Thermal stability of the nanocrystalline Fe–Co–Hf–B–Cu alloy

Hirofumi Iwanabe
Japan Energy Corporation, 10-1, Toranomon 2-Chome, Minato-ku, Tokyo 105-8407, Japan

Bin Lu, Michael E. McHenry, and David E. Laughlin
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Nanocrystalline $(Fe_{1-x}Co_x)_{88}Hf_7B_4Cu_1$ alloys have been investigated as candidates for soft magnetic materials for high temperature applications. Four samples were obtained in annealed or as-spun ribbons with $x=0,0.10,0.30,0.44$. Magnetic properties and thermal stability were studied focusing on the $x=0.30$ alloy by means of different thermal analysis, hysteresisgrapher, impedance analyzer, transmission electron microscope, etc. © *1999 American Institute of Physics.* [S0021-8979(99)17608-4]

I. INTRODUCTION

Nanocrystalline $(Fe_{1-x}Co_x)_{88}Hf_7B_4Cu_1$ alloys have been studied as candidates of soft magnetic materials for internal generators in the so-called more electric aircraft. The materials are to be used at elevated temperatures (773–873 K) and are expected to have: (a) a 2 T (1592 emu/cm^3) or higher induction at the working temperature (773 K); (b) thermal stability at 873 K for 5000 h; (c) core losses less than 480 W/kg at 5 kHz and 773 K and 2 T induction. These are very severe conditions for existing materials. Besides, high temperature mechanical properties of the soft magnetic material should also be concerned. In searching new materials, the CMU MURI program has concentrated on the following materials: (1) Fe–Co base alloys for high magnetization, (2) crystalline materials for thermal stability and higher magnetization, and (3) nanocrystalline materials for better soft magnetic properties.

In this work, amorphous materials are used as precursors for the nanocrystallization process. Hf and B were selected as the glass formers. A small amount of Cu was added to provide nucleation sites for the nanocrystals so as to optimize the grain size. Additional alloying elements are minimized so as to keep the magnetization large. In this article, we present results of studies of $(Fe_{1-x}Co_x)_{88}Hf_7B_4Cu_1$ alloys and assess their potential as high temperature soft magnets.

II. EXPERIMENT

Fe (99.97% pure), Co (99.9%), Hf (99.6% including 2–3.5% of Zr), FeB (99% pure), and Cu (99.999%) were mixed and melted in the arc melting furnace to make $(Fe_{1-x}Co_x)_{88}Hf_7B_4Cu_1$ alloy ingots with $x=0$, 0.10, 0.30, and 0.44. Ribbon samples were obtained from the ingots by the single-roll melt-spinning technique. A copper wheel was used, except for the $x=0.44$ alloy ribbons which was spun on a low C steel wheel. The linear velocity of the wheel was about 35 m/s x-ray diffraction (XRD), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were used to study the phases in the ribbons. Magnetization was measured using a Quantum Design SQUID magnetometer. ac magnetic property measurements were performed at room temperature using a hysteresisgraph tracer and impedance analyzer. The size of the sample for ac magnetic property measurements was 1.6 mm×41 mm×27 μm. Demagnetization field corrections were neglected.

The as-spun ribbons were studied with a DSC using a constant heating rate of 0.167 K/s. The heat flow was monitored and heating was suspended just after the crystallization so as to perform XRD, SQUID, and transmission electron microscope (TEM) experiments on the as crystallized specimens. For thermal stability tests, as-spun ribbons were enclosed in evacuated glass capsules and annealed in a tube furnace at 873 K for various times. The microstructures were observed with an EM420 TEM and JEM4000 high resolution TEM (HRTEM). TEM samples were prepared by mechanical polishing and subsequent ion milling.

III. RESULTS AND DISCUSSION

The phase in as-spun ribbons of $x=0,0.10,0.30$ alloy spun on the Cu wheel was confirmed to be amorphous by the broad XRD peak, the absence of any crystalline peaks, as well as the crystallization peaks in the DTA. The as-spun ribbon of $x=0.44$ alloy spun on the steel wheel was confirmed fully crystallized by XRD results. The XRD results for the crystallized samples of four different compositions showed distinct peaks of bcc structure (with significant Scherrer broadening) without detectable peaks from any other phases. It was found by TEM that all four samples are nanocrystalline phases with the grain size of about 10 nm. The magnetization of as-spun and crystalline ribbons with different Co content was measured at 5 and 300 K, respectively. The results are shown in Fig. 1. The $x=0.30$ Co alloy has the highest magnetization, 170 (at 300 K) or 1411 emu/cm^3, assuming the density of the alloy is about 8.3 g/cm^3. Therefore, it was chosen for the study of thermal stability.

Figure 2 shows the frequency dependence of permeability for field amplitudes of 0.68–0.82 A/m for $x=0.30$ Co samples annealed for various times at 873 K. ac magnetic response was measured using an impedance analyzer. Figure 3 shows coercive forces determined by measurement on a

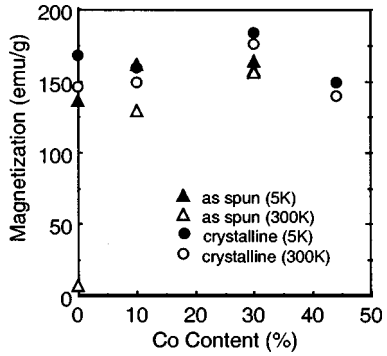

FIG. 1. Magnetization data of as-spun and crystalline $(Fe_{1-x}Co_x)_{88}Hf_7B_4Cu_1$ ribbons with different Co contents measured at 5 and 300 K, respectively.

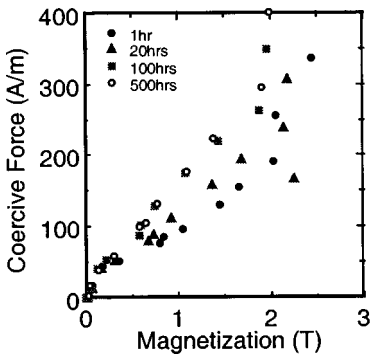

FIG. 3. Magnetization dependence of the coercivity for the $x=0.30$ sample with different annealing times at 873 K.

hysteresisgraph tracer. The coercive force worsened for samples annealed between 20 and 100 h, but was relatively stable for short and long times. In this period, grain growth was observed with TEM, as shown in Fig. 4. Grains grew from ~10 nm at 20 h to ~30 nm at 100 h, but no apparent grain growth between 1 and 20 h was observed. Further annealing pass 100 h did not lead to further increasing of the coercive force, but the magnetization was observed to decrease at room temperature. Both samples annealed for 500 and 1000 h have a larger temperature dependence of magnetization than those for shorter times.

TEM observations were performed which revealed precipitates in long-time annealed samples. Figure 5 show TEM images of 500 and 1000 h annealed samples. There are small precipitates everywhere among large grains in the 500 h annealed sample. In the 1000 h annealed sample, precipitates are large in size and quantity and the original grain boundaries became unclear. From electron diffraction rings, the precipitates were identified to be Co_2Hf in the 500 h annealed sample and $Co_{23}Hf_6$ in the 1000 h annealed one. Also a weaker but similar diffraction pattern to that of the 500 h annealed sample was observed in the 100 h annealed sample although precipitates were not observed in images.

Figure 6 shows the magnetization change with annealing time. Magnetization started varying after 100 h, which coincides with that of commencement of precipitation. The change is larger at room temperature than that at 5 K implying that both the magnetization dipole moment and the Curie temperature were diminished by the precipitation (secondary crystallization).

This alloy system showed excellent nanocrystalline forming ability for wide range of Co contents. The importance of the grain size to soft magnetic properties is clearly shown by Herzer[1] as the grain size dependence of coercivity. To obtain excellent magnetic materials, the grain size should be small compared with the so-called ferromagnetic exchange length. $L_{ex}=\sqrt{A/K}$, where A is the exchange stiffness, and K is the magnetic anisotropy.

The ferromagnetic exchange length of an equiatomic ordered Fe–Co alloy is estimated to be 46 nm by assuming $A=1.7\times10^{-11}$ J/m and $K=8$ kJ/m^3.[2] If a larger anisotropy is assumed for the $x=0.30$ Co alloy, i.e., $K\sim25$ kJ/m^3 but all other parameters are equivalent to the equiatomic alloy has, the exchange length will be about 26 nm. The two numbers bracket Herzer's estimate of 35 nm for Fe–Si alloy.[1] For grains smaller than the exchange length, a random anisotropy model should be considered. Here the anisotropy is replaced with the effective anisotropy that is a statistical (random walk) average over grains coupled within an exchange length. The Herzer plot predicts that a material with a ~30 nm grain size should be expected to have a coercivity of 100 A/m, which is comparable with our data. Coercivities on the

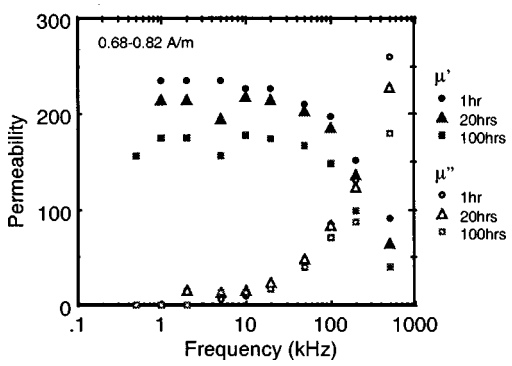

FIG. 2. Frequency dependence of the real (μ') and the imaginary (μ'') components of the permeability for the $x=0.30$ sample with different annealing times at 873 K.

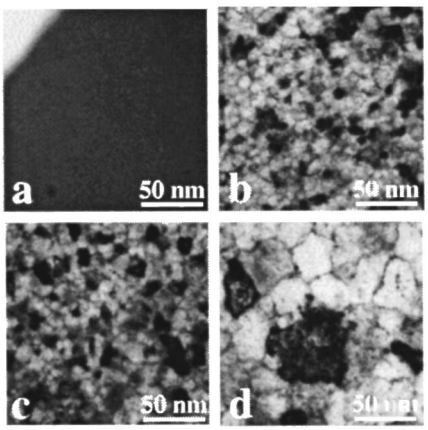

FIG. 4. TEM micrographs of the $x=0.30$ sample annealed at 873 K for different times: (a) as-spun, (b) 1 h, (c) 20 h, (d) 100 h.

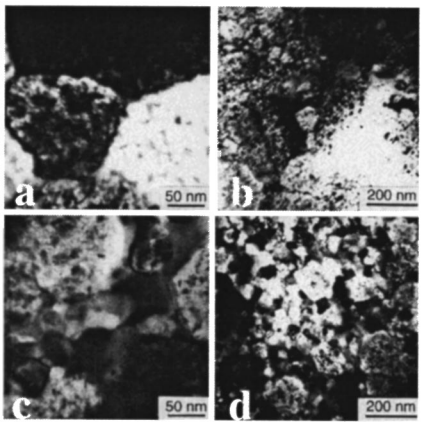

FIG. 5. TEM micrographs of the $x=0.30$ samples annealed at 873 K for different times: (a) and (b) 500 h (c) and (d) 1000 h.

order of 10^{-2} A/m are predicted for 10 nm particles suggesting that further refinement of our grain size could result in even softer magnets.

Figure 2 shows a relatively invariant permeability as a function of frequency out to several kHz. The permeability at 5 kHz is not very different from those at lower frequencies. If the frequency does not influence the coercive force either at higher fields, the high coercive forces observed should be attributed to the higher anisotropy or shorter exchange length than expected.

The theory[3] of grain growth driven by the grain boundary energy predicts the highest growth rate at the beginning. Our results shown in Fig. 4 do not fit this as it seems to have an incubation time. This suggests the grain growth in this material would be controlled by two or more processes. Figure 7 shows HRTEM images. It can be seen that the nanocrystalline grains are separated by an amorphous phase. The thickness of the amorphous phase between the grains remains almost same after 20 h annealing compared with 1 h annealed sample. This amorphous phase at boundaries may hinder grain growth by inhibiting diffusion.

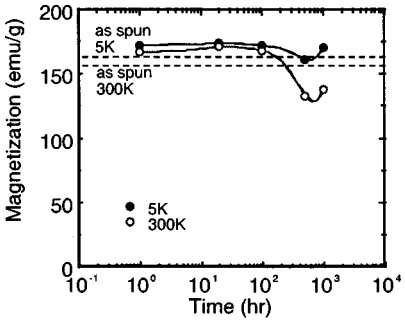

FIG. 6. Magnetization change (at 5 and 300 K) of the $x=0.30$ sample with annealing time.

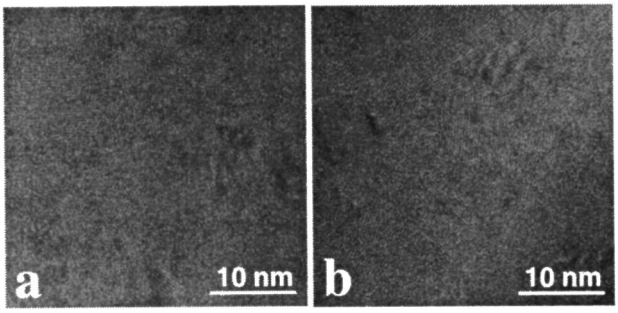

FIG. 7. High resolution TEM micrograph of the $x=0.30$ sample annealed at 873 K for (a) 1 h and (b) 20 h.

Precipitation occurred after longer anneals. In the grains of the 500 h annealed sample, the precipitates were revealed to be Co_2Hf, while in the sample annealed for 1000 h, the precipitates are $Co_{23}Hf_6$. It is natural to consider that second phases may affect the magnetization of the material. Because of the formation of these compounds consume Co, the Co content of the matrix decreases, contributing to the stronger reduction of magnetization at room temperature.

Also, if $Co_{23}Hf_6$ has a small nonzero magnetization and a low Curie temperature, its existence will cause larger difference of magnetization between low and high temperatures.

In this study, the amorphous phase at the grain boundary seems to play an important role in both stability and magnetic properties. To improve the properties, we may need to make this phase more thermally stable and probably the magnetization of the phase higher to obtain stronger coupling among grains. The magnetization decrease at higher temperatures of long annealed samples is another issue. There must be effects of precipitation on magnetization although the relation between them is not clear yet. If the larger temperature dependence is due to the precipitation, it must be avoided.

ACKNOWLEDGMENTS

The authors would like to express great thanks to H. Okumura and Professor W. A. Soffa at University Pittsburgh for sample preparations. This study was supported by the Air Force Office of Scientific Research, Air Force Material Command, USAF, under Grant No. F49620-96-1-0454. D.E.L. was partially supported by a NEDO grant. Dr. Bin Lu was supported by Intevac.

[1] G. Herzer, IEEE Trans. Magn. **26**, 1397 (1990).
[2] H. Iwanabe, M. E. McHenry, and D. E. Laughlin (unpublished).
[3] J. S. Kouvel, in *Magnetism and Metallurgy*, edited by E. Berkowitz and E. Kneller (Academic, New York, 1969), Vol. 2A, p. 523.