Magnetic softness and magnetization dynamics of FeSiBNbCu(P,Mo) nanocrystalline alloys with good high-frequency characterization

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ARTICLE INFO

Keywords:
Nanocrystalline alloy
Magnetic softness
Dynamic magnetization
High-frequency
Magnetic domain

ABSTRACT

In this study, the microalloying effects of P and Mo on thermal behavior, magnetic softness and magnetization process of FeSiBNbCu(P,Mo) nanocrystalline alloys were investigated systematically. The P and Mo bearing alloys exhibit pronouncedly improved magnetic softness, including extremely low coercivity of about 0.7 A/m, high saturation magnetic flux density of about 1.40 T, high permeability over 3.0 × 10^4 at 1 kHz. The excellent magnetic softness could be attributed to uniform dual-phase microstructure and wide strip magnetic domains after optimum annealing. The P and Mo containing alloys also have good high-frequency characterization, especially, the permeability at 100 kHz is still over 1.53 × 10^4. These alloys also have relatively low pinning field of 20–30 A/m, which means lesser defects and easier magnetization. Through observing the changes of magnetic domains and μ with applied field increasing, we found that the increase of μ is corresponding to reversible and irreversible movement of domain walls, after reaching the maximum, the decrease of μ is related to the rotation of magnetic moment and the split of domains.

1. Introduction

As soft magnetic functional materials, Fe-based nanocrystalline alloys with excellent magnetic softness containing quite low coercivity (Hc), low core loss (P), and high permeability (μ) [1–3], have been widely used in common mode chokes, inductors, high-frequency transformers, and other electrical devices. With the emergence of the global energy crisis and the progress of the science and technology, the development tendency of electrical devices is miniaturization, high efficiency and energy conservation [4]. This correspondingly desires Fe-based nanocrystalline alloys have higher saturation magnetization (Bs), lower P, higher μ, and better high-frequency stability than that of current alloys. Finemet nanocrystalline alloys not only have relatively low Hc and high μ, but also have been widely industrial used. However, the Finemet alloys also have two shortcomings which become increasingly obvious for low Bs of only 1.24 T and high material costs due to addition of 3 at.% precious element Nb [5,6]. By devoting subsequent great efforts, a variety of high Bs of FeZrB [7], (Fe0.5Co0.5)ZrB [8], FeSiBCu [9], FeSiBCu [10], FeSiBPCu [11] and etc. were successfully developed. Yet, these nanocrystalline alloys exhibit high Hc above 3 A/m, poor high-frequency characteristic and low amorphous forming ability (AFA) due to high content of Fe element [12] and low content of amorphous forming elements [13]. Recently, Fe76Si13B8Nb2Cu1 nanocrystalline alloy with low Hc of 1.5 A/m, high Bs of 1.4 T, and high μ near 1.0 × 10^4 at 100 kHz have been successfully developed [14], showing an attractive application prospect. Nevertheless, the Fe76Si13B8Nb2Cu1 alloy also needs further optimization to meet the demands of the high-frequency applications, which requires further reduction of Hc and increment of μ up to frequencies of several hundred kilohertz.

Compared with Fe-based alloys without addition of P element, the P containing FeSiBCu [11,15] alloys had higher nanocrystallization activation energy and frequency factor which were benefit to form more uniform microstructure with high density of α-Fe (Si) grains. Accordingly, FeSiBCP [13] and FeSiPCu [16] alloys also had low Hc and high AFA. Moreover, it found that adding Mo could improve oxidation resistance, thermal stability [17–19] and high-frequency performance [20]. Besides, the addition of Mo also could improve the local packing efficiency and energy conservation [4]. This correspondingly desires Fe-based nanocrystalline alloys with good high-frequency characterization.

Received 24 October 2018; Received in revised form 31 January 2019; Accepted 31 January 2019

Available online 01 February 2019

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efficiency, inhibit grain growth, and restrain the long-range diffusion of atoms, which leading to reduction of Hc and improvement of AFA [18, 21, 22].

In this study, via addition of P and Mo elements, Fe_{76}Si_{13}B_{7}P_{1}Nb_{2}Cu_{1} and Fe_{76}Si_{13}B_{8}Nb_{1.5}Mo_{0.5}Cu_{1} nanocrystalline alloys with good soft-magnetic performances are developed. The origin of excellent magnetic softness of the FeSiBNbCu(P, Mo) alloys were discussed. Furthermore, because of the nanocrystalline soft-magnetic alloys widely used as electric devices in various magnetic fields, the relations among the dynamic magnetic properties, magnetic domains, and magnetization fields on the nanocrystalline alloys are illustrated.

2. Experimental procedures

Multi-component alloys with nominal atomic compositions of Fe_{76}Si_{13}B_{7}P_{1}Nb_{2}Cu_{1} and Fe_{76}Si_{13}B_{8}Nb_{1.5}Mo_{0.5}Cu_{1} were prepared by induction melting with the mixtures of pure Fe (99.99 mass%), Si (99.99 mass%), B (99.9 mass%), Cu (99.99 mass%), Mo (99.9 mass%), and pre-alloy of Fe-3P under Ar atmosphere after high vacuum of about 1 × 10^{-2} Pa. Amorphous ribbons with width of about 1.3 mm and thickness of about 24 µm were prepared through a single-roller melt-spinning method. The thermal properties of ribbons were identified by a differential scanning calorimetry (DSC, NETZSCH 404C) at a heating rate of 0.67 °C/s. Isothermal annealing were carried out under a certain temperature from 500 to 600 °C for 10 min followed by water-quenching. In order to avoid oxidation of the samples, the annealing process was performed in a furnace with a vacuum degree of about 5 × 10^{-3} Pa.

The microstructures of as-quenched and annealed ribbons were investigated by an X-ray diffraction (XRD, Bruker D8 Advance) with Cu-Kα radiation and a high-resolution transmission electron microscopy (TEM, TF20). B$_1$ was evaluated through a vibrating sample magnetometer (VSM, Lake Shore 7410) at the maximum applied field of 800 kA/m. $\mu$ was measured by an impedance analyzer (Agilent 4294 A) in alternating magnetic fields from 1 to 60 A/m. $H_c$ was conducted using a DC B-H loop tracer (EXPH-100, Riken Doshi Co., Ltd.) under the maximum applied field of 800 A/m. The magnetic domain images were observed by a Magneto-optical Kerr Effect Microscopy using an Evico Magnetics Kerr Microscope (4-873K/950MT, Germany) in the longitudinal mode. The Kerr microscopy was measured on the air-bare surface of ribbon samples without further sample preparation such as polishing or coating. In order to deeply investigate the domain model and magnetization process, the changes of the domains were performed via the Magneto-optical Kerr Microscopy with in-situ applying an increasing external magnetic field with direction along the ribbon axis. The magnetic softness measurements were conducted on melt-spun or annealed ribbons with length of 75 mm. All the measurements were conducted at room temperature.

3. Results and discussion

3.1. Thermal behavior and amorphous forming ability

Thermal behavior and amorphous forming ability (AFA) were investigated after developed FeSiBNbCu(P, Mo) ribbons with good surface quality, as shown in Fig. 1. XRD measurements from 30° to 90° were performed on ribbon samples and shown in the inset (a) of Fig. 1. It can be found from the XRD patterns that P added Fe_{76}Si_{13}B_{7}P_{1}Nb_{2}Cu_{1} (PA) and Mo added Fe_{76}Si_{13}B_{8}Nb_{1.5}Mo_{0.5}Cu_{1} alloy (MA) ribbons prepared at a low wheel speed of 25 m/s exhibit only a halo peak at 2θ = 45° corresponding to complete amorphous structure, indicating high AFA of two alloy ribbons. The DSC curves of the melt-spun basic Fe_{76}Si_{13}B_{8}Nb_{2}Cu_{1} (BA), PA, and MA ribbons all exhibit two distinct exothermic peaks with the onset temperatures marked as $T_{x1}$ and $T_{x2}$ [23]. Inset Fig. 1(b) illustrates partial enlarged graph of the DSC curves. The decrease of $T_{x1}$ for the PA and MA ribbons means easier to precipitate α-Fe (Si) phase [23]. The result is consistent with the trend of previously reported at FeSiBPCu alloy system [11, 24]. It has been already reported that, in the amorphous precursor with a large $\Delta T_x$ ($\Delta T_x = T_{x2} - T_{x1}$), there is a large possibility to form single nanocrystalline α-Fe(Si) phase without precipitation of any compounds, i.e., boride by heat treatment within the annealing temperature region between the two crystallization peaks [25]. The wide temperature interval $\Delta T_x$ of PA and MA ribbons are 152 °C and 151 °C, respectively, which are slightly lower than BA ribbon but a sufficient wide temperature interval to precipitate ultrafine single nanoparticles and obtain excellent magnetic properties in the annealing process [26].

3.2. Magnetic softness dependence on annealing temperature

The magnetic properties were then investigated systematically focusing on the 10 min annealed ribbons according to optimum annealing time of BA ribbons [14]. The coercivity ($H_c$) dependence on annealing temperature ($T_a$) of annealed PA, MA, and BA ribbons exhibit similar tendency, as shown in Fig. 2(a). The $H_c$ of both PA and MA ribbons exhibit extremely low value of 0.7 and 0.6 A/m annealed at 580 °C,
between typical loops of soft magnetic nanocrystalline alloys. It is found that the
then measured with VSM. As shown in Fig. 3, all ribbons exhibit the
(henceforth designated as optimum
loys. The hysteresis loops of three alloys annealed at optimum
field.
respectively. Fig. 2(b) presents the permeability ($\mu$) as a function of $T_A$
for the annealed PA, MA, and BA ribbons, which show the same trends. With the increase of $T_A$, the $\mu$ of ribbons moderately decreases at first, then it increases and reach a peak value. Especially, the peak values of PA and MA ribbons reach to $2.83 \times 10^4$ and $3.0 \times 10^4$ at $580^\circ$C (henceforth designated as optimum $T_A$), respectively. It is noted that $H_c$ and $\mu$ of PA and MA ribbons follow the rule of $\mu \propto H_c^{-1}$. The relations between $H_c$ and $\mu$ are also existed in the many amorphous and nanocrystalline alloys [27]. The addition of P or Mo to the BA alloy could effectively improve $\mu$ and greatly reduce $H_c$. Furthermore, compared with commercial nanocrystalline Finemet alloys [3], the PA and MA ribbons are expected to have more advantages in the future applied field.

The hysteresis loops of three alloys annealed at optimum $T_A$ were then measured with VSM. As shown in Fig. 3, all ribbons exhibit the typical loops of soft magnetic nanocrystalline alloys. It is found that the $H_c$ of PA and MA ribbons have similar low value, which is equivalent to the $H_c$ of Finemet alloy, as shown in inset (a) of Fig. 3. But, the $B_s$ gains a great improvement, increase from 1.24 T for the Finemet alloy to 1.41 T for the PA alloy, as illustrated in inset (b) of Fig. 3. Similarly, compared with BA ribbons, the $B_s$ of PA and MA ribbons have slight increase or decrease, but the $H_c$ has been greatly optimized. It has reported that $B_s$ is related to the ratio of the volume fraction of the crystalline phase ($V_c/V$) and to that of the amorphous phase ($V_a/V$). The $B_s$ can be expressed as:

$$B_s = B_{sc} V_c/V + B_{sa} V_a/V$$  \hspace{1cm} (1)

where $B_{sc}$ and $B_{sa}$ are the saturation magnetic flux densities of the crystalline and amorphous phases, respectively, the $B_{sc}$ is larger than $B_{sa}$ [28,29]. The $B_s$ of PA ribbons is slightly higher than that of BA ribbons mainly due to easy precipitation of $\alpha$-Fe (Si) phase with the additive of P element.

From the above, the specific value parameters of thermal behavior and magnetic softness of three ribbons were summarized and shown in the Table 1. It is found that the PA and MA ribbons exhibit excellent thermal behavior and magnetic properties, which is promising to be widely applied in electronics fields.

In order to obtain more convincing and detailed microstructure to prove the excellent magnetic softness of PA and MA ribbons, the XRD and TEM characterizations of the PA and MA after annealing under optimal conditions were carried out on ribbon samples, and shown in Fig. 4(a) and Fig. 4(b-c). It can be found that PA and MA ribbons both exhibit three sharp crystalline peaks at about $2\theta = 45^\circ$, 65$^\circ$, and 83$^\circ$, respectively, which can be identified as $\alpha$-Fe phase from XRD patterns according to the reports [9,30]. The grain size of PA and MA ribbons were obtained with $Scherrer$ formula [31] and the values are 12.8 nm and 11.6 nm, respectively. The grain size was further confirmed by TEM, the ultra-fine $\alpha$-Fe nanocrystalline grains uniformly embed in the amorphous matrix and the grain sizes are 13.2 nm and 12.9 nm, respectively, which are consistent with the XRD patterns. The uniform microstructure with the fine grains is the main reason for the excellent magnetic properties of the PA and MA sample [32], Fig. 4(d-e) show the magnetic domains of PA and MA alloy ribbons after optimum annealing. Two wide alternately bright and dark stripe domains over 70 µm with preferred orientation can be easily observed, and continuous stripe domains with alternating bright and dark could be observed in many nanocrystalline alloys after normal annealing [33–35], so sketched striped domain arrangements were shown in Fig. 4(d-e), which can directly prove that both PA and MA ribbons exhibit extremely low $H_c$.

### Table 1
Thermal behavior and magnetic softness parameters of three nanocrystalline alloys.

<table>
<thead>
<tr>
<th>System</th>
<th>$T_x$ (°C)</th>
<th>$T_{x1}$ (°C)</th>
<th>$T_{x2}$ (°C)</th>
<th>$\Delta T_x$ (°C)</th>
<th>$H_c$ (A/m)</th>
<th>$\mu_e$ (1 kHz)</th>
<th>$B_s$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>332</td>
<td>490</td>
<td>642</td>
<td>152</td>
<td>0.7</td>
<td>28,300</td>
<td>1.41</td>
</tr>
<tr>
<td>MA</td>
<td>338</td>
<td>487</td>
<td>638</td>
<td>151</td>
<td>0.6</td>
<td>30,000</td>
<td>1.38</td>
</tr>
<tr>
<td>BA</td>
<td>340</td>
<td>492</td>
<td>650</td>
<td>158</td>
<td>1.5</td>
<td>21,500</td>
<td>1.39</td>
</tr>
</tbody>
</table>

3.3. Dynamic magnetization and high-frequency characterization

For the consideration of the high-frequency applications tendency of the nanocrystalline alloy, the relative permeability of the annealed
ribs under different AC magnetic field amplitude (H_m) and frequency is an important parameter [36]. The high-frequency characterization of ribbons, which were annealed at optimum condition were measured by the impedance analyzer (Agilent 4294 A) with characterization of ribbons, which were annealed at optimum condition. The high-frequency characteristic, which will make the two alloys prospectively candidate for various electric devices at a high frequency field. As we know, H_p is directly related to the domain motion, and could be identified through investigating the degree of difficulties in domain movements [33,38]. The μ is also closely related to the magnetization process. Furthermore, when the investigated frequency of the ribbon is lower than the magnetic relaxation frequency, the dynamic magnetization model could be treated as a quasi-static model [39]. The relaxation frequency of PA and MA ribbons is over 100 kHz, which is wider than frequency range of this study. Therefore, the changes of domain were in-situ investigated by applied fields at optimum annealing temperature for 10 min; (c) the changes of μ for PA and MA ribbons with H_m at 1 kHz; (d) the permeability spectra of the PA, MA and BA ribbons at H_p.

Compared with other high magnetic softness alloys such as FeZrB [7], FeSiBCu [10], FeSiBPCu [11] and FeSiPCu [16] alloys, PA and MA nanocrystalline alloys have huge advantage in high frequency characteristics, which will make the two alloys prospectively candidate for various electric devices at a high frequency field. When the H is higher than H_p, only irreversible movement such as refinement, split and reversal of domains occurred, which corresponds to μ began to decrease. Therefore, as shown in Fig. 6 A, the variation trend of μ is consistent with change of domains wall, before the value of μ reaches its maximum, the domain wall moves reversible and then irreversible. After μ reaches the maximum, the magnetic moment begins to rotate and the domain splits up and then disappears. The vanishing of

![Diagram](image_url)

Fig. 5. (a-b) permeability spectra of the PA and MA ribbons with various applied fields at optimum annealing temperature for 10 min; (c) the changes of μ for PA and MA ribbons with H_m at 1 kHz; (d) permeability spectra of the PA, MA and BA ribbons at H_p.
domains means the magnetic moment reverses completely and tends to saturation, leading the \( \mu \) decreases to a low value and even close to zero.

4. Conclusion

After microalloying P and Mo, the thermal behavior, magnetic softness and dynamic magnetization process of FeSiBNCu(P,Mo) nanocrystalline alloys were investigated systematically. As a result, both Fe\(_{76}\)Si\(_{13}\)B\(_7\)P\(_1\)Nb\(_2\)Cu\(_1\) (PA) and Fe\(_{76}\)Si\(_{13}\)B\(_8\)Nb\(_1.5\)Mo\(_0.5\)Cu\(_1\) (MA) ribbons exhibit good thermal behavior and high AFA, together with good magnetic softness including extremely low \( H_\mathrm{c} \), of 0.6–0.7 A/m, high \( \mu \) over 3.0 \( \times \) 10\(^4\) and high performance are attributed to the low pinning force, which makes the two nanocrystalline ribbons prospectively candidate for various electric devices at a high frequency field. The excellent high frequency performance are attributed to the low pinning field and easy movement of domain walls during dynamic magnetization process due to the fine homogeneous dual-phase microstructure, and wide strip domains.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2017YFB0903902), and the National Natural Science Foundation of China (Grant No. 51801224, 51601206, 51771083, 51571047), the Zhejiang Provincial Natural Science Foundation (LQ18E010006), and the Ningbo Municipal Natural Science Foundation (2018A610172).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmmm.2019.01.116.

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