Synthesis Method and Absorption Application of Nanocrystalline Alloy Flakes

Pei-Heng Zhou and Long-Jiang Deng

Abstract—The soft magnetic Fe-Si-B nanocrystalline/amorphous flakes were fabricated by ball milling from the elemental powders and annealing the amorphous precursor, respectively. The microstructure, magnetic and microwave properties were evaluated by different synthesis methods. By computation, ball-milled Fe$_{78}$Si$_{13}$B$_9$ flakes demonstrated potential application in absorption.

Index Terms—Absorption, alloy, flake, nanocrystalline.

1. Introduction

With the development of wireless communications, absorbers of electromagnetic waves having thin absorption layer, wide applicable frequency range and large absorption loss above gigahertz are needed. To address this need, materials with high microwave permeability and matching permittivity must be explored, as the traditional ferromagnetic absorbing materials are limited in this application[1]-[4]. Fe-based nanocrystalline alloys with nano-effects and two phase nature, first investigated by Yoshizawa et al.[5], combine high-saturation magnetization with very small coercivity and very low effective saturation magnetostriction and are, therefore, of potential to improve microwave electromagnetic performance.

In recent years, ferromagnetic nanoparticles and ultrafine metallic flakes have attracted much scientific attention in the area of microwave electromagnetic properties, due to the advance of nano-effects and shape dependence of microwave properties, respectively[6][7]. Combining these two effects together, our previous works find that Fe-based nanocrystalline alloy flakes can improve microwave performance effectively by high permeability and multi-resonance[8][9].

In this paper, we investigate the Fe-Si-B nanocrystalline flakes in same nominal composition but prepared by two different synthesis methods, ball milling from the elemental powders and annealing the amorphous precursor. The characterizations of microstructure, magnetic and microwave properties are compared and discussed. Finally, absorption application of these flakes is explored by computation.

2. Experimental Details

For ball milling synthesis, experiments are carried out using Fe, Si, B elemental powders of purity ≥99%. Ball milling of powder mixture is done by a QMC1 planetary mill firstly without medium for 30 hours and then with anhydrous grain alcohol as medium for 30 hours.

For annealing synthesis, amorphous Fe-Si-B ribbons (about 1 mm wide and 18 μm thick) are prepared by melt-spinning. In the first step, amorphous ribbons are annealed at the temperature of 450 °C to 650 °C for 1 hour. Then, as-annealed ribbons are broken up into flake powders by ball milling with medium for 30 hours. Milling hours mentioned in this paper all mean the time spend on the secondary milling process (milling with medium).

The phases of the samples are determined by X-ray diffraction (XRD), and the microstructures are characterized using a transmission electron microscope (TEM/EDX). The magnetic hysteresis loops are measured using a vibrating sample magnetometer (VSM). For microwave test, as-milled powders are firstly dispersed with paraffin solvent at weight ratio 3:1, then filled in a coaxial die after cooling, and finally compacted to a toroidal shape of thickness less than 3mm. The microwave properties $\varepsilon_r(\omega)$, $\mu_r(\omega)$ of flakes-paraffin composites are measured in the 0.5-18 GHz range with a APC7 coaxial line associated with a Agilent 8720 ET vector network analyzer. The reflection loss (RL) curves are calculated from the complex permeability ($\mu_r$) and permittivity ($\varepsilon_r$) at given frequency and absorber thickness $d$ with the following equations[10]:

$$RL = 20\log[(Z_{in} - Z_0)/(Z_{in} + Z_0)]$$  \hspace{1cm} (1)

$$Z_{in} = Z_0\sqrt{\mu_r/\varepsilon_r}\tanh\left\{j(2\pi fd/c)\sqrt{\mu_r\varepsilon_r}\right\}$$  \hspace{1cm} (2)

where $Z_{in}$ is the input impedance at absorber surface, $Z_0$ the impedance of air, $f$ the frequency of microwave, and $c$ the velocity of light.

3. Results and Discussion

Ball milling is a mechanical non-equilibrium process for crystallization (called as mechanical alloying in this case), while annealing process denotes the thermal stability of solid-states. Both methods are widely used to form the nanocrystalline/amorphous two phase structure[11], but material’s microstructures differ with each other by varied
growing mechanism. Consequently, the value of magnetic and microwave parameters are distinguished.

Table 1: The mean grain size calculated by Sherrer formula and saturation magnetization

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size (nm)</th>
<th>Saturation magnetization (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₇₈Si₁₃B₉</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>11.23</td>
<td>137.43</td>
</tr>
<tr>
<td>B</td>
<td>10.55</td>
<td>145.14</td>
</tr>
<tr>
<td>Fe₇₈Si₉B₁₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>14.76</td>
<td>138.33</td>
</tr>
<tr>
<td>B</td>
<td>9.73</td>
<td>148.02</td>
</tr>
</tbody>
</table>

We have studied the effect of medium during ball milling, and it is interesting that with certain amount of medium the energy of ball milling can not introduce any new phase to material’s composition but only reducing the particle/grain size\(^1\). Therefore, the crystal structure of Fe-Si-B samples is determined by mechanical alloying and thermal crystallization and labeled as sample A and B, respectively.

![Fig. 1. SEM graphs of Fe₇₈Si₁₃B₉ flakes: (a) sample A and (b) sample B.](image)

The XRD and TEM/EDX results denote that two kinds of samples contain only bcc α-Fe phase and form the nanocrystalline/amorphous structure. The value of mean grain size and saturation magnetization \(M_s\) are listed in Tab.1. It is clear that samples in A type possess relatively high value of grain size but low \(M_s\), comparing to B type. For the reason, grain size are tailored by the competitive result of cold-welding and fracture effect during mechanical alloying, which is a confusing process, while silicon and amorphous component restrain the growth of crystallites in case of thermal crystallization, therefore, B samples have a finer microstructure and higher \(M_s\). Additionally, Fig.1 shows that B sample flakes are coarser than the other one. It is known that \(M_s\) decreases with diminishing grain size\(^1\), which is in line with the data in Table 1.

![Fig. 2. Frequency characteristics on the permeability and permittivity of Fe₇₈Si₁₃B₉ nanocrystalline alloy samples in A and B type: (a), (b) are the real and imaginary part of complex permeability, (c), (d) are the real and imaginary part of complex permittivity.](image)
As can be seen from Fig. 2, B sample provide improved permeability due to the fine microstructure and high $M_s$, as $\mu_r=4.48$ at 2.25 GHz, $\mu''=2.70$ at 6 GHz. However, both the real and imaginary part of complex permittivity is extremely high for B sample in the whole frequency range and a peak is observed at low frequencies. The great increase of permittivity deteriorates the absorption ability of sample B, as shown in Fig. 3, but the reflection loss is improved in 2GHz. It is believed that annealing process produces large amount of interface area with smaller grain size, then enhances the dielectric interface polarization effect, and finally improves the complex permittivity at GHz. For A sample, assuming as an absorber, it has broad band absorption with $RL\leq-4$ dB at 3 GHz to 10 GHz, $RL_{\text{max}}\leq-10$ dB at 4 GHz.

**Fig. 3.** Frequency dependence of reflection loss for Fe$_{78}$Si$_{13}$B$_9$ nanocrystalline flake samples with absorber thickness $d=1$mm.

### 4. Conclusion

This study investigates the microstructure, magnetic and microwave properties of Fe-Si-B nanocrystalline flakes prepared by mechanical alloying and annealing crystallization. The nanocrystalline/amorphous two phase structure and fine flake shape are successfully synthesized by two methods respectively. It is found that FeSiB flakes synthesized by annealing method possess small grain size and so introduce high value of saturation magnetization and microwave parameters to the material. However, the extremely high complex permittivity deteriorates the absorption ability of flakes. Fe$_{78}$Si$_{13}$B$_9$ nanocrystalline flakes prepared by mechanical alloying show broad band absorption in GHz, with $RL\leq-4$ dB at 3 GHz to 10 GHz, $RL_{\text{max}}\leq-10$ dB at 4 GHz.

### References


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