Microstructural evolution and nanocrystalline formation kinetics in FeCo based alloys during mechanical alloying

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Abstract. Mechanical alloying (MA) is a widely used processing technique to prepare metastable or nanophase materials in a cost effective fashion. In this study, mechanically alloying FeCo based nanomagnetic alloys was included. Scanning electron microscope (SEM), X-ray diffractometer (XRD), transmission electron microscope (TEM), vibrating sample magnetometer (VSM) were used to characterize the as milled powders. The effect of additional elements P and B on the powder size, microstructures and magnetic properties is discussed. It showed that the addition of P and B could reduce the powder size more effectively. The addition of elements P and B during MA of FeCo magnetic alloy also led to the formation of spherical nanocrystallines instead of banded microstructures in MA FeCo without these additions.

Introduction
Nanostructured magnetic materials have attracted considerable interest from various researchers in the areas of defense, bioengineering, power electronics and data storage industries [1-3]. FeCo based alloys, which have highest magnetic induction among all the magnetic materials, as well the high Curie temperature, were one state of art topic of the nanomagnetic research. A successful example was HiTperm alloys (typical composition (FeCo)₈₈M₇B₄Cu₁), showing superior soft magnetic properties and potential applications in high temperature [4-6]. The significant character of this alloy family was that the α-FeCo or α'-FeCo nanocrystalline phase embedded in the amorphous matrix. These alloys are generally produced by nanocrystallization from melt spun amorphous ribbon.

MA had been widely used in processing metastable or nanophase materials [7]. It shows some advantages to melt spinning processing technique, such as simplification of processing and low cost. Investigations of mechanical alloying FeCo binary alloys were reported by several researchers [8-14]. From these reports, nanophases could be obtained but the magnetic properties were not superior. Mechanical alloying of FeCo based alloys with additions has been seldom reported [15]. However, these additions can affect the microstructures as well the magnetic properties. In this study, mechanical alloying FeCo based alloys basing on the HiTperm alloy compositions was carried out.

Experimental
Starting from elemental powders Fe (99.9%, 22 mesh), Co (99.9%, 100 mesh) and compounds powders Fe₃P (99.5%), FeB (98%), mechanical alloying was carried out in Fritsch Pulverisette 5 (F5) planetary ball milling with attachments of hardened steel balls and vials. The powders were filled according to the nominal composition Fe₅₀Co₅₀, Fe₄₁Co₄₄₅P₇B₄, Fe₄₁Co₄₁P₁₄B₄ and Fe₄₂Co₄₂₅P₇B₈. The balls to powder weight ratio was 10:1. The milling speed was set to 300 rpm for all the milling experiments. Reverse mode after every 5min milling was selected during the milling process to decrease the sticking of powders to the balls and vials, and also to make the milling more effective. Argon gas was used to protect the powders from oxidation during all the
milling process. After different periods of milling, the powders were retrieved and then characterized using SEM, XRD, TEM and VSM for morphological observation, phase analysis, microstructural observation and magnetic properties study. The powder size was determined from SEM micrographs; generally more than 200 powders were included. TEM samples were prepared by mixing the as milled powders with epoxy resin and ion milling after properly grinding.

**Results**

The size of as milled powders after different periods of milling is listed in Table 1. A significant decrease in powder size from 5 h to 15 h milling was observed for all the four different nominal compositions. Typical morphologies of as milled powders after 15 h milling are shown in Fig. 1. It can be seen that the addition of elements P and B had a strong effect on the morphology and the reduction of powder size. The powders were alloyed after 5 h milling for all the four compositions, as there were no peaks corresponding to Co after 5 h milling as well as a change in the position of the Fe peaks in the XRD analysis (Fig. 2), indicating the formation of FeCo alloy. Fig. 3 is the magnetization and coercivity of the powders as milled after different periods. The microstructure of the powders was observed using TEM, as shown in Fig. 4.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Milling time</th>
<th>5 h</th>
<th>10 h</th>
<th>15 h</th>
<th>20 h</th>
<th>50 h</th>
<th>70 h</th>
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<tbody>
<tr>
<td>Fe&lt;sub&gt;50&lt;/sub&gt;Co&lt;sub&gt;50&lt;/sub&gt;</td>
<td>19.6 µm</td>
<td>12.3 µm</td>
<td>5.0 µm</td>
<td>4.6 µm</td>
<td>4.3 µm</td>
<td>3.3 µm</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sub&gt;44.5&lt;/sub&gt;Co&lt;sub&gt;44.5&lt;/sub&gt;P&lt;sub&gt;7&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;</td>
<td>3.2 µm</td>
<td>2.1 µm</td>
<td>1.7 µm</td>
<td>1.5 µm</td>
<td>1.4 µm</td>
<td>1.1 µm</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sub&gt;41&lt;/sub&gt;Co&lt;sub&gt;41&lt;/sub&gt;P&lt;sub&gt;14&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;</td>
<td>2.6 µm</td>
<td>3.1 µm</td>
<td>1.6 µm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sub&gt;42.5&lt;/sub&gt;Co&lt;sub&gt;42.5&lt;/sub&gt;P&lt;sub&gt;7&lt;/sub&gt;B&lt;sub&gt;8&lt;/sub&gt;</td>
<td>9.4 µm</td>
<td>1.8 µm</td>
<td>1.9 µm</td>
<td>-</td>
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</table>

Fig. 1 Typical morphologies of as milled powders
Discussion

MA (generally practiced using high-energy ball milling technique) is accomplished through mixing, impaction, shearing, cold-welding and fracturing [7]. These mechanisms of milling can lead to a decrease in powder size, as well increase in powder size when cold welding is dominant. From Table 1, it can be seen that the powder size decreased a lot with the milling time for mechanical alloying Fe_{50}Co_{50}. However, compared to the compositions with P and B, the decrease in powder size during mechanical alloying Fe_{50}Co_{50} was much slower. Only after 5 h milling of Fe_{44.5}Co_{44.5}P_{7}B_{4} and Fe_{41}Co_{41}P_{14}B_{4} or after 10 h milling of Fe_{42.5}Co_{42.5}P_{7}B_{8}, the powders had a size comparable with 70 h milled Fe_{50}Co_{50} powders. This is because during the milling Fe_{50}Co_{50} cold welding was more effective than during the milling FeCoPB, i.e., P and B may increase the brittleness of the powders. The ductility of powders also depends on the powder size. Thus, when the powder size reach some value, it is difficult to decrease it further. A small increase in powder size of Fe_{41}Co_{41}P_{14}B_{4} and Fe_{42.5}Co_{42.5}P_{7}B_{8} for 10 h milling and 15 h milling respectively was therefore considered to be this size effect. The typical morphology of the as milled powders also proved this point. It can be seen that some powders in Fig. 1 (c) have a very sharp edge which is different from that in Fig. 1 (b) and (d). The large powders with sharp edge in Fig. 1 (c) were due to the sticking of the small powders (cold welding effect) and fracturing of the stuck large powders. The difference in powder size of powder underwent 5 h milling (Table 1) and the morphologies of
the as milled powders (Fig. 1) also indicate that P has strong effect on the reducing of powder size but B tries to make the powder more spherical.

The Fe and Co was alloyed after 5 h milling, as shown in Fig. 2, the XRD results of 5 h milled Fe$_{50}$Co$_{50}$ and Fe$_{44.5}$Co$_{44.5}$P$_7$B$_4$. The saturation magnetization ($M_s$) of the as milled powders also indicated the Fe and Co was alloyed after 5 h milling (Fig. 3). For the unalloyed Fe$_{50}$Co$_{50}$ and Fe$_{44.5}$Co$_{44.5}$P$_7$B$_4$, the $M_s$ was 175.7 emu/g and 167.2 emu/g respectively. Later stage of milling led to a homogenization in composition and microstructural modulation, which gave higher $M_s$ for 10 h milling and small variation in $M_s$ up to 70 h milling. From Fig. 2, it also can be seen that the FeCo peaks of 5 h as milled Fe$_{44.5}$Co$_{44.5}$P$_7$B$_4$ powders was broader than 5 h milled Fe$_{50}$Co$_{50}$. The broadening of XRD peaks can be due to the strain, small grains and some other reasons. The TEM microstructure observation shown in Fig. 4 showed the reason: 10 h milled Fe$_{50}$Co$_{50}$ had a banded structure with a lot of dislocations while 10 h milled Fe$_{44.5}$Co$_{44.5}$P$_7$B$_4$ consisted of roughly spherical grains about 35 nm in diameter.

The as milled powders were not magnetic soft (Fig. 2). The coercivity of as milled Fe$_{50}$Co$_{50}$ powders showed a monotonous increase up to 50 h milling from 58.3 G to 75.0 G and a slight decrease for 75 h milling. However, the as milled Fe$_{44.5}$Co$_{44.5}$P$_7$B$_4$ powders showed a monotonous decrease after 15 h milling. This coercivity variation was related to the microstructural evolution. For Fe$_{50}$Co$_{50}$, the refinement of the banded structure generally introduced more dislocations and strains until a critical characterize was reached; for Fe$_{44.5}$Co$_{44.5}$P$_7$B$_4$, the refinement of the grain size formed smaller nanocrystals. This fits the Herzer model quite well [2].

Conclusions

MA FeCo based alloys with P and B additions were investigated. The following could be concluded: (a) P and B had strong effect on the powder size and morphology; (b) Fe and Co was alloyed after 5 h milling, further milling led to a homogenization in composition and microstructural modulation; (c) Banded microstructure with a lot of dislocations in MA Fe$_{50}$Co$_{50}$ and spherical nanocrystals with 35 nm in diameter in MA Fe$_{44.5}$Co$_{44.5}$P$_7$B$_4$ were observed; (d) The as milled powders were not magnetic soft but the variation in coercivity with milling time was related the microstructural evolution and fit the Herzer model.

References