Magnetic properties of Fe–Zr metastable phases

L.F. Kiss a,*, G. Huhn b, T. Kemény a, J. Balogh a, D. Kaptás a

a Research Institute for Solid State Physics, P.O. Box 49, H-1525 Budapest, Hungary
b Eötvös University, Solid State Department, Múzeum krt. 6–8, H-1088 Budapest, Hungary

Abstract
Amorphous Fe_{100-x}Zr_x (7 < x < 12) alloys were crystallized up to the first and second crystallization peak of the respective DSC thermogram. The phases obtained were compared with those detected in Fe–Zr ingots (10–33 at% Zr) by Mössbauer spectroscopy and Curie point measurements. The partially crystallized samples contain, besides α-Fe, a possible amorphous phase with Zr content near 17–20 at%. α-Fe and Fe₂Zr were found in the fully crystallized samples; the Fe₃Zr intermetallic phase of the ingots was not present.

Keywords: Crystallization; Fe–Zr alloys; Magnetic properties; Metallic glasses; Metastable phases; Mössbauer spectroscopy

1. Introduction
Fe_{100-x}Zr_x amorphous alloys can be produced by melt-spinning near both eutectic minima (x = 8.8 and 76 at% Zr) of the equilibrium phase diagram [1]. Fe-rich amorphous Fe–Zr alloys (7 < x < 12) have been studied intensively for more than a decade because of their peculiar magnetic properties as well as in order to identify their crystallization processes and crystallization products [2–6]. However, the crystallization sequence of these alloys is not well understood. There is general agreement that the crystallization of these alloys consists of two distinct processes [2] according to differential scanning calorimetry (DSC) results. In the first process, bcc α-Fe is precipitated. However, the results are contradictory as far as the compositions of the evolving crystallization products after the first and second processes are concerned.

Osamura et al. [3] found by X-ray diffraction and small angle X-ray scattering that, in Fe₉₀Zr₁₀ after phase separation (Fe/Fe₂Zr) in the amorphous state, Fe₂Zr appeared in the first crystallization stage while both Fe₃Zr and Fe₂Zr were detected in the second stage (apart from α-Fe in both stages). Sostarich and Khan [4] studied the same alloy by X-ray diffraction during annealing and observed that the reflections due to Fe₃Zr were immediately followed by those due to Fe₂Zr. Therefore, they could not decide which of the two phases is associated with the second exothermal peak in the DTA thermogram (differential thermal analysis). Altounian et al. [5] identified the phase evolving in the second DSC stage, in addition to (δ, α)-Fe, as Fe₂Zr.

The crystallization kinetics of Fe₉₀Zr₁₀ were also studied by transmission electron microscopy (TEM), initial susceptibility and DSC measurements. The results depend very much on the preparation conditions of the melt-quenched alloys. Zárubová et al. [2] report on quenched-in nuclei in the as-quenched state of the alloy, whereas there were no detectable nuclei in the as-quenched alloy of Sostarich and Khan [4]. This is consistent with the fact that the ribbon was thicker (prepared with lower cooling rate) in the former case than in the latter. Consequently, the activation energy determined by Zárubová et al. [2] for the first crystallization peak (precipitation of α-Fe) was found to be lower than that determined by Sostarich and Khan [4].

In the present work the crystallization sequence and products for the Fe-rich Fe_{100-x}Zr_x amorphous alloy system were investigated in the concentration range 7 < x < 12, which is wider than those available in the literature. Furthermore, Fe–Zr ingots were prepared for a wide Zr concentration range of 10–33 at% to compare the crystallization products with the phases found in the ingots. All phases were identified by Mössbauer spectroscopy and Curie temperature (T_c) measurements.

2. Experimental
Amorphous Fe_{100-x}Zr_x (7 < x < 12) alloys were produced by melt-spinning in the form of ribbons with an average cross section of 0.5–1 mm × 10–20 μm. The amorphous state of the ribbons was checked by X-ray diffraction and Mössbauer spectroscopy. One of the alloys
(Fe₀ᵦZr₁₀) was prepared in Stuttgart and was much wider (1 cm) and thicker (25–30 µm) than the others. The DSC measurements were performed using a Perkin-Elmer DSC-2-type calorimeter with a heating rate of 20 K/min. The samples used for the Mössbauer study and for the Curie point measurements were partially and fully crystallized in the DSC operating under Ar atmosphere by heating the amorphous samples at 20 K/min up to the end of the first and second DSC peak, respectively, followed by rapid cooling at 320 K/min.

Mössbauer measurements were performed at room temperature using a conventional constant acceleration spectrometer with a 50 mCi ⁵⁷CoRh source. The Curie temperature was measured in a Foner-type vibrating sample magnetometer using the kink-point method, i.e. Tₐ was detected as the inflection point of the decrease in magnetization measured in a low field (10 Oe) as a function of temperature. The heating and cooling rate was about 4–5 K/min and the sample temperature was measured using a CuKα thermocouple. There was a systematic increase in Tₐ of up to about 10 K measured on cooling after heating the sample slightly above Tₐ (probably due to ordering). In the present analysis the Curie points measured on cooling were used.

### 3. Results and discussion

Fig. 1 shows DSC thermograms of the amorphous Fe₁₀₀₋ₓZrₓ (7 < x < 12) alloy system. In agreement with the available literature data [2–5] all the thermograms consist of two peaks, indicating two distinct crystallization processes. The initial crystallization temperature and the crystallization enthalpy for the thicker Fe₉₀Zr₁₀ do not fit the data set for the thinner ribbons. It is well known that crystallization properties are influenced by the amount of quenched-in nuclei (i.e. by the thickness) [2,4]. The DSC curve of Fe₉₃Zr₇ has a very irregular shape. This composition is very close to the concentration range where the alloy cannot be amorphized using the usual quenching rates (around 10⁵ K/s). Although the Fe₉₃Zr₇ alloy is found to be amorphous by conventional methods, a heterogeneous distribution of quenched-in nuclei is evident from the crystallization.

To help identify the crystallization products of the glasses, the crystalline phases present in the Fe–Zr ingots were studied. Fig. 2 shows the Mössbauer spectrum and hyperfine field distribution of the stoichiometric Fe₂Zr ingot. This contains only one phase: the Fe₂Zr equilibrium phase has a Cu₂Mg-type structure with two inequivalent Fe sites and can be off-stoichiometric in the Zr composition range 27–34 at% [1]. On reducing the nominal Zr content of the ingots down to 10 at%, two phases appear in the spectra: an increasing amount of bcc α-Fe and a decreasing amount of Fe₂Zr. This is illustrated in Fig. 3 where the intensity ratios of α-Fe, Iₐ₋Fe, vs. the nominal Zr content, x, are shown for the Fe₂Zr ingots. Iₐ₋Fe is the relative ratio of the Fe atoms having a bcc α-Fe environment. Furthermore, it follows from the figure that below 28 at% nominal Zr content, the Fe₂Zr phase present in the ingots is off-stoichiometric with a Zr content of about 28 at%.

The Curie temperatures of the Fe₂Zr compounds were determined from the magnetization vs. temperature curves measured on the Fe–Zr ingots. The Tₐ values displayed as a function of the nominal Zr content, x (Fig. 4), show that Tₐ increases steeply (34 K/at%) with decreasing Zr content from the stoichiometric composition (33 at%) down to 28 at%, and then stays constant down to 15 at% Zr.
content. This means that the Fe$_2$Zr phase found in the Fe–Zr ingots in the nominal Zr composition range of 15–28 at% is an off-stoichiometric phase with a constant Zr content of 28 at%. As was shown before, the same conclusion could be drawn from the α-Fe content of the samples (Fig. 3). The Curie temperature values obtained and the steep increase of $T_c$ observed in the off-stoichiometric range (28–33 at%) agree well with literature data [6].

Fig. 5 shows the Mössbauer spectra for the partially crystallized Fe$_{90}$Zr$_{10}$ alloy (upper figure: solid line), the α-Fe phase (upper figure: dashed line) and their difference (middle figure), together with the hyperfine field distribution for the latter. Obviously, the alloy spectrum can be satisfactorily described by assuming two dominant phases: α-Fe and an alloy phase with a broad hyperfine distribution. A similar data analysis was performed for all partially crystallized Fe$_{100-x}$Zr$_x$ alloys ($7 < x < 12$) giving the same result. The intensity ratios of α-Fe, $I_{\alpha,Fe}$, for these alloys are displayed in Fig. 3 as a function of the nominal Zr content, $x$. They suggest that the alloy phase found after the first crystallization peak has a composition near 17–20 at% Zr in the whole concentration range investigated ($7 < x < 12$). (It is difficult to decide whether this composition corresponds to a stoichiometry of Fe:Zr = 5:1 or 23:6.) The Curie temperature of this phase was estimated to be about 320 K from kink-point measurements, although the very smooth decrease of magnetization indicated a peculiar microstructure for this phase. The true amorphous structure of this phase needs further confirmation.

Mössbauer spectra for the fully crystallized Fe$_{90}$Zr$_{10}$ alloy (upper figure: solid line), the α-Fe phase (upper figure: dashed line) and their difference (middle figure) are shown in Fig. 6, together with the hyperfine field distribu-
As can be seen from the Mössbauer results, fully crystalline Fe\textsubscript{100-x}Zr\textsubscript{x} alloys (7 < x < 12) are composed of dominantly two phases: α-Fe and an alloy phase with a composition close to Fe\textsubscript{3}Zr. The Curie points, T\textsubscript{C}, for the latter phase are shown in Fig. 4 as a function of the nominal Zr content, x, of the starting amorphous sample. (The decrease of magnetization for this phase takes place over a very broad temperature range for each composition, indicating a significant degree of inhomogeneity.) The significant dependence of the Curie point of the Fe\textsubscript{3}Zr phase on the nominal amorphous composition may indicate a slight off-stoichiometry, which is not evident within the precision of Fig. 3. The T\textsubscript{C} values, increasing with decreasing Zr content of the parent amorphous phase, cannot exclude that this phase is slightly off-stoichiometric Fe\textsubscript{3}Zr with 31–35 at% Zr. However, a Curie point as low as 590 K has never been observed for the Fe\textsubscript{3}Zr structure. Besides that, the very distinct values of the Mössbauer parameters for the two phases (mainly those of the half-width of the hyperfine field distribution seen in Fig. 2 and Fig. 6) exclude this possibility, suggesting that the fully crystallized state of Fe–Zr amorphous alloys does not contain the off-stoichiometric Fe\textsubscript{3}Zr phase. This finding is in agreement with that of Altounian et al. [5].

In conclusion, Curie point determination by magnetization measurements and Mössbauer spectroscopy indicates that the final crystallization products of the amorphous Fe\textsubscript{100-x}Zr\textsubscript{x} alloy system (7 < x < 12) are α-Fe and an alloy phase which is identified as (slightly off-stoichiometric) Fe\textsubscript{3}Zr.

Acknowledgement: The authors are indebted to L. Bujdosó who prepared all the samples, except for the amorphous Fe\textsubscript{90}Zr\textsubscript{10} which was kindly supplied by Dr. N. Moser, Stuttgart. DSC measurements of N. Víťáz are appreciated. Financial support from the Hungarian Research Fund (grant No. OTKA-T4469) and the Copernicus project (ERBCIPACT 940155) is greatly acknowledged.

References