Mössbauer Measurements for a Nanocrystalline $Fe_{44}Co_{44}Zr_7B_4Cu_1$ Alloy

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***Abstract*—A two phase microstructure, consisting of nanocrystallites surrounded by an amorphous matrix, was produced by a melt spinning processing route. Alloys of this type have extrinsic properties that are dependent on the relative amounts of the amorphous and nanocrystalline phases. One method for examination of the properties of the nanocrystalline and amorphous phases is by Mössbauer spectroscopy. This paper examines ribbons with the composition of $Fe_{44}Co_{44}Zr_7B_4Cu_1$, both as-spun and after annealing at 650 °C for 1 hour. Three Mössbauer techniques were used to examine these materials, including: transmission measurements, conversion electron Mössbauer spectroscopy, and radio frequency Mössbauer. The transmission spectrum for the annealed HITPERM alloy is composed of two superimposed sextets corresponding to the nanocrystalline FeCo and retained amorphous phases. The rf-Mössbauer results fail to show collapse of the sextet, indicating a large magnetocrystalline anisotropy of the nanocrystalline phase.**

***Index Terms*—HITPERM, Mössbauer, nanocrystalline soft magnetic material.**

I. Introduction

MÖSSBAUER spectroscopy has been an effective tool in the characterization of Fe-based and FeCo-based nanocrystalline soft magnetic alloys [1]–[6]. Previous work on FeCo-based nanocrystalline soft magnetic materials have revealed high magnetization and permeability to high temperatures (above 600 °C). The average grain sizes were near 30 nm for the standard annealing procedure. However, the residual amorphous phase hypothesized to remain at the grain boundaries was not readily seen by conventional transmission electron microscopy (TEM) due to its small fraction, intergranular distribution, and poor contrast. High resolution TEM has been used in previous work to provide confidence in the existence, quantity, and distribution of the remaining amorphous phase [7]. This work provides clear evidence of the residual amorphous phase by fitting two sextets with discrete hyperfine field values to the collected data of annealed Fe–Co–Zr–B–Cu alloy ribbons. By transmission Mössbauer measurements, the bulk properties of the ribbon are accessed while the surface effects are isolated by conversion electron Mössbauer spectroscopy (CEMS). Finally, the radio frequency (rf) Mössbauer technique is used to examine the anisotropic magnetic effects of the hyperfine field.

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II. Experimental Methods

Samples with composition $Fe_{44}Co_{44}Zr_7B_4Cu_1$ (HITPERM) were produced from high purity elemental components by single wheel melt spinning, as described in [8], [9]. Ribbon samples were annealed at 650 °C for one hour in an argon atmosphere. Mössbauer measurements were carried out using a constant acceleration spectrometer with a ^{57}CoRh source. Data analysis was performed by the histogram method of Hesse and Rübartsch [10] with constraints introduced by Le Caer and Dubois [11].

Transmission Mössbauer measurements and CEMS were performed by the standard methods. Radio frequency Mössbauer measurements were conducted with a radio frequency magnetic field (61.3 MHz) and field amplitudes between 0 and 20 Oe. Data fitting of the spectra was accomplished for all data except the rf-Mössbauer spectra. No reasonable theory quantitatively describes the rf-Mössbauer data, however, qualitative interpretations give important information about the magnetic anisotropy.

The transmission spectrum for the as-cast ribbon shows a broadened sextet that is typical of an amorphous ferromagnetic alloy [Fig. 1(a)]. The hyperfine field distribution was extracted from the spectrum by the Hesse–Rübartsch method and is characteristic of an amorphous ferromagnet [Fig. 1(a′)]. It consists of a main broad peak (0.8 mm/s) with average hyperfine field, $\langle H_{hf}\rangle$, of 29.3 T. The width of the distribution, $\Delta P(H)$, was ∼4.6 T. This value of $\langle H_{hf}\rangle$ is quite large compared with NANOPERM ($Fe_{88}Zr_7B_4Cu_1$) and FINEMET ($Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$) alloys. This is due to FeCo as a basis for the alloy composition. Typical Fe-based alloys reveal much smaller $\langle H_{hf}\rangle$.

The CEMS technique provides surface structure information from the top 120 nm of the ribbon. CEMS measurements were conducted for each sample on each side of the ribbon. The spectrum for the dull side of the ribbon of the as-cast sample was similar to the transmission spectrum. There was little evidence for a crystalline phase for the dull side of the ribbon [Fig. 1(b)]. The $\langle H_{hf}\rangle$ was ∼28.2 T and $\Delta P(H)$ ∼6.9 T [Fig. 1(b′)].

The CEMS spectrum for the shiny side of the as-cast ribbon showed both crystalline and amorphous phases on the surface [Fig. 1(c)]. The sextet with narrow lines corresponds to the crystalline phase with $\langle H_{hf}\rangle$ ∼35 T and ∼18% contribution to the

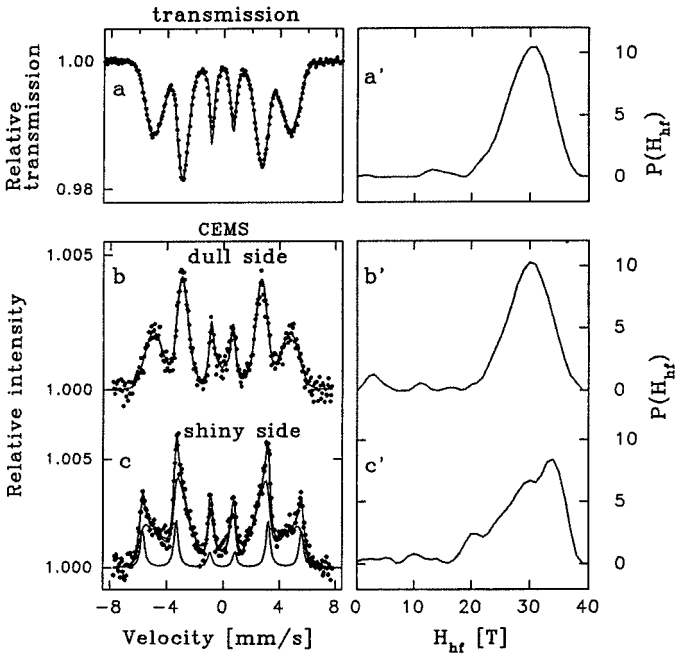

Fig. 1. Mössbauer data for a $Fe_{44}Co_{44}Zr_7B_4Cu_1$ as-cast ribbon sample. (a) Transmission spectrum. (a′) Hyperfine field distribution. (b) and (c) CEMS spectrum for dull and shiny sides of the ribbon, respectively. (b′) and (c′) CEMS hyperfine field distribution for dull and shiny sides of the ribbon, respectively.

total spectral area. The amorphous phase makes up the majority of the spectrum, with $\langle H_{hf} \rangle$ of 28.2 T and $\Delta P(H) \sim$7.2 T [Fig. 1(c′)].

The transmission spectrum for the HITPERM alloy annealed at 650 °C for 1 hr is composed of two superimposed sextets [Fig. 2(a)]. The first sextet corresponds to the FeCo nanocrystalline phase, with narrow lines (0.4 mm/s), $H_{hf} \sim$35 T and isomer shift of $\delta = +0.02$ mm/s (relative to the Fe standard). The second sextet has broad lines (0.8 mm/s) and is related to the retained amorphous phase. This phase has $H_{hf} \sim 30$ T and $\delta = +0.05$ mm/s. The spectral area fractions were 81.5% and 18.5% for the nanocrystalline phase and amorphous phases, respectively.

The CEMS spectra for the annealed sample showed greater extent of crystallization on the surfaces than in the bulk of the sample [Fig. 2(b) and (c)]. Both surfaces of the annealed ribbons show similar characteristics. There is a paramagnetic component that accounts for about 3% of the spectral area with a quadrupole doublet splitting of 0.35 mm/s. The origin of this phase found only on the surface is not easily identified. The surface seems to be full crystallized without retained amorphous phase present.

Transmission Mössbauer measurements were made for as-cast and annealed ribbons exposed to a rf-magnetic field with a frequency of 61.3 MHz. Each set of data was collected at fixed field amplitudes of 4, 6, 8, 12, 16, and 20 Oe. After each rf field exposure, an additional experiment without the rf field was collected as a control.

As seen in Fig. 3, the rf field was not able to collapse the magnetic hyperfine structure to a quadrupole doublet. Collapse of the hyperfine field for Fe-based amorphous alloys is generally possible by the same experiment.

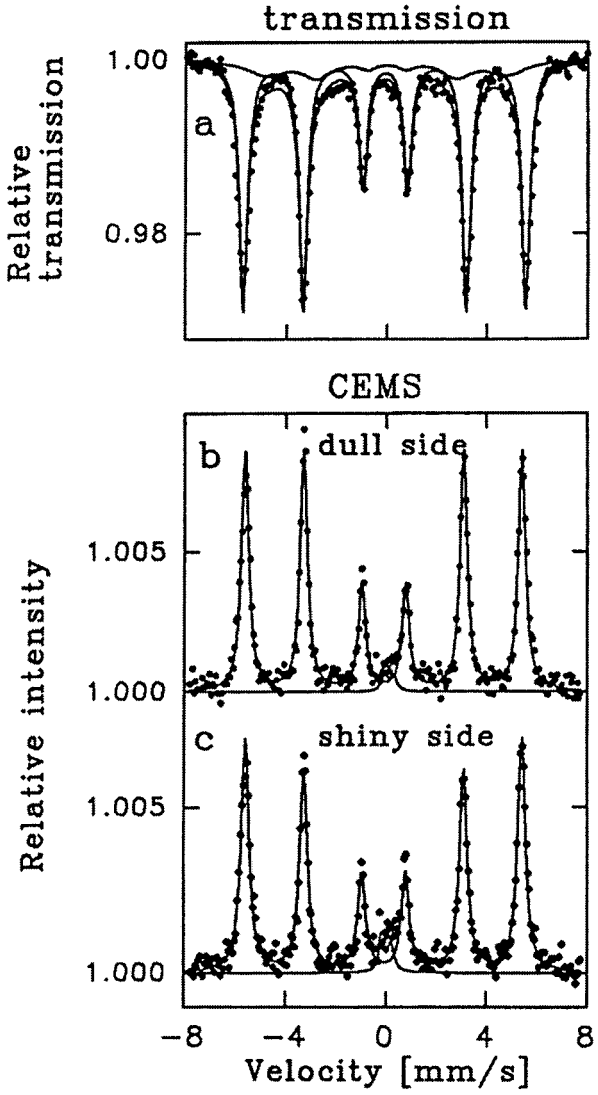

Fig. 2. Mössbauer data for a $Fe_{44}Co_{44}Zr_7B_4Cu_1$ ribbon sample annealed at 650 °C for 1 hour. (a) Transmission spectrum. (b) and (c) CEMS spectrum for dull and shiny sides of the ribbon, respectively.

The spectrum recorded after the sample was exposed to the 8 Oe field [Fig. 3(d)] is almost identical to that of the starting alloy [Fig. 3(a)]. However, the increase of the rf field intensity to 12 Oe did not induce further narrowing of the spectrum, but caused partial crystallization of the amorphous alloy [Fig. 3(e)]. The spectra recorded after this experiment clearly shows partial crystallization. The parameters of the new sextet show a relative fraction of 35% crystalline phase with a H_{hf} of 34.8 T with an isomer shift of $\delta = +0.01$ mm/s. The retained amorphous phase makes up the remaining 65% and has a $\langle H_{hf} \rangle$ of 30 T.

Further increase in the rf field intensity did not induce significant narrowing of the spectrum but instead increased the degree of crystallization [to 85% nanocrystalline phase in Fig. 3(h)]. The spectrum in Fig. 3(g) recorded during sample exposure to the 20 Oe rf field consists of only marginally rf-narrowed sextet corresponding to the crystalline FeCo phase. In the center of the spectrum, a single line appears, which may correspond to very soft nanocrystals that exhibit the complete rf-collapse effect. This single line is not found in the spectrum recorded after the 20 Oe rf field.

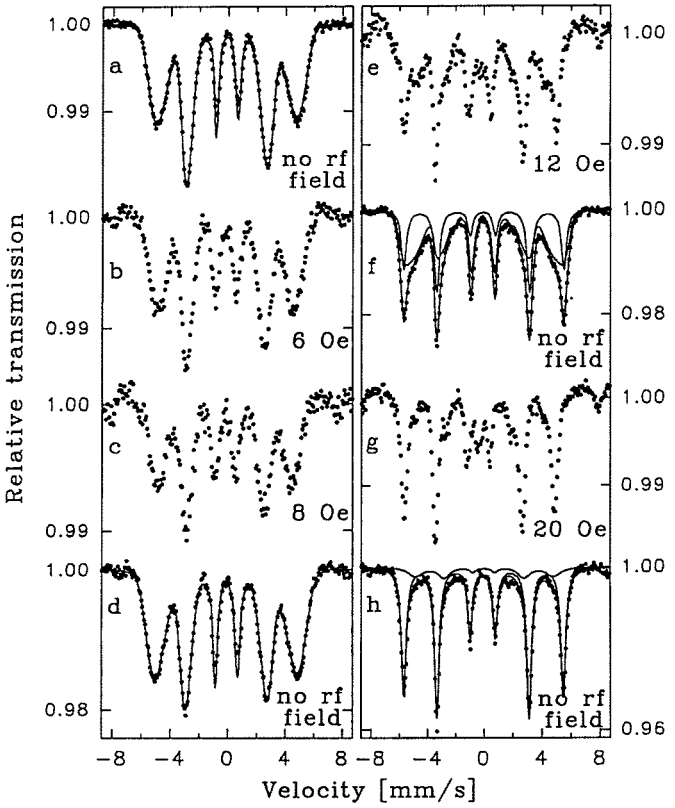

Fig. 3. Mössbauer data for a $Fe_{44}Co_{44}Zr_7B_4Cu_1$ as-cast ribbon sample with a rf-magnetic field applied with frequency 61.3 MHz. (a) No rf-field. (b) Field amplitude of 6 Oe. (c) Field amplitude of 8 Oe. (d) No rf-field. (e) Field amplitude of 12 Oe. (f) No rf-field. (g) Field amplitude of 20 Oe. (h) No rf-field.

The rf field induced crystallization is probably a side effect from magnetostrictive energy during the field application. The isomer shift can be used to estimate the temperature of the sample during the experiment. For this reason, crystallization due to heating of the sample is excluded. The second order Doppler shift is small, indicating that the temperature of the sample during the rf field exposure did not increase above 200 °C, so was far below the sample's crystallization temperature.

The rf-Mössbauer spectra for the annealed sample are shown in Fig. 4. At 8 Oe and 12 Oe rf fields, the spectra consist of only slightly narrowed sextets [Fig. 4(b) and (c)]. At higher fields (16 Oe and 20 Oe), the rf collapsed single line appears in the center of the spectra [Fig. 4(d) and (e)]. The origin of the singlet is probably very soft nanocrystallites. The marginally narrowed sextet corresponds to the nanocrystalline FeCo phase whose anisotropy is quite large. The singlet appears when the rf field induces fast magnetization reversal and collapse of the hyperfine structure results.

III. Conclusion

The transmission data show a hyperfine field of 29.3 T for the as-spun alloy and hyperfine fields of ∼35 T and ∼30 T for the crystalline and amorphous phases of the annealed sample. The respective spectral areas for the two phases were 81.5% and 18.5% after annealing. The CEMS spectra were measured for each side of the ribbon, showing differences for the dull and shiny sides of the ribbons. The CEMS data showed greater

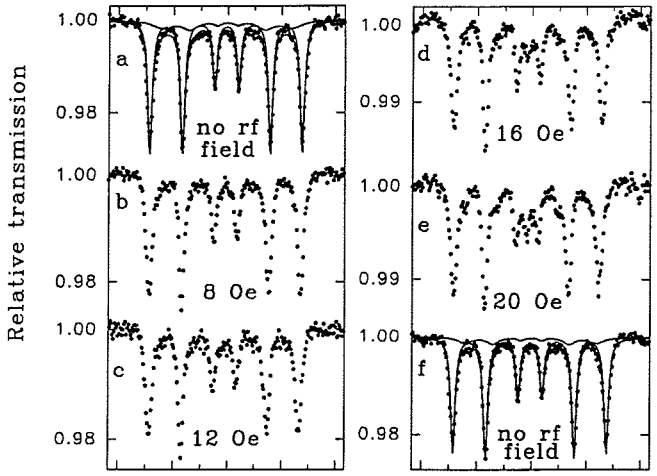

Fig. 4. Mössbauer data for a $Fe_{44}Co_{44}Zr_7B_4Cu_1$ ribbon sample annealed at 650 °C for 1 hour with a rf-magnetic field applied with frequency 61.3 MHz. (a) No rf-field. (b) Field amplitude of 8 Oe. (c) Field amplitude of 12 Oe. (d) Field amplitude of 16 Oe. (e) Field amplitude of 20 Oe. (f) No rf-field.

extent of crystallization on the surfaces of the ribbons than the ribbon bulk. The rf-Mössbauer results reveal that the nanocrystalline FeCo phase has a fairly large magnetic anisotropy. However, a small fraction of the nanocrystalline grains are very soft and rf-collapse is possible in this case. The larger anisotropy of the FeCo phase is expected for these alloys due to the compositional (magnetostriction and magnetocrystalline anisotropy) and microstructural (larger nanocrystallite size) effects. Optimization of alloy processing can provide improved performance.

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