Syntheses and Fundamental Properties of Cr/Mo-Adoped Fe-Rich Alloys With Metastable Phase and Saturation Magnetization Near 1.9 T

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The Fe-rich alloys of Fe_{90-x}Si_{5}B_{x}M_{x} (M= Cr or Mo; x=1, 2) are synthesized in the present study. The as-spun structure mainly consists of bcc phase plus a minor amount of metastable phase (Fe_{5}B and/or Fe_{8}B). Comparing with the base alloy Fe_{90}Si_{5}B_{5}, the corrosion resistance is improved significantly due to the formation of the passive film. Saturation magnetic flux density reaches 1.9 T for the melt-spun alloys Fe_{89}Mo_{1}Si_{5}B_{5}. The alloys present a nearly constant high permeability in a rather high magnetic field up to coercive field which can be used as a new kind of sensor material with good fundamental properties and low cost.

Keywords: Fe-rich metastable alloys; Magnetic sensor materials; High Bs; Corrosion resistance

1. Introduction

Recently, there has been an increasing emphasis on the development of magnetic component with high performance and high integration level, which requires the exhibition of high saturation magnetic flux density (B) in combination with good mechanical strength and corrosion resistance for soft and hard magnetic materials. In our previous study, we have been developing amorphous and nanocrystalline soft magnetic alloys and nanocomposite hard magnetic alloys with B which is much higher than that of the commercialized composition in conjunction with good fundamental performance such as good corrosion resistance, wear resistance and bending ductility even after annealing.

Meanwhile, a series of Fe-rich crystalline-based Fe_{90}Si_{5}B_{5} alloys (x=2.5–7.5) alloys were developed as well. These alloy ribbons consist mainly of bcc phase plus a minor amount of metastable phase such as amorphous and Fe_{5}B phase. Besides, the alloys exhibit unique magnetic properties of high B exceeding 1.9 T, moderately large coercivity (Hc) in conjunction with the nearly linear B–H relation in coercive field. In addition, these alloys show good bending ductile nature even after annealing. Such alloys are expected to provide unique magnetic behavior in moderately wide magnetic field for highly integrated magnetic sensor component.

However, their crystalline-based feature results in the low corrosion resistance than that of the Fe-Si-B amorphous alloy ribbons. This situation limits the application and increase in cost as a new kind of magnetic material. Therefore, there is a strong demand on improving the corrosion resistance for such alloys. It is expected to obtain the combination of such good properties by compositional modification. The study of Cr-adopted Fe-Si steel and Mo-adopted amorphous glassy alloys indicate that the corrosion resistance can be improved by a small addition of Cr/Mo element. On the contrary, however, the B value decreases simultaneously.

Based on our recent research of Fe_{90}Si_{5}B_{5} alloy, Fe-rich alloys of 1 and 2 at% Cr / Mo substituted for Fe, i.e. Fe_{89}Si_{5}B_{x}M_{x} (M=Cr or Mo; x=1, 2) are synthesized with the aim of improving the corrosion resistance and mechanical properties with no significant decrease in B in the present study.

2. Experiment procedure

Quaternary alloys Fe_{90}Cr_{1}Si_{5}B_{5}, Fe_{90}Cr_{1}Si_{5}B_{5}, Fe_{90}Mo_{1}Si_{5}B_{5} and Fe_{90}Mo_{1}Si_{5}B_{5} ribbons were prepared for this study. Their alloy ingots were prepared by arc melting the mixtures of pure elements in an argon atmosphere. Rapidly solidified ribbons were prepared by melt spinning and the resulting alloy ribbons have a thickness of about 20μm and a width of about 0.8 to 1.0 mm. The structure was examined by X-ray diffraction (XRD) with Cu-Kα radiation and transmission electron microscopy (TEM). XRD patterns were obtained on the free solidified side of the ribbon samples. Mechanical properties were measured by tensile testing machine (WDW-20) at room temperature. Tensile specimens had a gauge length of 10 mm in length and the strain rate was 0.05 s^{-1}. Bending ductility was evaluated by bending the specimens through 180 degrees. The bent surface was examined by scanning electron microscopy (SEM). The B and Hc were measured with a vibrating sample magnetometer (VSM) under a field of 800 kA/m and a DC B–H loop tracer under a field of 800 A/m, respectively. Corrosion behavior was evaluated for the ribbon samples which were degreased, washed and dried in air.

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before immersion by electrochemistry test. Electrochemistry measurements were performed by an electrochemistry workshop (Gamry Reference 600 redefining electrochemical measurement) in 3.5mass% NaCl solution at 298 K. Ribbon samples were set as working electrode; a platinum electrode was working as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. Polarization curves were measured by a potentiodynamic process from 250mV under open circuit potential (OCP) to 250mV above OCP value at a scanning rate of 1mV/s.

3. Results and Discussion

Figure 1 (a) shows the X-ray diffraction patterns of the present melt-spun ribbons. The major phase in these alloys is identified as bcc-Fe from the ordinary XRD patterns. Besides, one can notice tiny peaks around 44 degree in the diffraction patterns of all alloys, which can be indexed as Fe₆B phase. This resulted structure is similar to that of the Fe₆Si₆B₄ alloy. Besides, from the high resolution XRD patterns of Fe₉Mo₆Si₆B₄ alloy shown in Figure 1 (b), it can be recognized the tiny peak appeared around the (110) peak of bcc-Fe, indicating the presence of another phase, which will be discussed later.

In order to clarify the structure feature and phase component in details, the Fe₉Mo₆Si₆B₄ alloy was studied by TEM. Figure 2 shows the bright-field TEM images and SAED patterns of Fe₈₅Mo₂₅Si₃₀B₁₀ alloys. The as-spun structure consists of bcc phase with a grain size of about 0.1 to 0.2 μm and nearly fine spherical precipitates with a size of about 20 nm. The diffraction patterns shown in Figure 2 (b) and (c) are identified as bcc-Fe and fcc-Fe₆B phases, respectively. Fe₂₂B₉ is a metastable boride phase present in different kind of steel and alloys. It can easily decompose into bcc-Fe and Fe-B. However, this phase is stabilized when Fe atom site is partially substituted by another transition metal atom. The larger atomic radius of Mo (0.140 nm) and the strong Mo-B interaction is deduced to impede the atomic migration for the decomposition of Fe₂₂B₉ phase. Thus the as-spun structure is composed of bcc + Fe₆B phase for Fe₈₅Cr₂₅Si₂₅, Fe₈₅Cr₇Si₇B₂₃, and Fe₉₀Mo₆Si₆B₄ alloys as well as bcc + Fe₆B phase + Fe₂₂B₉ phase for Fe₈₅Mo₂₅Si₃₀B₁₀ alloy, respectively.

Figure 4 shows the B-H hysteresis loops for the present Fe-Si-B-TM alloys in as-spun state, and the Bₓ and Hc of the alloys annealed at 823 K for 600 s are summarized in Table 1. For the as-spun ribbons, the Fe₉₀Mo₂₅Si₃₀B₁₀ ribbon exhibits the highest Bₓ value, and then followed by Fe₈₅Cr₂₅Si₂₅. Adding 2 at% Mo does not affect as harmful as 2 at% Cr on the Bₓ value, which is presumably due to the presence of the remaining Fe₂₂B₉ phase. According to recent theoretical studies about the structure and magnetic properties of Fe₂₅Mₓ-type phase (M=C or B) using first-principles theory, it is revealed that the Fe₂₅Mₓ phase has strong ferromagnetic characteristics and large magnetic moment. After annealing, the Fe₉₀Mo₂₅Si₃₀B₁₀ alloy maintains high Bₓ value of 1.9 T in spite of the presence of Fe₆B precipitates. Besides, these Fe-rich crystal-based alloys exhibit moderately large coercivity,
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Figure 3: (a) outer surface and (b) SEM image obtained near the crease mark of the bent alloy ribbon Fe$_{88}$Mo$_2$Si$_5$B$_5$ annealed at 823 K for 600 s.

Figure 4: $B$-$H$ hysteresis loops of Fe$_{90-x}$Si$_5$B$_5$M$_x$ (M=Cr, Mo; x=1, 2) ribbon as-spun alloys under an applied field of 800 kA/m.

Table 1: Saturation magnetic flux density ($B_s$), coercivity ($H_c$), corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$), tensile fracture strength ($\sigma_f$) and elongation rate ($\varepsilon$) of the Fe$_{90-x}$Si$_5$B$_5$M$_x$ (M=Cr or Mo; x=1, 2) alloys annealed at 823 K for 600 s.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$B_s$ (T)</th>
<th>$H_c$ (A/m)</th>
<th>$I_{corr}$ ($\mu$A/cm$^2$)</th>
<th>$E_{corr}$ (V)</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{89}$Cr$_1$Si$_5$B$_5$</td>
<td>1.68</td>
<td>189</td>
<td>7.1</td>
<td>-0.716</td>
<td>1151</td>
<td>0.363</td>
</tr>
<tr>
<td>Fe$_{89}$Cr$_2$Si$_5$B$_5$</td>
<td>1.49</td>
<td>654</td>
<td>6.7</td>
<td>-0.683</td>
<td>1158</td>
<td>0.444</td>
</tr>
<tr>
<td>Fe$_{89}$Mo$_1$Si$_5$B$_5$</td>
<td>1.90</td>
<td>790</td>
<td>9.7</td>
<td>-0.738</td>
<td>1250</td>
<td>0.373</td>
</tr>
<tr>
<td>Fe$_{88}$Mo$_2$Si$_5$B$_5$</td>
<td>1.63</td>
<td>945</td>
<td>9.4</td>
<td>-0.799</td>
<td>1380</td>
<td>0.575</td>
</tr>
</tbody>
</table>

which is related to the irregular shape and wide size range of the grains to obtain significant magnetic anisotropy. As recognized previously, the present alloys maintain the unique magnetic features of showing a nearly constant permeability (slope) up to relatively high magnetic field corresponding to a moderately large coercivity.

Figure 5 shows the polarization curves of the annealed ribbons and their electrochemistry parameters are summarized in Table 1. By addition of Cr or Mo into the Fe$_{90}$Si$_5$B$_5$ alloy ($I_{corr}$=15.65 A/cm$^2$, $E_{corr}$=-0.796 V), the corrosion current density decreased by an order of magnitude and the corrosion potential distinct increased as well. Moreover, one can notice that among these alloys, composition containing Cr exhibit relatively lower corrosion current and higher corrosion potential than those of the Mo-containing alloys, which is caused by the formation of stable protective passive films made of Cr-rich oxides. Although Cr and Mo belongs to the same subgroup in the periodic table which seems to exhibit the similar chemical properties, stable Mo-rich passive film cannot form on the surface deducing by the low Mo content than normal level detected by XPS. This can be explained by the difficulty of atomic migration of Mo to the surface resulting from the stronger bond than Cr to other metalloid elements due to the larger atomic radius. It is thus can be concluded that by adopting 1 at% to 2 at% of Cr and Mo, the corrosion resistance is improved significantly as compared with the base alloy Fe$_{90}$Si$_5$B$_5$.

The mechanical strength of the present alloy ribbons are estimated by tensile test. The obtained mechanical properties parameters such as tensile fracture strength, elongation of the annealed alloys are summarized in Table 1. Comparing with the base alloy Fe$_{90}$Si$_5$B$_5$ (1028 MPa), the tensile fracture strength has been significantly increased. The reason for the annealing-induced enhancement of mechanical strength can be regarded caused by the changes of structure feature. Figure 6 (a) shows the high resolution XRD patterns of the annealed Fe$_{88}$Mo$_2$Si$_5$B$_5$ alloy. Tiny peaks besides the bcc-Fe (110) peak can be recognized, which are indexed as precipitated Fe$_2$B and remaining Fe$_3$B phase. Figure 6 (b) shows the TEM bright-field image of this annealed alloy. One can notice the growth of the compound phase from...
Figure 5: Polarization curves of the Fe$_{90-x}$Si$_5$B$_5$M$_x$ (M= Cr or Mo; x=1, 2) ribbon alloys in 3.5mass% NaCl solution at 298K. The ribbons were annealed at 823 K for 600s.

Figure 6: (a) High resolution XRD patterns (Cu-Kα) and (b) Bright-field image with corresponding (c) selected area electron diffraction pattern of Fe$_{88}$Mo$_2$Si$_5$B$_5$ ribbon after annealing at 823 K for 600 s.

20 nm (as-spun state) to 80 nm (annealed state). Thus the enhancement of mechanical strength is caused by the growth of Fe-B compound. Besides, here it is necessary to point out that the suitable growth of Fe-B precipitate is not harmful for the alloys to exhibit good bending ductility.

4. Conclusion

We examined the formation, structure, mechanical properties, magnetic properties as well as corrosion resistance of the alloys with the composition of Fe$_{90-x}$Si$_5$B$_5$M$_x$ (M= Cr or Mo; x=1, 2). The results obtained are summarized as followed:

1. The as-spun structure is composed of bcc + Fe$_3$B phase for Fe$_{89}$Cr$_1$Si$_5$B$_5$, Fe$_{89}$Cr$_2$Si$_5$B$_5$, and Fe$_{89}$Mo$_2$Si$_5$B$_5$ alloys as well as bcc + Fe$_3$B + Fe$_{23}$B$_6$ phase for Fe$_{88}$Mo$_2$Si$_5$B$_5$ alloy, respectively.
2. All as-spun ribbon samples exhibit good bending ductility in as-spun state and even after annealing. Tensile fracture strength of the present alloys increased after annealing, caused by the growth of the Fe-B compound phase.
3. Corrosion resistance has been improved significantly by adopting Cr to the base alloy Fe$_{90}$Si$_5$B$_5$, contributing from the formation of the stable Cr-rich passive film.

4. High $B_s$ of 1.9 T is obtained for the present study, in conjunction with moderately large coercivity. Besides, all samples present a nearly constant high permeability in a rather high magnetic field up to coercive field which can be useful for special application in a rather wide magnetic field.

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6. References


