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Enhanced microwave absorption properties of flake-shaped FePCB metallic glass/graphene composites

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ABSTRACT

A novel kind of composite absorber, i.e. FePCB/graphene composite, with excellent microwave absorption properties was successfully fabricated by a simple and scalable ball milling method. After being milled, the FePCB particles displayed flaky morphology with large aspect ratio. The complex permittivity and permeability of the flaky FePCB distinctly increased compared with those before milling. Furthermore, with the introduction of graphene, the flaky FePCB/graphene composite exhibited excellent microwave absorption performance with strong absorption and wide absorption band. In particular, for FePCB/graphene composite with an absorber thickness of 2 mm, the reflection loss (RL) reached a minimum of −45.3 dB at 12.6 GHz and the effective absorption bandwidth (RL < −10 dB) covered 5.4 GHz. The enhanced microwave absorption performance of the FePCB/graphene composite was attributed to the high magnetic loss and improved impedance matching which were closely related to the flake-shaped FePCB particles and the introduction of graphene sheets.

1. Introduction

With the high demands for the reduction of the electromagnetic (EM) radiation and improvement of anti-electromagnetic interference, microwave absorbing materials with the capability of absorbing EM signal are widely applied in industry and military [1–3]. Among the candidates for EM wave absorbers, Fe-based soft magnetic metals/alloys such as Fe [4], FeNi [5], FeCo [6] and FeSiAl [7] have attracted considerable interest because of their outstanding soft magnetic properties and potential applications in high-frequency devices and micro-transductions which require high saturation magnetization, large susceptibility and high Curie temperature. However, the metal/alloy magnetic absorbers often suffer from narrow absorbing frequency bandwidth, large layer thickness, EM mismatch, easy oxidation and corrosion, which hinder their applications in absorbing EM wave.

Fe–P–C metallic glass is an important soft magnetic material and has been widely used as the key parts in many magnetic devices due to its high saturation magnetization, high permeability, good mechanical property and low cost [10]. These advantages also endow the Fe–P–C metallic glass an attractive microwave absorbing material in practical applications. Moreover, the amorphous structure and unique composition of the Fe–P–C metallic glass causes the decrease of conductivity relative to the Fe-based crystalline alloy, which is favorable to reducing the impedance mismatch. Nevertheless, to the best of our knowledge, the microwave absorbing properties of the Fe–P–C based metallic glass have not been reported yet.

Recently, the synthesis of magnetic–dielectric composite absorbers, which can take advantages of both a unique permittivity and strong magnetic properties, have received increasing attention [8,9]. Compared with other dielectric additives, carbon-based materials including carbon nanotubes [14], carbon black [15], graphite [16] and graphene [10–13] possess exceptional advantages of low density, high thermal stability and high chemical stability. Until now, many carbonaceous material-alloy composites have been prepared and exhibited strong EM wave absorbing property. For example, Liu et al. prepared (Fe, Ni)/C nanocapsules using arc discharge technique and obtained an optimal reflection loss of −32 dB with 2 mm thickness layer [9]. Chen et al. deposited Fe nanoparticles on graphene nanosheets, and this material exhibited good microwave absorbing properties with the minimum reflection loss of −31.5 dB at 14.2 GHz with a thickness of 2.5 mm

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[14]. Bateer et al. found that the Fe_3C/graphitic carbon/paraffin composite containing 70 wt.% Fe_3C/graphitic carbon displayed good microwave absorption abilities with an optimal reflection loss of −26 dB for the 2 mm thickness layer [1]. All of these encourage us to develop a novel FePCB–carbonaceous material composite absorber. The addition of carbonaceous material may play important roles in tuning the permittivity and improving the impedance matching, which benefit the enhancement of microwave absorption performance.

In this work, FePCB alloy powder with a potato-like shape mixed with light-weight graphene sheets, was ball-milled to achieve a flake-shaped FePCB–graphene composite absorber. The obtained FePCB flakes have higher permeability in gigahertz frequency due to their large aspect ratio, and exhibited strong magnetic loss. Simultaneously, graphene sheets are used as a light-weight dielectric addictive to improve the impedance matching of the FePCB metallic glass. Relative to other carbonaceous materials, graphene sheets have larger surface areas, and their flexible laminated structure benefits the close contact with FePCB particles during ball milling process. The prepared FePCB/graphene composite displayed an excellent microwave absorption performance with strong absorption, wide absorption bandwidth and a thin layer thickness.

2. Experimental method

2.1. Preparation of FePCB/graphene composite

A micrometer-sized $Fe_{0.2}P_{0.05}C_{0.45}B_{0.3}$ alloy powder fabricated by a water spray method was used as the starting material. The shape of the raw powder was potato-like and the size was in the range of 2–32 μm. The graphene sheets with diameter and thickness of 5–10 μm and 3–10 nm, respectively, were purchased from Nanjing XFNANO Materials Tech (Nanjing, China). The conductivity of the graphene was 500–1000 S/cm. The SEM images of the graphene sheets are given in the supporting information (Fig. S1). The FePCB/graphene composite was obtained by ball milling the mixed powders of FePCB and graphene for 4 h. The mass fraction of graphene to FePCB was 4 wt.%. The ball-to-powder ratio was set at 40:1 by weight with the rotation speed of 178 rpm. Certain content of anhydrous ethanol was added into the powder as the process control agent. After ball milling, the powders were collected and dried in oven at 60 °C.

2.2. Characterization

The crystal structure was determined by X-ray diffraction (XRD, Rigaku, model D/max-2500 system at 40 kV and 100 mA of Cu Ka). The morphology and the size of the powder were characterized by scanning electron microscopy (SEM, JEOL JSM-7500F). Raman spectra were obtained using an in Via Laser Raman spectrometer (LabRAm HR Evolution). The magnetic properties were measured by a vibrating sample magnetometer (VSM, Lake Shore 7307) at room temperature. The measurements of the room-temperature conductivity were carried out on four-point probes resistivity measurement system (RTS-8).

For electromagnetic (EM) parameter measurements, the powder samples with weight ratio of 60 wt.% were uniformly mixed with paraffin. The as-prepared mixture was then pressed into toroidal-shaped specimens with outer diameter of 7.00 mm and inner diameter of 3.04 mm. EM parameters were measured by a vector network analyzer (Agilent Technologies, PNA-L, N520C) in the range of 2–18 GHz.

3. Results and discussion

XRD measurements were used to investigate the crystalline structure of the samples. As shown in Fig. 1, the XRD pattern of the raw FePCB powder displays a broad diffraction hump at 45° and three sharp diffraction peaks at 43°, 50°, 74°, respectively. It reveals that the raw FePCB alloy consists of both nanocrystalline and amorphous phases. The broad hump corresponds to the bcc structured α-Fe with metallic glassy feature, while the three sharp peaks can be indexed to Fe_3P phase. After ball milling, the three sharp peaks become indistinct indicating the disappearance or significant decrease of Fe_3P phase during the milling process. As for FePCB/graphene composite, the XRD curve exhibits strong diffraction peaks of α-Fe phase along with a weak peak at 25.6°. The new peak could be attributed to the disordered (002) stacking layers of graphene [15].

Fig. 2 shows the morphology of the raw FePCB, as-milled FePCB and FePCB/graphene composite. The raw FePCB alloy exhibits potato-like shape with wide distribution of particle size from 2 to 32 μm. After ball milling, the FePCB particles deformed into flake shape with an increase of plane size and a decrease of thickness (Fig. 2b). Hence, the aspect ratio of the as-milled particles (plane size/thickness) considerably increases relative to the raw powder. Since the large aspect ratio of the particle could suppress eddy currents in high-frequency electromagnetic field and limit the magnetic moments to the plane of the particles thereby increasing permeability, such shape deformation would benefit the microwave absorption capability of the FePCB alloy. As presented in Fig. 2(c), the stacking structure of the graphene sheets did not change during the ball milling process, and the stacking layers of graphene were uniformly mixed with the FePCB alloy flakes. The compositions of the three samples were determined by EDS. As illustrated in Fig. 2(d)–(f), the elemental ratio of the as-milled FePCB alloy is consistent with that of the raw material. The C ratio of the FePCB/graphene composite obviously increases due to the addition of graphene.

Raman spectroscopy is a powerful tool to distinguish ordered and disordered crystal structures of carbon [16]. Fig. 3 presents the Raman spectra of the graphene and FePCB/graphene composite. Two characteristic peaks at ~1340 and 1600 cm^{-1} appear in graphene spectrum, which correspond to the D band and G band, respectively [17]. The D band is a first-order zone boundary phonon mode associated with defects in the graphene or graphene edge, while the G band is a radial C–C stretching mode of sp^2 bonded carbon [18]. In general, the intensity ratio of D band to G

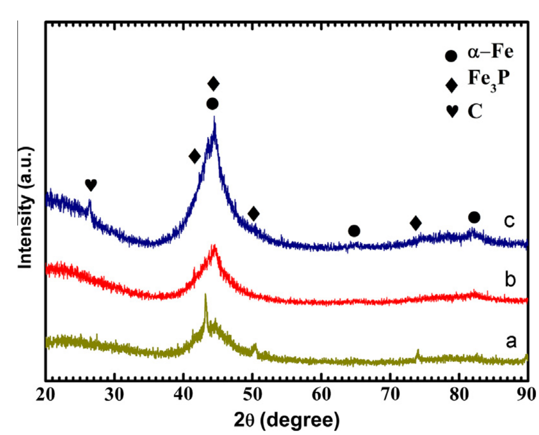

Fig. 1. XRD patterns of raw FePCB (a), as-milled FePCB (b) and FePCB/graphene composite (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)