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**PAPER**

Tb$_{0.2}$Dy$_{0.8}$(Fe$_{0.8}$Co$_{0.2}$)$_{1.93}/$Polyaniline composites as an excellent absorber against electromagnetic pollution

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**Abstract**

A soft magnetic alloy Tb$_{0.2}$Dy$_{0.8}$(Fe$_{0.8}$Co$_{0.2}$)$_{1.93}$ (TDFC) was prepared by combining the arc-melting process and high-energy ball-milling method. The obtained alloys were further modified by polyaniline (PA) via chemical oxidation polymerization method. The magnetic properties, microstructures and microwave-absorption properties of fabricated TDFC/PA composites were investigated in detail. The results show that the reflection loss of TDFC/PA composites reached $-38.3$ dB at 17.8 GHz with merely 1.6 mm thickness. The effective bandwidth $4.6$ GHz was obtained at 1.9 mm, which almost covered the whole Ku-band (12–18 GHz). The results of impedance matching indicate that the TDFC/PA composites possess good impedance matching due to the suitable complex permeability and complex permittivity, which contribute to excellent microwave absorption. Hence, the TDFC/PA composites have great potential in the microwave-absorption field. This work is significant for the further investigation and application of magnetostrictive magnets.

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**1. Introduction**

Serious electromagnetic interference and pollution have given a priority toward research on microwave absorption materials with low reflectivity [1–4]. Among all of the candidates, magnetic fillers have attracted a great deal of attentions in recent years due to their unique properties [5, 6]. Therefore, it is urgent to find a magnetic and multifunctional microwave-absorption material. As a microwave absorber, it is important to possess matched property of complex permittivity and complex permeability. The soft magnetic R$_x$M$_y$-type alloys with planar anisotropy possess appropriate conductivity [7], high initial permeability and high resonance frequency [8–12], which provide a great possibility that these materials possess good microwave-absorption properties. Tb-Dy-Fe-type alloy as a kind of typical magnetostriction material with planar anisotropy have appropriate conductivity and high initial permeability, which has been widely applied in the areas of medicine, electronics, military, agriculture and so on [13–17]. In addition, it was found that Co substitution for Fe will result in an increasing of Curie temperature $T_C$ [18, 19]. However, very few studies are associated with the microwave-absorption properties of (Tb-Dy-Fe-Co)-alloys.

Although the bulk alloy has good conductivity, the conductivity of corresponding powder system is poor. Therefore, it is necessary to introduce a medium with high conductivity for enhancing the permittivity to achieve suitable impedance matching [20–22]. Polyaniline (PA) modified with proton acid (e.g. hydrochloric acid) possesses excellent dielectric property due to the effect of conjugated $\pi$ electrons [23]. Besides, PA has the simple preparation process and the stable chemical properties. Thus, PA is a great candidate as a conductive medium to enhance the permittivity of alloy powers. It is expected to obtain excellent microwave-absorption properties of (Tb-Dy-Fe-Co)/PA composites.

In this work, we report a soft magnetic Tb$_{0.2}$Dy$_{0.8}$(Fe$_{0.8}$Co$_{0.2}$)$_{1.93}$ (TDFC) alloys with high permeability. The alloy was modified by dielectric PA via chemical oxidation polymerization method, forming TDFC/PA...
composites with wrapped structure as an excellent microwave absorber. The high-frequency electromagnetic parameters and microwave-absorption properties of samples were studied in detail. The results reveal that the TDFC/PA composites possess excellent microwave-absorption performances for their high absorption intensity and wide absorption bandwidth at a rather low thickness. This work is significant for the further investigation and application of magnetostrictive magnets.

2. Experimental

2.1. Synthesis of TDFC particles

TDFC alloys were prepared in high-pure argon atmosphere by arc-melting method using 99.8% pure metallic substance (Tb, Dy, Fe and Co) as raw materials. The bulk TDFC was obtained by cooling to room temperature. In order to obtain submicron powders, the bulk samples are pulverized into small-sized powders by a simple vibration-pulverization method. Subsequently, the prepared TDFC powders were further smashed into submicron powders by high-energy ball-milling method using ethanol as medium.

2.2. Polymerization reaction of aniline and preparation of samples

PA was employed to wrap the TDFC particles by in situ chemical oxidation polymerization method [24]. The detailed process is as below: 1 g TDFC powders were mixed with 10 ml deionized water under continuous mechanical stirring. 19.5 ml diluted hydrochloric acid was added into 1.5 ml aniline with continuous magnetic stirring. The above two solutions were mixed together. Subsequently, 3.2 g ammonium persulfate (\((\text{NH}_4)_2\text{S}_2\text{O}_8\)) was added dropwise into the above mixed solutions for sufficient polymerization reaction. The obtained products were centrifuged and dried for 24 h at 70 °C. The TDFC/PA composites were mixed with paraffin at the mass percent of 30 wt% and 50 wt%, respectively. Afterward, circular specimens with outer diameter of 7 mm and inner diameter of 3.02 mm were prepared by a mould for next electromagnetic parameter measurement.

2.3. Material characterization

X-ray diffraction (XRD) was implemented with Cu Kα radiation in a Rigaku D/max-2500PC diffractometer at a scan rate of 8° min⁻¹ from 15° to 90°. The magnetic hysteresis loop of samples was measured by a vibrating sample magnetometer (VSM Lakeshore-7410, America). Scanning electronic microscope (SEM) images were obtained by Sirion 200. The electromagnetic parameters of samples were determined in the frequency range of 1-18 GHz using an Agilent N5230C network vector analyzer. The relevant calculations for data in this work were achieved by Matlab tool.

3. Results and discussion

Figure 1(a) shows XRD patterns of TDFC powders, which well matched the patterns of DyFe₃ phase [PDF#39-1473], revealing that the alloys have the hexagonal structure of DyFe₃-type. The strong peak of (116) represents the preferable orientation of crystallographic plane of TDFC alloys. A few very weak peaks at 62° and 66° can be attributed to the existing of DyFe₂ phase, which resulted from local heterogeneous mixing during the process of electric arc-melting of raw materials. The hysteresis loop of the TDFC powders at 300 K is shown in figure 1(b). A
low coercivity ($H_c$) (about 100 Oe) and a high saturation magnetization ($M_s$) (63 emu g$^{-1}$) can be observed. The magnetism comparisons of TDFC and another two homotypic ferrites [25, 26] were given in Table 1. It can be observed that the $M_s$ of TDFC is obviously larger than those of another two ferrites due to its ferromagnetic nature.

Figure 2 depicted the micromorphology of TDFC alloys and TDFC/PA composites. In Figure 2(a), it can be observed that the particles have irregular shape with distinct sizes. The higher magnification of TDFC particles is shown in Figure 2(b). After the polymerization reaction, the TDFC surfaces nearly have been wrapped entirely by PA layers, as shown in Figure 2(c). The detailed structure of PA was shown in Figure 2(d). Owing to the fluffy and porous structure of PA layers, the microwave can be reflected repeatedly and absorbed multiply inside the TDFC/PA composites [27], which would be beneficial for microwave absorption. Meanwhile, such a structure formed by PA can protect alloys from oxidation.

Figures 3(a) and (b) illustrated the frequency dependence of complex permittivity and dielectric loss tangents for (TDFC/PA)/paraffin samples at different mass ratios of TDFC/PA in paraffin. In Figure 3(a), the two $\varepsilon'$ values decrease to a constant at higher frequencies, which can be explained by Debye relaxation mechanism [28]: $\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega \tau)^2}$. Meanwhile, the $\varepsilon''$ values of two samples in the frequency range of 1–18 GHz have a slight fluctuation around 10 and 3, respectively. As shown in Figure 3(b), dielectric loss of 50 wt% sample is obviously higher than those of 30 wt% due to the higher content of dielectric PA. To better understand the dielectric loss mechanism, the Cole-Cole semicircle was introduced. The relationship between $\varepsilon'$ and $\varepsilon''$ can
be obtained by Debye relaxation, which can be expressed as following equation [29, 30]:

\[
(\varepsilon' + \varepsilon_\infty)^2 + (\varepsilon'')^2 = (\varepsilon_s - \varepsilon_\infty)^2
\]

Where \(\varepsilon_s\) is static permittivity and \(\varepsilon_\infty\) is relative permittivity at infinite frequency. It can be concluded that the \(\varepsilon' - \varepsilon''\) curves would be a semicircle, named as Cole-Cole semicircle. Each Cole-Cole semicircle presents one Debye relaxation process. As shown in figure 3(c) and figure 3(d), some distinguishable Cole-Cole semicircles appear in the two \(\varepsilon' - \varepsilon''\) curves, indicating multiple dielectric polarization relaxation occurred in composites. Irregular profiles of \(\varepsilon' - \varepsilon''\) curves may stand for other relaxation mechanism. For \((\text{TDFC/PA})/\text{paraffin}\) composites, the fluffy and porous structure is believed to play an important role in the electron relaxation mechanism. A large amount of interfacial polarizations formed at the interfaces of TDFC and PA as well as the multielectron polarization in the polymer chain of PA.

In figure 4(a), the \(\mu'\) values of both of two samples slightly fluctuated around 1, while the \(\mu''\) curves of 30 wt% and 50 wt% samples present a strong peak at 15 GHz and 9 GHz, respectively. The curve of \(\tan\delta\mu\) had the same variation trend with that of \(\mu''\) as shown in figure 4(b). For the TDFC alloys, the magnetic loss is generally believed to be the eddy current effect [31, 32] and natural resonance [11, 33]. The eddy effect can be judged by equation [34]: \(\mu''(\mu')^{-2}f = 2\pi\mu_0f^2\sigma\), where \(f\) is applied frequency, \(\mu_0\) is permeability in free space, \(d\) is diameter of particles and \(\sigma\) represents electric conductivity. According to the equation, if the eddy effect presents in the composites, the values of \(\mu''(\mu')^{-2}f^{-1}\) should be constant. The results of the dependence of \(\mu''(\mu')^{-2}f^{-1}\) on frequency are shown in figure 4(c), it can be observed that the values of \(\mu''(\mu')^{-2}f^{-1}\) have a large fluctuation in the range of 1–3 GHz, while keep a constant in the range of 3–18 GHz, indicating that the eddy current effect mainly occurred in the range of 3–18 GHz. The fluctuation may be attributed to ununiform particle sizes and the natural resonance effect. The natural resonance was described as the following formulas [11]:

\[
K = \mu_0 M_s H_c / 2
\]

\[
H_a = 4|K| / (3\mu_0 M_s)
\]

\[
2\pi f_r = rH_a
\]

Where \(K\) is anisotropy constant, \(\mu_0\) is permeability in free space, \(M_s\) and \(H_c\) are saturation magnetization and coercive force, respectively, \(r\) is gyromagnetic ratio, \(H_a\) is the anisotropy energy. From the above formulas, it can be easily known that a low \(H_a\) will results in a low \(H_a\) and \(f_r\). For TDFC alloys, the value of \(H_a\) is only about 100 Oe. Thus, influence of natural resonance is slight compared to the eddy effect.
In order to further study the microwave absorption performance of samples, the corresponding reflection loss values (RLs) were calculated by equations [35]:

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

(5)

\[
RL = 20 \log \left| \frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0} \right|
\]  

(6)

The frequency dependences of RLs for samples are shown in figures 5(a) and (b). It can be observed that the peaks of RLs shift to lower frequency with increasing the sample thicknesses, which can be explained by Quarter-wave theory [36]:

\[
d_m = nc / \{ 4 f_m (\mu_r \varepsilon_r)^{1/2} \} (n = 1, 2, 3, 4 \ldots)
\]  

(7)

Where \(d_m\) and \(f_m\) stand for the matching thickness and frequency of RL_{min} peaks, respectively, \(\mu_r\) and \(\varepsilon_r\) represent complex permittivity and permeability under matching frequency and \(c\) is the velocity of light.

For 30 wt% sample, when the thickness is 2.0 mm, the RL reached \(-22.5\) dB at 14.5 GHz, and the corresponding bandwidth is 4.5 GHz (12.5–17.0 GHz). Meanwhile, the minimum RL reached \(-38.4\) dB at 1.6 mm thickness. As shown in the figure 5(b), it is found that the RLs lower than \(-10\) dB corresponding to 90% microwave attenuation can be obtained in 3–7 GHz frequency range for the given absorber thickness of 2.5–5.0 mm, and the minimum RL reached \(-12.4\) dB at 4.8 mm. Figures 5(c)–(e) display the thickness dependence of effective bandwidth (\(\leq -10\) dB) and RLs maps for 30 wt% and 50 wt% samples, respectively. For 30 wt% sample, the effective bandwidth reached 4.6 GHz (13.2–17.8 GHz) with thickness of 1.9 mm, which almost covers Ku-band. The results show that the TDFC/PA composites have excellent microwave-absorption performance, which is very suitable for engineering applications in microwave-absorption field.

For an excellent absorber, the impedance matching should be equal or close to that of free space. To explain the excellent microwave absorption performance of TDFC/PA composites, the impedance matching degree was calculated by a delta-function method, which can be defined by equation [37]:
Where $K$ and $M$ can be calculated by \[37\]. A small delta value ($\Delta \leq 0.4$) implies better impedance matching. In figures (a) and (b), it can be found from the large effective areas that the impedance matching of TDFC/PA composites is excellent ($\Delta \leq 0.4$), which accords well with the calculated RLs.

### 4. Conclusions

In summary, the TDFC/PA composites were successfully synthesized by combining the arc-melting process and \textit{in situ} oxidative polymerization method. The coated PA with fluffy and porous structure is beneficial for the repeated reflection, multiple absorptions and effect of interfacial polarizations inside the TDFC/PA composites. The sample of TDFC/PA composites in the paraffin matrices has an excellent microwave-absorption performance for their high absorption intensity and wide absorption bandwidth at low thickness. When thickness is 2.0 mm, the minimum of RL reaches $-22.5$ dB at 14.5 GHz with 4.5 GHz bandwidth (12.5–17.0 GHz). The RL reached $-38.4$ dB at a high frequency of 17.8 GHz with merely 1.6 mm. Furthermore, the effective bandwidth reached 4.6 GHz (13.2–17.8 GHz) at 1.9 mm thickness, which covers most of Ku-band. Totally speaking, the RLs results show that the TDFC/PA is an excellent absorber against electromagnetic pollution. This work provides a new idea to further study microwave absorption properties of magnetostrictive materials.
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