SYNTHESIS OF Fe-Co BASED NANOMAGNETIC MATERIALS

H.F. Li and R.V. Ramanujan
School of Materials Science and Engineering, Nanyang Technological University, Singapore, 639798
Email: ramanujam@ntu.edu.sg

(Received 5 October 2004; in revised form 5 April 2005)

ABSTRACT

Processing of FeCo based nanomagnetic materials was carried out by chemical synthesis, crystallization from amorphous precursors and mechanical alloying. It was found that the products from chemical synthesis depended on the concentration of reaction solution. Uniform fiber like and spheroidal nanopowders were produced using Fe$^{+2}$ rich and Co$^{+2}$ rich reaction solutions respectively. The chemically synthesized FeCo based alloys was found to be amorphous. Through crystallization of melt spun amorphous precursors, high density nanocrystalline Fe$\text{_{44.5}}$Co$\text{_{44.5}}$Zr$\text{_{7}}$B$\text{_{4}}$ alloy was obtained; the nanocrystals had a compacted dendritic morphology. Spheroidal nanocrystalline structure was successfully obtained after mechanical milling of Fe$\text{_{44.5}}$Co$\text{_{44.5}}$P$\text{_{7}}$B$\text{_{4}}$ for more than 20 h at 300 rpm. The fiber like and compact dendritic morphology was not suitable for soft magnetic properties. Due to the pinning of magnetic domains, the powder nanostructured FeCo based alloys had inferior soft magnetic properties to the ribbon form alloys. The fiber like chemically synthesized and mechanically alloyed FeCo based alloys powders showed large coercivities. The magnetization of chemically synthesized FeCo alloy powders was low, which was considered to be due to solid solution contaminations, amorphous phase formation and the oxidation layer.

1. INTRODUCTION

The booming development of nanoscience and nanotechnology in recent years provides opportunities for the design of new magnetic materials$^{1-3}$. Nanomagnetic materials containing nanocrystals of about 10 nm in size are expected to have superior soft magnetic properties$^{3-6}$. The recently explored Finemet (Fe-Si-B-Cu-Ni), Nanoperm (Fe-Zr-B-Cu) and HiTperm (Fe-Co-Zr-B-Cu) alloys, which have as small coercivity as that of amorphous magnetic alloys, as large magnetization as their crystalline counterparts and near zero magnetostriction, are good examples of nanocrystalline soft magnetic materials. Iron cobalt based magnetic alloys have the highest magnetization among the existing magnetic materials; processing nanostructures in these alloys has thus attracted a large amount of research effort$^{7-11}$. Processing of FeCo based nanomagnetic materials is under development; investigation work has been carried out using crystallization from an amorphous matrix$^{7}$, mechanical alloying$^{8}$, mechanochemical method$^{9}$, sputtering$^{10}$, chemical synthesis$^{11}$, etc. The materials processed can be in the form of bulk, fine powders, fibers or thin film, corresponding to the novel applications in electromagnetic devices, bioengineering, data storage and silicon integration technology. HiTperm FeCo based alloys nanocrystallized from melt-spun amorphous precursors, showed a stable nanocrystalline structure at high temperatures of up to 600°C and superior soft magnetic properties$^{7}$. The Cu free HiTperm amorphous precursor Fe$\text{_{44.5}}$Co$\text{_{44.5}}$Zr$\text{_{7}}$B$\text{_{4}}$ also exhibits a nanocrystallization behavior. Characterization of Cu free HiTperm alloy Fe$\text{_{44.5}}$Co$\text{_{44.5}}$Zr$\text{_{7}}$B$\text{_{4}}$ was studied earlier$^{12}$. Processing of FeCo based nanostructured magnetic alloys was also carried out by mechanical alloying$^{13-14}$. Although the nanocrystalline structure formed after sufficient milling time, the powders were not magnetically soft. In this paper, chemically synthesis of FeCo based alloy nanoparticles is included. The nanostructures and magnetic properties of the materials prepared using the above three techniques are compared and discussed.
2. MATERIALS AND METHODS

Chemical synthesis of FeCo nanoparticles used the reduction reaction

\[ Fe^{+2} + Co^{+2} + 4BH_4^{-1} \rightarrow FeCo(B) + \ldots \]

Solutions of specific molar concentrations were prepared respectively from FeCl$_2$.4H$_2$O (99%, Merck, Germany), CoCl$_2$.6H$_2$O (98%, Reagent Fine Chemicals), NaBH$_4$ (Fluka, Sigma Aldrick, Steinheim). The FeCl$_2$ solution was mixed with CoCl$_2$ solution and homogenized, then the solution mixture and solution NaBH$_4$ were dropped simultaneously into a beaker with 10 ml deionized water; reduction reaction then occurred in the beaker. The mixing and reaction of the solution was conducted in an ultrasonic vibrator. After about 30 min of reaction, the powders were collected using a magnet and cleaned at least 5 times using deionized water. The cleaned powders were then characterized using field emission scanning electron microscope (JEOL, JSM-6340F) transmission electron microscope (TEM JEOL 200kV) and vibrating sample magnetometer (LakeShore VSM 736).

The details of processing of nanostructured FeCo based alloys by crystallization and mechanical alloying has been stated in Ref. 12 and Ref. 13 respectively.

3 RESULTS

Figure 1 shows the morphology of chemically synthesized powders. The chemical synthesized powders have uniform morphologies and size: the Fe$^{+2}$ rich solution yielded nanofibers (Fig. 1 a); the Co$^{+2}$ rich solution yielded spheroidal powders (Fig. 1 b). TEM micrographs suggested that the nanofibers consisted of powder agglomerate (Fig. 2 a) and the spheroidal powders are single powders (Fig. 2 b). The average sizes of the powders are 30 nm and 80 nm respectively. The chemically synthesized FeCo based alloy powders appeared to be amorphous since lattice fringes were never observed in the HRTEM of the powders, only diffuse ring pattern was observed in SADP of the powders and the XRD results did not show crystalline peaks. The magnetic hysteresis loops of the powders are shown in Fig. 3. The saturation magnetization and coercivity of Fe rich powders are 42 emu/g and 104 Oer respectively; the magnetization and coercivity of Co rich powders are 22 emu/g and 13 Oer respectively.

The microstructure of high-density nanocrystals embedded in an amorphous matrix is generally observed in the 450°C ~ 600°C annealed Fe$_{44.5}$Co$_{44.5}$Zr$_5$B$_4$ melt spun amorphous alloy. Nanocrystalline structure was also obtained after mechanical alloying of FeCo based alloys. Fig. 4 and Fig. 5 are the typical nanostructures of FeCo based alloys prepared by crystallization and mechanical alloying respectively.
Fig. 2: TEM micrographs of chemical synthesized FeCo base alloy nanoparticles. The morphology of powders varied with solution concentrations. (a) 0.05M Fe$^{+2}$, 0.05M Co$^{+2}$ and 0.2M BH$_4^{-1}$ and (b) 0.02M Fe$^{+2}$, 0.05M Co$^{+2}$ and 0.2M BH$_4^{-1}$.

Fig. 3: Magnetic hysteresis loop of chemical synthesized powders.
4. DISCUSSION

4.1 Chemical synthesis of FeCo based nanomagnetic materials.

Chemical synthesis methods have the advantage of easier control of particle size by varying the reaction environment, such as concentration of solution, surfactant and magnetic field. From Fig. 1 and Fig. 2, it can be seen that the concentration of solutions had a significant effect on the powder morphology of chemically synthesized FeCo based alloys: with equal concentration of Fe+2 and Co+2 in the reaction solution, the powders have a fiber like morphology and when the concentration of Fe+2 was reduced to half of Co+2, the powders were spheroidal. This difference in behavior was due to the competition of surface energy and anisotropy energy of the powders formed. For the Fe+2 rich solution, the anisotropy energy of the product dominated; fiber like powders were thus formed. For the Co+2 rich solution, surface energy was dominated, in order to reduce the total surface area, spheroidal powders were formed. From the Fe-Co phase diagram, the equilibrium phases are f.c.c (or h.c.p) and b.c.c (or simple cubic) FeCo solid solution for the atomic percent iron in the range of 0~23% and 23%~100% respectively. We expected that the phase formed from Fe+2 rich solution should be b.c.c (or simple cubic) and the phase from Co+2 solution should be f.c.c (or h.c.p). From the HRTEM and SADP and XRD analysis, it was found that these crystalline phases did not form. The different morphologies of powders seem to indicate that the packing of atoms of the powders may be close to b.c.c and f.c.c phase respectively. That the ordered crystalline phase was not observed is due to the low mobility of atoms once they were attached to the particles. This process was different from the crystallization from the melt and precipitation of solute from over saturated solutions.

Compared to mechanically alloyed FeCo alloyed powders, which have a size of more than 1 μm and a wide powder size distribution range, the chemically synthesized powders have uniform powder size and morphology. The diameter of the fiber like FeCo alloy powder is less than 50 nm and the diameter of the spheroidal powders is about 80 nm.

The magnetic properties of chemically synthesized FeCo alloy powders varied significantly with preparation conditions. In Fig. 3, it can be seen that the Fe rich powders have much larger magnetization and coercivity than the Co rich powders. The different magnetization behavior was due to their different compositions, phases and morphologies. The b.c.c (or simple cubic) FeCo is magnetically soft phase, however the chemically synthesized FeCo alloy powders were not magnetically soft. This is mainly because of the fiber like powders and the presence of other nanomagnetic elements in the FeCo alloy powders. Chemically synthesized Co rich FeCo alloy powder showed relatively soft magnetic properties, possibly due to the amorphous native of the powders. The magnetization of chemically synthesized powders is low for both Fe rich and Co rich powders because of boron in the alloy, oxidation and lack of crystallinity. It is odd to see that the magnetization of Fe rich FeCo alloy powders decreased just during the measurement (as indicated in Fig. 3).

4.2 Nanostructures and magnetic properties of FeCo based alloys

The correlation of processing techniques, microstructures and magnetic properties is now discussed. By crystallization of melt spun Fe_{44.5}Co_{44.5}Zr_{7}B{4} amorphous precursors, high density of nanocrystalline α-(Fe,Co) solid solution can be readily formed. A typical microstructure is shown in Fig. 4; it can be seen that the nanocrystals are clustered. From our detailed microstructural analysis, it was found that the “cluster” morphology were actually due to single crystals. The “cluster” morphology resulted from the compact dendritic growth of crystals and thickness effect in transmission electron microscopy. Nanocrystalline structure was also obtained by mechanical alloying of FeCo based alloys. Fine nanocrystalline structure was observed in 300 rpm, 20 h milled Fe_{44.5}Co_{44.5}P_{7}B{4} powders. Such nanocrystals had a spheroidal morphology. It may be recalled that the chemically synthesized FeCo based alloy with near equal atomic percent of Fe and Co had a fiber like morphology (Fig. 2 a). The different morphologies of nanostructures are related to their processing techniques. For crystallization and chemical synthesis, the nanostructures were formed by nucleation and growth; the morphologies were controlled by
interfacial energy (surface energy) and anisotropy energy. Therefore, these nanostructures showed the similarity due to anisotropy growth rate. However for crystallization, the anisotropy growth was suppressed because of the segregation of Zr at the grain boundaries\textsuperscript{17}. The mechanical alloying of nanocrystals is through introduction of disordering into the lattice, deformation of lattice and recrystallization\textsuperscript{18}. The introduction of mechanical energy into powders can be considered as a process of shock wave absorption by atoms, particularly for high energy of milling for which impact is dominant. Thus the fiber-like or dendritic morphology will be easily destroyed by mechanical milling. Due to the random impact, spheroidal nanocrystals are generally formed after sufficient long time of high energy of ball milling. Since the nanocrystals are from the initial large grains and shearing of powders is not avoidable, weak texture is often observed in mechanical alloyed nanocrystals\textsuperscript{19}.

The magnetic properties of the materials depend on their composition, morphologies and microstructures. The FeCo based nanocrystalline alloys obtained by crystallization of amorphous precursors showed superior soft magnetic properties\textsuperscript{7,12}. The mechanically alloyed FeCo based alloy powders had much larger coercivity than the crystallization products although they also showed a nanocrystalline microstructure\textsuperscript{13,14}.

The magnetization of the nanostructured FeCo based alloys prepared by crystallization and by mechanical alloying is comparable. The chemical synthesized FeCo based alloy powders, as stated in section 4.1, showed very low magnetization and coercivity was quite different between Fe rich powders and Co rich powders. The inferior soft magnetic properties of mechanical alloyed nanocrystalline FeCo based alloys are caused by the large stress induced by the milling, weak texture of the nanocrystals and powder morphology. Since magnetization is insensitive to stress, textures and morphology, the magnetization is very close for crystallized and mechanical alloyed nanocrystalline FeCo based alloys. The fiber like morphology led to the large coercivity in chemically synthesized Fe rich FeCo based alloy powders. Although the fibers have small diameter, averaging out the anisotropy is difficult in the loose packed powders. It can also be seen that the compact dendritic morphology of nanocrystals in crystallized FeCo based alloys has deleterious effect on the soft magnetic properties; this type of morphology of nanocrystals is also observed in Nanoperm alloys\textsuperscript{5,17}. The fine powder morphology will increase the coercivity because of the surface pinning of magnetic domains. Alloys in powder form generally showed larger coercivity than nanocrystallized soft magnetic ribbon counterparts\textsuperscript{12}. The magnetic properties of chemically synthesized Co rich FeCo based alloy powders is a
little larger than that of high density nanocrystalline soft magnetic alloys but much smaller than chemically synthesized Fe rich FeCo alloy powders and mechanically alloyed FeCo alloy powders. Since chemically synthesized FeCo based alloy powders contained of B and other nonmagnetic elements, surface oxide layer and amorphous phase, they have much lower magnetization than crystallized and mechanically alloyed FeCo based alloys.

4. CONCLUSIONS

Three techniques, chemical synthesis, crystallization from amorphous precursor and mechanical alloying, have been carried out to process nanostructured FeCo based alloy powders. The processing techniques, nanostructures formed and magnetic properties of these alloys are correlated.

(1) Powder morphology varied with the concentration of reaction solutions during the chemical synthesis of FeCo alloy powders. Fiber like powders and spheroidal powders were synthesized from Fe rich and Co rich solutions respectively.

(2) The morphology of nanostructures and magnetic properties of FeCo based nanostructured alloys varied with the preparation techniques.

(3) Mechanically alloyed FeCo based alloys are magnetically harder than the alloys obtained from crystallization although both of the techniques yielded nanocrystalline structure.

(4) Fiber like morphology as well as the compact dendritic nanocrystalline morphology had an undesirable effect on the soft magnetic properties, the coercivity increased in this morphology.

(5) The chemically synthesized FeCo alloy powders have very low magnetization due to the dissolution of nonmagnetic elements such as boron and the lack of crystallinity.

REFERENCES

12. Li H F and Ramanujan R V, unpublished work.