Effects of heat treatment on magnetic properties of Co–Fe-plated hollow ceramic microspheres

Xiang LI, Yue-xin DUAN, Yan ZHAO, Lei ZHU
School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100191, China
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Abstract: Functional hollow ceramic microspheres plated with Co–Fe were obtained through electroless plating technique for the application of lightweight microwave absorbers. They were treated at different temperatures by vacuum annealing method. The surface-coated hollow microspheres were characterized by scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). The microwave electromagnetic loss and absorbing properties of hollow microspheres plated with Co–Fe were tested by network vector analysis. The magnetic properties were tested by vibrating sample magnetometer (VSM). The results show that the annealing treatment changed the crystal phase of Co from HCP to FCC, simultaneously increased the crystallinity and crystal size of Co and Fe in coating layers. Additionally, after annealing at 800 °C or 1 000 °C, the microwave absorbing properties and soft magnetic properties of hollow microspheres plated with Co–Fe were further improved.

Key words: electroless plating; hollow ceramic microspheres; magnetic properties; heat treatment; Co–Fe

1 Introduction

In recent years, microwave absorption materials have attracted considerable attention due to the fast development of modern telecommunications and technology. As one of the new functional materials, microwave absorption material is not only increasing valued by people in the application of the military, but also has an extremely widespread application prospect in the civil aspect [1–5]. For microwave absorption materials, fine magnetic materials, such as powders of iron [6] and ferrites [7], have been widely used. However, the conventional absorptive materials have difficulties in improving the permeability in gigahertz region owing to Snoek’s limit for ferrites [8] or eddy current loss for magnetic metals [9]. Meanwhile, these materials possess relatively high density, which restricts their usefulness in the applications on requiring lightweight mass [10–11]. To date, lightweight microwave absorption materials such as CNTs, electric polymer and functional hollow microspheres, have drawn more attention due to their good electromagnetic performance and low density [12].

Hollow microspheres composed of SiO₂ and Al₂O₃ have low density as well as other excellent physical performance, such as high thermal stability, high wear resistance and good chemical stability [13]. Therefore, it is a good substrate for synthesizing the wave absorption materials. With a magnetic metal layer deposited on their surface, hollow microspheres can obtain electromagnetic properties, and can be dispersed into different matrix, such as polyester resin, ceramic and metal, as lightweight microwave absorbent for electromagnetic shielding applications [2].

Magnetron sputtering deposition [14, 15], chemical vapor deposition (CVD), physical vapor deposition (PVD) and electroless plating [16] were selected as deposition technologies for hollow microspheres. Recently, electroless plating has been used to coat microspheres with metallic layer [17–19]. As a well-established coating technique, electroless plating is a method for obtaining a thin metallic coating layer on metals, ceramics, or plastics by just immersing the substrate into an electrolyte solution [20]. Various metal particles and their oxides, such as Co [21, 22], Ni [23, 24], Cu [25], Ag, Fe₂O₃ [26, 27], and SnO₂ [28] can be deposited on the surface of hollow microspheres via this technology.

Fe has a higher magnetic moment than Co and Ni due to its 4 holes in 3d state. Therefore, depositing Fe on
the surface of hollow microspheres can enhance magnetic loss and the absorbing properties, and widen the absorbing bandwidth, accordingly improving the magnetic properties. However, it is still a critical issue to well-plating Fe on the surface of hollow microspheres via electroless plating, resulting from the weak autocatalytic reductive ability of Fe. As one effective approach to resolve this problem, Co–Fe alloy-plated hollow microspheres are expected to be obtained owing to the induced co-deposition effects of Co on Fe$^{2+}$.

In this work, Co–Fe alloy thin film instead of Fe was proposed to coat the surface of hollow microspheres. A preliminary work was conducted on the effects of heat treatment on magnetic properties of these Co–Fe alloy-plated microspheres.

2 Experimental

2.1 Activating and electroless plating processes

The hollow microspheres (diameter: 1–20 μm; apparent density: 1.4 g/cm$^3$) were supplied by Qinhuangdao Glass Microspheres Co., Ltd. of China. Cobalt (II) sulfate (CoSO$_4$·7H$_2$O), ferrum (II) sulfate (FeSO$_4$·7H$_2$O), sodium citrate (C$_6$H$_5$Na$_3$O$_7$·2H$_2$O), sodium hypophosphite (NaH$_2$PO$_2$·H$_2$O), tin (II) chloride (SnCl$_2$·2H$_2$O), palladium (II) chloride (PdCl$_2$), sodium hydroxide, hydrochloride acid, ammonia and ethanol were purchased from Xilong Chemical Reagent Factory. All chemicals were of reagent grade and were used as received. De-ionized water was used during sample preparation.

Before electroless plating, activating pretreatment was performed. The hollow microspheres were immersed into sodium hydroxide solution and stirred at 70 °C for 40 min. Then, the microspheres were filtered off, immersed into a solution which involves SnCl$_2$ and PdCl$_2$. Stirring at 40 °C for 30 min, the activated hollow microspheres were obtained. The Sn–Pd activating process was used to deposit Pd particles on the surface of hollow microspheres.

After the pretreatment procedure, the general sequential steps involved in the present electroless Co–Fe plating process were as follows. The activated hollow microspheres were immersed into a plating bath which involved CoSO$_4$·7H$_2$O, FeSO$_4$·7H$_2$O, C$_6$H$_5$Na$_3$O$_7$·2H$_2$O, NaH$_2$PO$_2$·H$_2$O and ammonia (used to adjust the pH value) for actual Co–Fe deposition at 80 °C, and stirred until there were no air bubbles in the bath. The Co–Fe coated microspheres were then filtered off, washed with de-ionized water, and dried in a vacuum oven at 60 °C for 2 h. Regulating the proportion of CoSO$_4$·7H$_2$O and FeSO$_4$·7H$_2$O in the bath, the Co–10%Fe microspheres were obtained, in which the ratio of Co to Fe equaled 9.

2.2 Heat treatment process

The Co–10%Fe microspheres were heated for 1 h annealing treatment in vacuum condition at 600, 800 and 1 000 °C, respectively.

2.3 Characterization

The chemical compositions of Co–Fe coating were analyzed by energy-dispersive X-ray detector (EDX, S530, Oxford, UK). Malvern laser particle analyzer (Hydro 2000MU, Malvern, UK) was used to analyze the particle sizes of microspheres. The surface morphologies of the Co–Fe deposits were examined by scanning electron microscopy (SEM, LEO–1530, LEO, Germany), while the phase structure analysis of products was identified (within 2θ range of 10°–80°) using an X-ray diffractometer (XRD, D/max 2200 PC, Rigaku, Japan) utilizing Cu K$_\alpha$ X-radiation of wavelength of 1.541 8 Å.

The measurements of the magnetic properties of composite microspheres were performed at room temperature (about 300 K) using a vibrating sample magnetometer (VSM, LDJ9600, LDJ Electronics Co., USA). Meanwhile, the electromagnetic parameters of the functional hollow microspheres were analyzed in the frequency range of 2–18 GHz, using vector network analyzer (8722ES).

3 Results and discussion

The mechanism of electroless plating can be explained by the following chemical equations:

$$H_2PO_3^- + H_2O \rightarrow HPO_4^{2-} + 2H^+ + H^+ \quad (1)$$

$$Co^{2+} + 2H \rightarrow Co + 2H^+ \quad (2)$$

$$Fe^{2+} + 2H \rightarrow Fe + 2H^+ \quad (3)$$

$$H + H \rightarrow H_2 \quad (4)$$

Firstly, reductive H is produced in the reaction of reducing agent and H$_2$O under the catalytic effect of Pd particles, as shown in Eq. (1), and the reductive H occurs on the surface of hollow microspheres where the Pd particles are deposited. Secondly, Co$^{2+}$ and Fe$^{2+}$ are reduced by the reductive H to Co and Fe, respectively, as shown in Eq. (2) and Eq. (3). These reactions occur mainly on the surface of hollow microspheres. Therefore, hollow microspheres are coated with the Co–Fe produced in these reactions. Finally, the Co–Fe deposited on microspheres acts as a self-catalyst (the same catalytic effect as Pd) for further deposition, and this self-catalytic effect intensifies the reaction shown in Eq. (2) and Eq. (3).

Ideally, the functional Co–Fe coated hollow microspheres can be obtained. However, there is a certain number of free Pd particles involved in the solution, where the reactions shown in Eq. (2) and Eq. (3)
can also occur by the catalytic effect of Pd. Therefore, free Co and Fe particles are produced. The precipitates of Co and Fe are formed with the increment of free Co and Fe particles, and the amount of Co–Fe deposited on the surface of hollow microspheres decreases as a result.

Moreover, $\text{H}_2$ is produced in the self-reaction of reductive $\text{H}$, as shown in Eq. (4). Consequently, the degree of electroless plating process can be estimated through this reaction. The electroless plating process continues until there are no more bubbles produced in the solution.

3.1 Morphology of Co–Fe-plated microspheres

Figure 1 shows the morphologies of Co–Fe-plated microspheres before and after heat treatment at different temperatures.

It can be observed clearly that most of hollow microspheres are coated with Co and Fe without much free Co and Fe produced, and good quality coating layers of Co–Fe are obtained.

Particle diameter distributions of microspheres before and after electroless plating are shown in Fig. 2. From Fig. 2, it can be seen that after electroless plating, the value of $d_{50}$ increases obviously. Furthermore, the average thickness of Co–Fe coating can be estimated, which approximately equals 2.6 $\mu$m.

In this work, the mass ratio of Co–Fe-plated microspheres to non-coated microspheres ranges from 3.5 to 4.0. Therefore, it can be inferred that the mass ratio of Co–Fe coating and microspheres approximately

![Fig. 1 SEM images of Co–Fe-plated microspheres: (a), (b) Un-heated; (e), (d) 600 °C; (e), (f) 800 °C; (g), (h) 1 000 °C](image-url)
equals 2.5–3.0, after electroless plating.

The SEM images also show that after annealing treatment, the spherical core-shell structure of the microspheres is well-maintained, while the metallic shells show the trend to be much coarser. Owing to the annealing treatment, the building units of the metallic shells begin to fuse and integrate with each other and grow up to larger ones. During this process, the morphology of these microspheres becomes irregular and their size varies in a broader range. Furthermore, with increasing annealing temperature to 1 000 °C, the spherical core-shell structure is destroyed and the microspheres collapse and melt into irregular particles. Therefore, the diameter and the surface area of microspheres annealed at 1 000 °C are the smallest in these four samples. This is consistent with the phenomenon of AN et al [29]. Consequently, it can be concluded that the 800 °C treatment enlarges the diameter of the microspheres while the annealing process shrinks their diameter when the temperature is increased to 1 000 °C.

In addition, it can be noted from Figs. 1(b), (d) and (f) that the size of those Co–Fe particles, which are coated on the surface of the microspheres, has a slight increase with elevating annealing temperature. However, when the annealing temperature is up to 1 000 °C, the size of Co–Fe particles decreases substantially. This phenomenon can be attributed to the fusion and collapse of those particles at a temperature high enough.

The elemental components of Co–Fe-plated microspheres at different heat treatment temperature are shown in Table 1. The elements of oxygen (O), aluminum (Al), silicon (Si), phosphorus (P), iron (Fe) and cobalt (Co) are found on the surface of Co–Fe-plated microspheres. Among these elements, elements Co and Fe are the main components. It should be noticed that the element compositions are similar when the heat treatment temperature is not higher than 800 °C. The sum percentages of Co and Fe are all above 90%, while the percentages of other elements are much lower than that. Consequently, it can be concluded that most of microspheres are coated by Co–Fe alloy, which leads to very low percentages of other elements content. When the heat treatment temperature reaches 1 000 °C, the sum percentages of Co and Fe reduce slightly and the percentages of Al and Si increase accordingly. This is mainly because when the temperature is higher than 1 000 °C, the integrity of coating layer is destroyed and some of the microsphere surface is uncovered.

### Table 1 EDX results of Co–Fe-plated microspheres

<table>
<thead>
<tr>
<th>Heat treatment temperature/°C</th>
<th>Mass fraction/%</th>
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<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Un-heated</td>
<td>1.34</td>
</tr>
<tr>
<td>600</td>
<td>2.74</td>
</tr>
<tr>
<td>800</td>
<td>1.24</td>
</tr>
<tr>
<td>1 000</td>
<td>3.70</td>
</tr>
</tbody>
</table>

### 3.2 XRD analysis of Co–Fe-plated microspheres

XRD patterns of the Co–Fe-plated microspheres before and after heat treatment at different temperatures are shown in Fig. 3.

The XRD spectra in Fig. 3 indicate that the annealing process changes the crystal phase of Co in the surface-coated microspheres. Before annealing, the crystal phase of Co is HCP, while after annealing process the FCC phase is observed. This is believed to be due to the annealing process which induces the allotropic transformation of Co. Furthermore, it is found that during the cooling circle, the Co particles within a wide size range still maintain their high structure (FCC) until
the temperature is reduced to room temperature. This is ascribed to the martensitic transformation, which is restrained mainly by the compression stress induced by surface tension of microspheres [30].

It should be noticed that the intensity of the characteristic peak at 44.28° is improved with the shrinking of its width (Fig. 3) due to the annealing treatment. It can be demonstrated that the annealing process increases the crystallinity and crystal size of Co and Fe in coating layers.

Furthermore, it also can be seen clearly from Fig. 3 that there is no characteristic peak of Fe observed in the pattern of un-heated. This is owing to the low percentage of Fe in the surface-coating (10%) and the relative low crystallinity of Fe. With the crystallinity increases after the annealing process, the characteristic peak of Fe emerges in the patterns.

3.3 Electromagnetic parameters and microwave absorbing properties analysis of Co–Fe-plated microspheres

The electromagnetic parameters of the functional hollow microspheres are analyzed in the frequency range of 2–18 GHz by vector network analyzer 8722ES. Each of the samples has a 50% filler proportion during the test.

Figures 4(a) and (b) show the real permittivity ($\varepsilon'$) and the imaginary permittivity ($\varepsilon''$) of Co–Fe-plated microspheres at different annealing temperatures. As shown in Figs. 4(a) and (b), all the $\varepsilon'$ and $\varepsilon''$ of microspheres annealed at 600 °C almost remain unchanged compared with those of un-heated composites microspheres, and the real and imaginary parts of permittivity remain constant in the whole frequency range. With the annealing temperature increasing to 800 °C, the values of $\varepsilon'$ and $\varepsilon''$ are improved. However, this rule reverses for both real and imaginary permittivity when the annealing temperature rises to 1,000 °C. The $\varepsilon'$ reaches 35 and $\varepsilon''$ reaches 18 when the microspheres were annealed at 800 °C for 1 h. This can be explained by the comprehensive effects of crystal size and fusion of the metal particles in the coating layers. As discussed before, the crystal size increases with the elevated annealing temperature, which improves the dielectric properties of microspheres. However, the gaps among these microspheres are limited, which restricts the increment of the crystal size. Furthermore, the spherical

![Fig. 4 Permittivity and permeability curves of Co–Fe-plated microspheres: (a) Real permittivity; (b) Imaginary permittivity; (c) Real permeability; (d) Imaginary permeability](image-url)
core-shell structure is destroyed and the microspheres collapse and melt into irregular particles with the annealing temperature rise to a critical value, which decreases the diameter and the surface area of microspheres and leads to a decrease of microwave absorbing properties. Therefore, the dielectric properties of microspheres are decreased.

It can be concluded that when the annealing temperature is 800 °C, the highest dielectric properties of Co–Fe-plated microspheres are achieved within the three annealing temperatures.

Meanwhile, Figures. 4(c) and (d) show the real permeability ($\mu'$) and imaginary permeability ($\mu''$) of the Co–Fe-plated microspheres at different annealing temperatures. As shown in Fig. 4(c), $\mu'$ reduces as the annealing temperature decreases, which demonstrates that the magnetic energy stored in microspheres decreases. It is attributed mainly to the improvement of the crystallinity and crystallite dimension of Co–Fe in coating layers induced by annealing process. On the other hand, the annealing process has little influence on $\mu''$.

For further investigation of microwave absorption, the reflection loss of Co–Fe-plated microspheres is calculated. The reflection loss curves are shown in Fig. 5. And the reflection loss of a microwave absorbing layer is given by [31, 32]

$$R = 20 \log_10 |\Gamma| = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|$$

(5)

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left[ \frac{j2\pi fd}{c} \sqrt{\varepsilon_r\mu_r} \right]$$

(6)

where $Z_{in}$ is the normalized input impedance; $Z_0$ is the impedance under vacuum (its value is 1); $c$ is the velocity of electromagnetic waves in free space; $f$ is the microwave frequency; and $d$ is the thickness of the absorbing layer. Therefore, microwave propagation in electromagnetic media is largely determined by the complex relative permeability and permittivity of the absorbing materials. All the calculated values were predicted based on a constant thickness of $d=2.0$ mm.

It is obvious that 600 °C annealing process has little effect on the calculated reflection loss curve, compared with the curve of the un-treated Co–Fe-plated microspheres. However, the microwave absorbing properties of microspheres increase substantially after annealing at 800 °C or 1 000 °C. After the annealing process, the increase of crystallinity and crystallite dimension promotes the absorption of Co–Fe-plated microspheres on microwave.

Non-coated hollow microspheres do not have the character of microwave absorbing. However, depositing magnetic metal layer on the surface of microspheres via electroless plating method can modify their surface properties, making modified microspheres show microwave absorbing properties. The composites of hollow microspheres and magnetic metal coating layer exhibit the advantages of both. Under the action of high frequency electromagnetic field, molecules and electrons of magnetic Co–Fe alloy in the coating layer move faster, facilitating magnetization and transforming more electromagnetic energy into heat. Meanwhile, Co–Fe alloy layer has strong interaction with high frequency electromagnetic field, producing eddy-current loss, hysteresis effect, domain wall resonance and so forth, which makes modified microspheres have ability to absorb microwaves. Furthermore, under the action of electromagnetic field, current is induced and flows through microscopic conductivity network formed among Co–Fe-plated microspheres, causing electromagnetic field power loss.

On the other hand, when the frequency range is 2–18 GHz, the corresponding wavelength range of microwaves is 150–16.7 mm, which is much larger than the diameter of microspheres. Therefore, the Rayleigh scattering is caused by the interaction of microwaves and modified microspheres, resulting in microwaves energy loss as well.

### 3.4 Magnetic properties analysis of Co–Fe-plated microspheres

The magnetic properties of Co–Fe-plated microspheres are measured by VSM at room temperature, as shown in Fig. 6, and the magnetic parameters such as saturation magnetization ($M_s$) and coercivity ($H_c$) are presented in Table 2.
Fig. 6 Hysteresis loops of Co–Fe-plated microspheres: (a) Un-heated; (b) 600 °C; (c) 800 °C; (d) 1 000 °C

<table>
<thead>
<tr>
<th>Heat treatment temperature/°C</th>
<th>Saturation magnetization, $M_s$(A·m$^{-2}$·kg$^{-1}$)</th>
<th>Coercivity, $H_c$(A·m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-heated</td>
<td>77.00</td>
<td>976 0</td>
</tr>
<tr>
<td>600</td>
<td>92.36</td>
<td>816 0</td>
</tr>
<tr>
<td>800</td>
<td>85.17</td>
<td>320 0</td>
</tr>
<tr>
<td>1 000</td>
<td>86.67</td>
<td>144 2</td>
</tr>
</tbody>
</table>

From Fig. 6 and Table 2, there is a slight hysteresis in the magnetization curve, which indicates that the core-shell structure microspheres show soft magnetic properties. In addition, it is clearly seen that the value of saturation magnetization increases after annealing, while the increased annealing temperature causes the reduction in the coercivity of the Co–Fe-plated microspheres.

When annealed at relatively low temperature, the crystal grain size of the sample is smaller and a large quantity of single domain exists. Moreover, the intergranular atomic arrangement of the nanocrystalline grain is rather disordered, which can weaken the ferromagnetic exchange coupling and enhance the disordered magnetic anisotropy between the single domains [29, 33, 34]. Therefore, coercivity of samples reduces with decreased grain size. During the annealing process, the crystalline grains grow up rapidly and the lattice structures of the samples become perfect. With the increase in annealing temperature, the resistance force of the domain wall movement decreases, and the surface magnetic swap of the magnetic particles becomes more intensive. Simultaneously, the interior stress and magnetic anisotropy constants decrease. All the changes in these factors induce much easier domain wall motion and spin rotation [35, 36]. As a result, when the annealing temperature rises to 800 °C, saturation intensity of products increases but coercivity reduces synchronously with increased temperature.

It can be concluded that the annealing process increases the crystallinity of Co and Fe in the coating layers, simultaneously enlarges their crystallite dimension. It is confirmed that the annealing process improves the soft magnetic properties of Co–Fe-plated microspheres.

Furthermore, it is also clearly indicated that the areas encompassed by the hysteresis loops are reduced
with the higher annealing temperature, which decreases the magnetic energy stored in the microspheres. And it matches with the results referred in Section 3.3.

4 Conclusions

1) Functional hollow microspheres plated with Co–Fe were obtained through electroless plating technique, and good quality coating layers of Co–Fe (about 2.6 μm thick) were achieved.

2) The annealing heat treatment increases the crystallinity and crystal size of Co and Fe in coating layers, and induces the Co crystal phase transformation from HCP to FCC.

3) The Co–Fe-plated microspheres possess soft magnetic character. The value of \( M_s \) decreases after the annealing process. In contrast, the coercivity of Co–Fe-plated microspheres decreases with higher annealing temperature.

4) When the annealing temperature is 800 °C, the highest dielectric properties of Co–Fe-plated microspheres can be obtained within the three annealing temperatures.

5) Co–Fe-plated microspheres are the most promising alternative candidates for microwave material due to their light, low cost, ease of processing and good dispersion.

References


