeSiAl/graphite composites with weight ratio of (a) FeSiAl/graphite = 8:2 and (b) 9:1 in different thickness (1–5 mm).

importance since the absorption frequency ranges of the milled FeSiAl/graphite composites can be tuned easily by changing the thickness of the absorbers, and broadband absorption can be achieved by means of multilayered absorbing structure [21].

Moreover, the absorption bandwidth with reflection loss lower than −10 dB of the composite with the thickness only of 1.5 mm can reach up to 2.4 GHz (from 13.68 to 16.08 GHz), which is wider than the reported Fe–Si–Al flakes with nylon (−10 dB bandwidth is 0 GHz) with the same thickness [6]. In conclusion, the as-prepared composite can be a potential microwave absorbing material with thin coating, lightweight, strong absorption and broadband absorption, and its microwave absorption property can by tuned easily by varying the mass content of graphite and layer thickness of the samples.

4. Conclusions

In summary, the irregular-shaped FeSiAl powder mixed with graphite was ball-milled and the as-prepared flake-shaped FeSiAl/graphite powder was used as the absorbent fillers in paraffin matrix. The results of this study have demonstrated that the milled FeSiAl/graphite absorbers possess higher permittivity, slightly increased permeability, and better microwave absorption properties than those of raw FeSiAl powders in the frequency range of 2–18 GHz. Additionally, the absorption frequency ranges of the milled FeSiAl/graphite composites can be tuned easily by varying the coating layer thickness. And the absorption bandwidth with reflection loss exceeding −10 dB can reach up to 2.4 GHz with the thickness only of 1.5 mm, indicating that the composite can be used as an attractive candidate for a thin microwave absorbing material. The results also indicate that, although the raw FeSiAl powder is a kind of good EM wave absorbers in the low GHz range, the milled flake-shaped FeSiAl/graphite composites exhibit superior microwave absorption performance due to the combination effects of high dielectric loss property of the added graphite and the high planar anisotropy of the flake-shaped particles obtained after the ball-milling.

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