CEMS AND RF-MÖSSBAUER STUDY
OF NANOCRYSTALLINE $Fe_{81}Zr_7B_{12}$ ALLOY

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The combined conversion electron (CEMS) and γ-transmission Möss-
bauer spectroscopy is used to investigate the differences in the bulk and sur-
face crystallization of the amorphous $Fe_{81}Zr_7B_{12}$ alloy. The radio-frequency
induced effects (rf collapse and side bands) are used to study the microstruc-
ture and magnetic behaviour of the alloy in the amorphous and nanocrys-
talline states. Rf-Mössbauer experiment permits us to distinguish soft mag-
netic nanocrystalline bcc-Fe phase from microcrystalline α-Fe.

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Amorphous FeZrBCu alloys are very promising systems for obtaining nano-
crystalline structure with high saturation magnetization and good soft magnetic
properties [1, 2]. Annealing of the amorphous precursor causes formation of nano-
scale grains of bcc Fe which exhibit high saturation magnetization combined with
low anisotropy and coercive fields and vanishing magnetostriction.

The crystallization and magnetic properties of nanocrystalline alloys have
been investigated by various techniques including the Mössbauer spectroscopy.
However, information regarding the grain size and magnetic anisotropy is not
available by conventional Mössbauer measurements. In order to investigate the
differences in the bulk and surface crystallization of amorphous FeZrB alloys we
used the combined conversion electron (CEMS) and transmission Mössbauer spec-
troscopy which allowed simultaneous study of the surface layer (about 100 nm
thick) and of the bulk of the sample. The magnetic properties were studied by an
unconventional technique which combines the Mössbauer effect with the phenom-
ena induced by an external radio-frequency field (rf collapse and side-band effects)
(see e.g. [3]). The collapse of the magnetic hyperfine splitting occurs due to fast
magnetization reversal induced by an external radio-frequency magnetic field as a
result of which the magnetic hyperfine field is averaged to zero at the Mössbauer
nuclei though the sample remains in the ferromagnetic state. The rf collapse is very
sensitive to small changes of local magnetic anisotropy, which allows distinction
of the soft nanocrystalline phase from the magnetically harder microcrystalline

phases formed by annealing of the amorphous precursor. The rf side-band effect, directly related to magnetostriction, allows identification of the nanocrystalline phase thanks to vanishing magnetostriction.

In this paper, we report on CEMS, transmission and rf-Mössbauer studies of $Fe_{93-x-y}Zr_7B_xCu_y$ alloys in amorphous and nanocrystalline states. Although a whole series of alloys with $x = 6, 8, 12$ and $y = 0, 2$ were studied only the results for the $Fe_{81}Zr_7B_{12}$ alloy are discussed here, since it reveals the highest Curie temperature in this set of samples.

In order to obtain the nanocrystalline phase, amorphous ribbons were annealed for 1 h at temperatures $T_A = 430–780°C$. The CEMS and conventional transmission Mössbauer measurements were performed for the as-quenched and annealed samples. The rf-Mössbauer measurements were performed during exposure of the samples to the rf field of 20 Oe at 60.8 MHz which was applied in the plane of the sample. The isomer shift data are given with respect to the α-Fe standard. The details of the experimental procedure are given elsewhere [4].

The transmission and CEMS spectra obtained are shown in Fig. 1. The spectra of samples annealed at $T_A \leq 600°C$ (Figs. 1a–e and 1a′–e′) were fitted by the combination of the hyperfine field distribution $(P(H))$ related to the amorphous phase and subspectra with discrete values of hyperfine fields (H_{hf}) and isomer shifts (δ) corresponding to the crystalline bcc Fe ($H_{hf} = 32.95$ T, $\delta = 0.00$ mm/s) and the tetragonal Fe_2B phase (two components with $H_{hf1} = 23.2$ T and $H_{hf2} = 24.2$ T and $\delta_1 = 0.12$ mm/s and $\delta_2 = 0.11$ mm/s, respectively [5]). The $P(H)$ distribution was calculated by the histogram method [6].

As can be seen from Fig. 1 the transmission and CEMS spectra of the as-quenched alloy are identical. However, clear differences between the bulk and surface crystallization appear already at $T_A = 430°C$. The transmission spectrum (Fig. 1b) consists of the spectral component characteristic of the purely amorphous state in which no crystalline phases could be detected, while the CEMS spectrum (Fig. 1b′) reveals, beside that component, the sextet characteristic of the bcc-Fe phase. Thus crystallization started at the surface already at $T_A = 430°C$. A similar situation was observed for the sample annealed at 500°C (Figs. 1c and 1c′). The spectral contribution in CEMS spectrum of the sextet characteristic of bcc Fe increases markedly with increasing T_A. At $T_A = 550°C$ the bcc-Fe phase appears in the bulk (Fig. 1d). The relative fraction of this phase is, however, much lower than that at the surface (Fig. 1d′).

In the spectra of the samples annealed at $T_A = 430, 500$ and $550°C$ beside the bcc-Fe sextet, a paramagnetic component, not observed in any transmission spectra, consisting of the quadrupole splitting (QS) doublet $(QS \approx 0.80$ mm/s and $\delta \approx 0.34$ mm/s) is clearly seen (Figs. 1b′, 1c′ and 1d′). The origin of this nonmagnetic component is uncertain. However, the observed QS and δ values correspond quite well to those characteristic of the iron-poor paramagnetic amorphous FeB phase [7]. Such a phase could appear at the surface as a result of segregation of some iron atoms from the amorphous matrix to form the bcc-Fe phase. The amorphous FeB phase is unstable and decomposes with progressing bulk and surface crystallizations which occur at higher annealing temperatures.

The CEMS spectrum of the sample annealed at $T_A = 600°C$ (Fig. 1e′) reveals
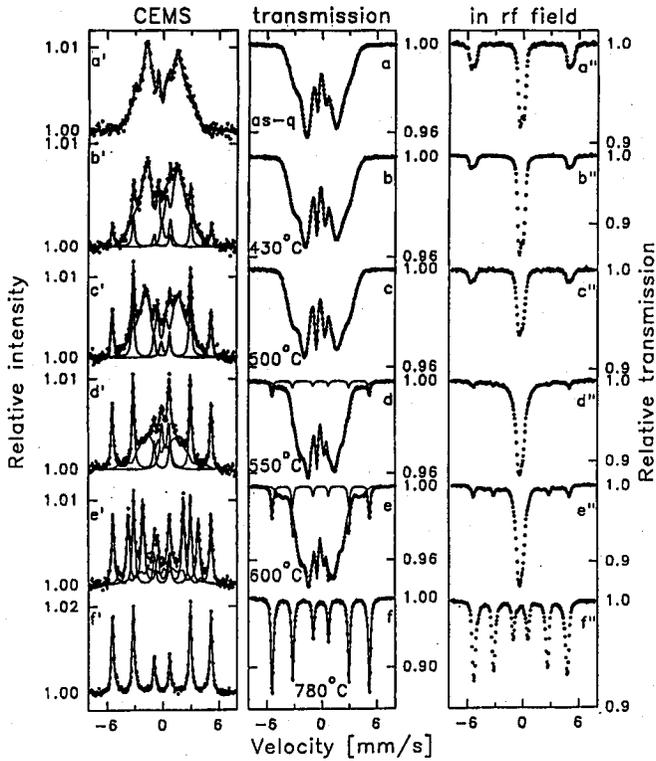
Fig. 1. CEMS ((a')–(f')) and transmission Mössbauer spectra recorded in the absence of the rf field ((a)–(f)) and during rf exposure ((a'')–(f'')) for $Fe_{81}Zr_7B_{12}$ alloy in the as-quenched state and after 1 hour annealing at 430–780°C.

that in addition to the bcc-Fe phase the crystalline Fe_2B phase was formed. This phase is formed only at the surface of the sample.

In all CEMS and transmission spectra of the samples annealed at $T_A = 500$, 550 and 600°C a spectral component with $H_{hf} \approx 27.5 \div 29$ T and $\delta \approx 0.04$ mm/s was observed. We attribute this sextet to the grain boundary regions between the nanocrystalline bcc Fe and the amorphous host.

The higher annealing temperature ($T_A = 780$°C) causes complete bulk crystallization of the alloy. Both transmission and CEMS spectra consist only of one sextet characteristic of the α-Fe phase (Figs. 1f and 1f') which suggests that iron atoms are completely separated from other alloy components.

The Mössbauer spectra measured during the exposure to the rf field are shown in Figs. 1a''–f''. A complete collapse of the magnetic hyperfine structure to a quadrupole doublet is observed for the amorphous alloy (Figs. 1a''–c''). The rf side bands clearly seen in the spectrum of the as-quenched alloy (Fig. 1a'') decrease markedly for the sample annealed at 500°C (Fig. 1c''). The formation of the nanocrystalline bcc-Fe phase causes a dramatic change of the shape of the rf-collapsed spectrum (Fig. 1d''). The central collapsed part consists now of a

superposition of a single line corresponding to cubic nanocrystalline bcc-Fe phase and a quadrupole doublet corresponding to the retained amorphous matrix. The rf side bands disappear completely which shows that magnetostriction almost vanished. However, the noncollapsed spectral component appears with sharp lines (Figs. 1d″, 1e″) corresponding to bcc-Fe phase in the form of grains with magnetic anisotropy large enough to prevent the rf collapse. The spectrum recorded during rf exposure for the microcrystalline sample (Fig. 1f″) shows noncollapsed six-line component similar to that corresponding to magnetically harder microcrystalline α-Fe (Fig. 1f). These results are discussed in detail elsewhere [4].

Conventional CEMS and transmission Mössbauer measurements allow identification of phases formed at the surface and in the bulk by annealing of the starting amorphous alloys but do not provide information concerning the magnetic anisotropy of the grains. The rf-Mössbauer experiments, in which the rf collapse and side band effects are observed, permit us to distinguish the soft nanocrystalline bcc-Fe phase from magnetically harder microcrystalline α-Fe. Some information concerning grain size distribution can be obtained. The nanocrystalline bcc-Fe phase is identified by the appearance of a single line component in the rf collapsed spectrum and by the disappearance of rf side bands due to vanishing magnetostriction.

Acknowledgments

References

[1] K. Suzuki, A. Makino, A. Inoue, T. Masumoto, *J. Appl. Phys.* **70**, 6232 (1991).

[2] K. Suzuki, A. Makino, A. Inoue, T. Masumoto, *J. Appl. Phys.* **74**, 3316 (1993).

[3] M. Kopcewicz, *Struct. Chem.* **2**, 313 (1991).

[4] M. Kopcewicz, A. Grabias, P. Nowicki, D.L. Williamson, *J. Appl. Phys.* **79**, 993 (1996).

[5] L. Takacs, M.C. Cadeville, I. Vincze, *J. Phys. F* **5**, 800 (1975).

[6] G. Le Caer, J.M. Dubois, *J. Phys. E* **12**, 1083 (1979).

[7] W. Hoving, F. van der Woude, K.H.J. Buschow, in: *Proc. Fifth Int. Conf. on Rapidly Quenched Metals*, Eds. S. Steeb, H. Warlimont, North-Holland, Amsterdam 1985, p. 549.