Effect of doping rare earth oxides on microwave absorbing properties of Polyaniline /Al-alloy foams composite materials

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Abstract. Porous metal as the new style structural—functional material is going to be exploited and utilized further. The absorbing properties of aluminium foams coated absorbing paint were studied and tested by making use of RCS in “the reflectivity testing measurement of radar absorbing material” of GJB 2038-94 in this work. The morphology and distribution of microwave absorbent were analyzed by scanning electron microscopy (SEM). The influence of electromagnetic wave rare earth oxides on absorbing properties of materials was discussed. The results indicated that in the 12~18GHz and 26.5~40GHz bands the absorbing properties increase with the increase of frequency, and after doping the rare earth oxide, the absorbability of the composite material was enhanced. Therefore, doping the rare-earth oxide is a way to improve absorbing properties of absorption materials, and the absorbability of Al-alloy foams can be improved by coating with composite powder of Polyaniline in reasonable proportion to the rare-earth oxide in is available to be improved.

1. Introduction
In the past years, electrically conjugated conducting polymers have rapidly become a subject of tremendous interest due to their interesting, magnetic, optical properties, and electronic [1-6]. Polyaniline belongs to electric for its high conductivity, this characteristic make challenge of facing reduce thickness and to enhance the bandwidth, improving and endowing the magnetic loss of conducting polymer are critical for its practical application [6]. It is known that rare earth ions have unpaired 4f electrons and the strong spin-orbit coupling of angular momentum. So their atoms and ions have special electromagnetic performance. A certain amount of rare earth elements will be added to Polyaniline which can improve the absorb efficiency of Polyaniline, which is an important research direction of absorbing materials [7-8]. This paper prepared Al-alloy foams absorbing compound materials, which combined the rare earth oxide doped Polyaniline with neotype porous metal foam material, and studied on its absorbing properties preliminary. By analyzed the configuration characteristics of Al-alloy foams and the advantage of antiradar coatings, the new efficient Al-alloy foams compound absorbing materials will be acquired.
2. Experimental

2.1. Experiment materials
Foam aluminum silicon alloy is the average porosity of 80% ~ 90%. Absorbent is dielectric loss type of polyaniline, the composite power is mixing polyaniline, La$_2$O$_3$, CeO and dy$_2$O$_3$; With epoxy resin as adhesive, polyurethane as curing agent, JN-115 as dispersing agent, KH-550 as coupling agent used in absorbing coating.

2.2. Surface degreasing treatment
Compared with the flat material, specific surface area of aluminum foam is large (as shown in figure1), the surface is roughness and porous, which easier to fitting coating, forming coating with strong adhesion. However, because of the characteristics of the surface of the aluminum foam, residual grease, debris and other impurities can easily stay in the surface pits and pores in the process of production. It is difficult to clean thoroughly; we have purified the surface of Al-alloy foams to remove oil and impurity in the residue pore. According to the surface characteristic of Al-alloy foams, weak high pressure spray wash was designed in this experiment, combined with purification treating technology of the combination of ultrasonic cleaning and wet abrasive blasting, then the cleanly surface of Al-alloy was obtained d for next coating work.

2.3. Preparing for absorbing composites coating
Polyaniline coupled with pretreatment before mixed the rare-earth oxide respectively. Compound absorbing materials were prepared by dry-mixed and wet-mixed for 5h. In order to electromagnetic wave absorber can disperse into the coating uniformly, coupling pretreatment were used before the coating was prepared. Filler (70%), dispersant and diluted binder were mixed. Electromagnetic wave absorber is dispersed uniformly after grinding, stirring, ultrasonic oscillation and sieving. And spray coating on Al-alloy foams surface, curing in 60°C, obtained the necessary materials.

2.4. Performance test
Absorbing Properties of material were tested according to the Standard GJB 2038-94 “Method to test the reflectivity of radar absorbing materials”, i.e., the RCS (radar cross-section) method, namely on the condition of the given wavelength and polarization, electromagnetic wave irradiates the plate of RAM and the plate of good conductor, from the same direction, at the same power density. Then, the reflected power of radar absorbed materials plate and the same size good conductor plate is calculated.

\[ R (f) = 10 \lg \left( \frac{P_1(f)}{P_0(f)} \right) \text{ (dB)} \]  

Formula (1), \( R (f) \) is the reflectance of RAM; \( P_0(f) \) is echo power of frequency changes, which was acquired during measuring frequency domain response of normal incidence of metal plate; \( P_1(f) \) is echo power of frequency changes, which was acquired during measuring frequency domain response of normal incidence of the same size RAM plate. Measurement is carried out in the microwave anechoic chamber (containing compact rang), the composition of measurement system is based on the HP8530A vector grid analyzer, the range of measurement frequency is 12.0~18.0GHz, 26.5~40.0GHz. The size of sample is 180×180mm$^2$, the template back liner metal floor.

Electromagnetic parameters tested by vector network analyser (E8363B), using waveguide methods test complex permittivity and permeability of the material in the Ku-band, the size of samples is 3.56mm×7.12mm×1.00mm, which was tested in China aerospace science and industry corporation the second 207 research Institute.
3. Experimental results and discussion

3.1. SEM analysis
Figure 1 is the rare earth oxide doped polyaniline, which reunion phenomenon is obviously, formed round sheet. The rare earth oxide has not changed polyaniline shape, and mixing uniformity dispersion.

![SEM micrographs of the rare earth oxide doped in PAn](image)

**Figure 1.** SEM micrographs of the rare earth oxide doped in PAn

3.2. The electromagnetic parameters test
The electromagnetic parameters including material complex permittivity \( \varepsilon \) and complex permeability \( \mu \), which can be expressed as [9]

\[
\varepsilon' = \varepsilon' - j \varepsilon''
\]

\[
\mu' = \mu' - j \mu''
\]

\( \varepsilon' \) and \( \mu' \) respectively represent the real part of the complex permittivity and permeability which indicates that the material on the storage capacity of electromagnetic energy. \( \varepsilon'' \) and \( \mu'' \) respectively represent imaginary part of the complex permittivity and permeability, which indicates that the material on electromagnetic energy reduction capability. The dielectric loss tangent \( \tan \delta_e \) and magnetic loss tangent \( \tan \delta_\mu \) indicated the loss magnitude:

\[
\tan \delta_e = \frac{\varepsilon'}{\varepsilon''}
\]

\[
\tan \delta_\mu = \frac{\mu'}{\mu''}
\]

The imaginary part of the complex permittivity \( \varepsilon'' \) and the imaginary part of complex permeability \( \mu'' \) is larger, the loss is greater, the more conducive to the absorption of electromagnetic waves. To
improve the medium wave absorption performance, we must improve $\varepsilon''$ and $\mu''$ value, at the same time as far as possible to make the impedance matching [101]. The table1 is shown that the real $\varepsilon'$ and imaginary $\varepsilon''$ part of the dielectric constant decreases with increasing frequency, but the change is not big; the dielectric loss angle tangent $\tan\delta_\varepsilon$ has no changes. The real part of the permeability $\mu'$ is nearly 1, the imaginary $\mu''$ is closed 0, and magnetic loss tangent is also 0. It is shown that polyaniline hasn’t virtually magnetic properties, belong to the dielectric loss materials.

Table 1. Electromagnetism parameter of PAN

| Absorbing agent | frequency /GHz | $\varepsilon'$ | $\varepsilon''$ | $\tan\delta_\varepsilon$ | $\mu'$ | $\mu''$ | $\tan\delta_\mu$ |
|-----------------|----------------|---------------|----------------|----------------------|-------|-------|--------|
| PAN             | 26.5           | 5.7189        | 1.6147         | 0.005                | 1.0047| 0.0247| 0.00   |
|                 | 28.0           | 5.6779        | 1.5438         | 0.005                | 1.0056| 0.0311| 0.00   |
|                 | 30.0           | 5.6804        | 1.503          | 0.005                | 0.9949| 0.0321| 0.00   |
|                 | 32.0           | 5.6589        | 1.5087         | 0.005                | 0.9879| 0.0247| 0.00   |
|                 | 34.0           | 5.5862        | 1.5026         | 0.005                | 0.9911| 0.0184| 0.00   |
|                 | 36.0           | 5.5281        | 1.4939         | 0.005                | 0.9925| 0.0129| 0.00   |
|                 | 38.0           | 5.4680        | 1.487          | 0.005                | 0.9955| 0.0074| 0.00   |
|                 | 40.0           | 5.4196        | 1.469          | 0.005                | 0.9969| 0.0056| 0.00   |

3.3. UV analysis

The preparation of PANI v-vis diffuse reflectance spectra was determined by uv-vis spectrophotometer with Japan Shimadzu uv-2550. Using small integral ball accessory, BaSO4 powders as reference to standards, scanning range is 240~800nm. Characterization of photoabsorption performance was often used by light absorption method in practical application, reflection absorbance defined by $A = \lg \frac{1}{R}$, which R is reflectivity of diffuse reflectance of sample, A is reflection absorbance [9-10].
Fig 2 shows that Uv-visible absorption spectrum of PANI and PAIN-coated the rare earth oxide composites was measured by solid reflection absorbance. The PANI has two absorbance peaks in 353nm and 680 nm, two absorbance peaks shift to 330nm and 720nm separately after doping 2% the rare earth oxide, and two absorbance peaks also shift to 325nm and 702nm(red shift) separately after doping 5% the rare earth oxide; This change in the absorption peak shows the molecular configuration of PANI changes in doping cerium oxide process. Two absorption peaks of polyaniline which correspond to \( \pi - \pi^* \) of benzene ring in molecular chains electron transition and benzene ring to the quinine electron transition; appears half-filled with pole in the conduction band [9], energy band structure after doped rare earth, when polyaniline doped with the rare earth oxide, macromolecular chain of H+ and N atoms combine to form valence electrons assigned to molecular structure forming conjugated, but is not to be "pocketed", the result is each nitrogen atom has the partial positive charges, aromatic ring is between the benzene and quinine-type, which forms large conjugated system. The electron transition needs the energy to reduce, thus make absorption band red-shifted to longer wavelength; On the other hand, molecular chains of PANI-coated rare earth oxide structure has changed, distorted defect of between the benzene ring and quinine ring is less, ordering of molecular chains is enhance, between adjacent dipole is strong, polar on band is more dispersed and energy gap reduces, these reflect on the absorption spectrum is absorbing peak broadening and red shift, the conductivity is larger.

3.4. Effect of doping rare earth oxides on microwave absorbing properties

The absorbing properties of coating doping the rare-earth oxides in PANi/Al-alloy foams materials is shown in figure 3. Each sample absorbing properties were detected in 12.0-18.0GHz and 26.5-40.0GHz bands, the coated aluminum foam for plate thickness, the average pore diameter and porosity are the same. The composite materials of polyaniline mixed rare earth oxide expected to adjust the equivalent electromagnetic parameters of absorbing coating, improve surface impedance of the foam aluminum composite absorbing material and the free space impedance matching conditions, so as to optimize the absorbing properties. As shown in figure 3, the absorbing performance of the sample Cp (Single Polyaniline), Cp2 (doped 2% rare earth oxide in PAN) and Cp5 (doped 5% rare earth oxide in PAN) increases with increasing frequency, reflectance curve have no obvious peak value in 12.0-18.0GHz and 26.5-40.0GHz bands, it showed the broadband characteristics of the material, the higher frequency, absorbability of materials is better. Absorption effect is not obvious in 12.0-18.0GHz band, absorbability of Cp did not meet the requirements of the absorbing material general field (less than -10dB), but absorbing effect is improved obviously after doping the mixed rare earth oxide. Doped with 2% the mixed rare earth oxide reaches -10dB nearly 6.5GHz, Cp5 inferior to Cp2, but also there is 3GHz to achieve 10-dB. In 26.5-40.0GHz band absorbing effect within the material has been significantly improved, tends to -10dB. Absorbing properties of single polyaniline-coated only reached -1.8dB in 12.0-18.0GHz band, the absorbing properties can reach -16dB after adding rare earth oxides, absorbing performance increased significantly. The bandwidth is 9GHz that coating absorbing properties of polyaniline can exceed -10dB, and all bandwidth reached -6dB; all absorbing properties reaches -10dB after the addition of rare earth oxides, the bandwidth increased Significantly, the highest absorbing reach -27dB, while single polyaniline can only reach -15dB.
Doped with a small amount of rare earth oxide can effectively improve the absorbing properties of polyaniline: Using rare earth ionic radius is relatively large, make lattice constant larger, which appears lattice distortion, increase physical activity, and improve the dielectric loss; The average crystal grain size is increased, so that the grain boundary resistivity is reduced, furthermore the resistivity of the whole crystal is reduced, improve the eddy current loss, meanwhile increased the domain wall resonance loss; Thereby the absorbing properties of polyaniline is increasing.

4. Conclusion
The influence of electromagnetic wave rare earth oxides on absorbing properties of materials was discussed in this paper, for aluminum foam absorbing materials research and design providing a good theoretical basis.
1. The absorption performance of the composite material was studied, which aluminum foam surface coated adding rare earth oxide in polyaniline. From UV spectroscopy, after doping rare earth oxides, the peak is redshift. Indicating electrical conductivity increase is helpful to improve of absorbing properties of polyaniline composite absorbents;

2. In the 12~18GHz and 26.5~40GHz bands the absorbing properties increase with the increase of frequency, and after doping the rare earth oxide, the absorbability of the composite material was enhanced.

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