Compositional dependence of and effects of hydrogen doping on coercive fields of Fe-rich Fe–Zr amorphous alloys

T Moyo

Department of Physics, University of Natal, Private Bag X10, Dalbridge 4014, South Africa

Abstract. Variation in low-temperature coercive fields $H_c(x)$ as a function of Fe concentration x and hydrogen doping are investigated for Fe-rich $Fe_x Zr_{1-x}$ amorphous alloys. The analysis is based on Fe density fluctuations in the alloys. We demonstrate a linear dependence between $\ln H_c(x)$ and $\ln(1-x)$. The drastic decrease in coercive field observed at low temperatures with hydrogen doping is also analysed.

1. Introduction

The study of the magnetic properties of Fe-rich $Fe_x Zr_{1-x}$ amorphous alloys has endured with time. A number of properties are still not well understood. This has always attracted a fresh review of available data and new measurements. For Fe concentrations $x > 0.88$, melt-spun alloys show a tendency towards non-magnetic behaviour with increasing x or pressure. The Curie temperature and spontaneous magnetization decrease [1–4]. This is associated with increased magnetic hardness and low-field magnetization behaviour at low temperatures. The effect of hydrogen doping is to enhance ferromagnetic order and to suppress coercivity and low-field behaviour drastically [5, 6].

The preparation technique and conditions affect the properties [2]. It now appears that many properties of Fe-rich alloys can be adequately described on the basis of density fluctuations in the alloys [7]. This is in the form of Fe-rich clusters with Fe atoms in the low-spin state embedded into a ferromagnetic matrix having Fe atoms in the high-spin state. Different spin states are determined by the proximity of Fe atoms to each other.

The objective of the present work is to consider the compositional and hydrogen doping effects on coercive field. The coercive field is a parameter that can be measured accurately and is very sensitive to the microstructure of the alloys. Our analysis is simple in formulation but gives results that appear to correlate well with the available experimental data.

2. Density fluctuation model

The Fe-rich alloys considered here have been prepared by melt spinning or sputtering. Their preparation methods and conditions have been reported elsewhere [8, 9]. Previous work has shown that coercive fields can be correlated with Fe-rich clusters which are responsible for domain wall pinning [8]. The clusters can be considered to be non-magnetic or weakly
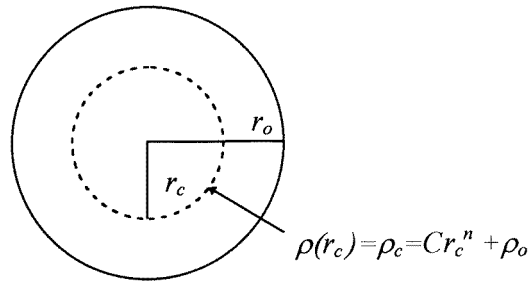
Figure 1. A spherical sample of radius r_0 with a representative Fe-rich cluster of radius r_c.
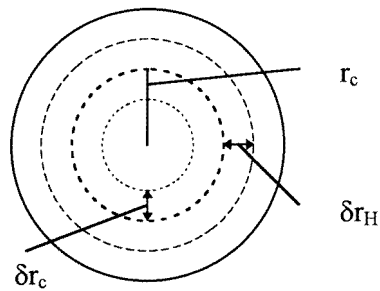
Figure 2. Effect of hydrogen doping on the size of an Fe-rich cluster.

magnetic inclusions in a ferromagnetic matrix. The coercive field of such alloys can be assumed to be approximately proportional to the volume fraction of the inclusions [8, 10, 11].

In order to define the clusters more precisely, we have assumed that they correspond to Fe atoms in regions with density $\rho > \rho_c$, where ρ_c is a critical density which separates Fe atoms into low-spin and high-spin states [7]. The clusters are distributed randomly in the ferromagnetic matrix having $\rho < \rho_c$. Density variation across a cluster can be taken to be of the form

$$\rho(r) = C_j r^n + \rho_{0j}. \tag{1}$$

ρ_{0j} is the density at the centre of a cluster. The index n describes the density variation. C_j are constants defined at the position of critical density. Hydrogen-doped and undoped samples are denoted by $j = H$ or $j = 0$ respectively. This is illustrated in figures 1 and 2. For simplicity, spherical clusters are assumed. It was shown previously [7], in the analysis of pressure and temperature variation in a coercive field, that we need to consider only a single cluster. A similar result was obtained by Golbazi *et al* [11] for a random distribution of inclusions in a ferromagnetic matrix. The spatial distribution of the clusters is ignored in the present analysis because the average distance between Fe-rich clusters is expected to be much larger than the average diameters of the clusters [7].

3. Compositional dependence

In order to analyse the compositional variation in coercive field, a sample of finite volume V_0 is selected. This includes a representative Fe-rich cluster of volume V_c whose extent is
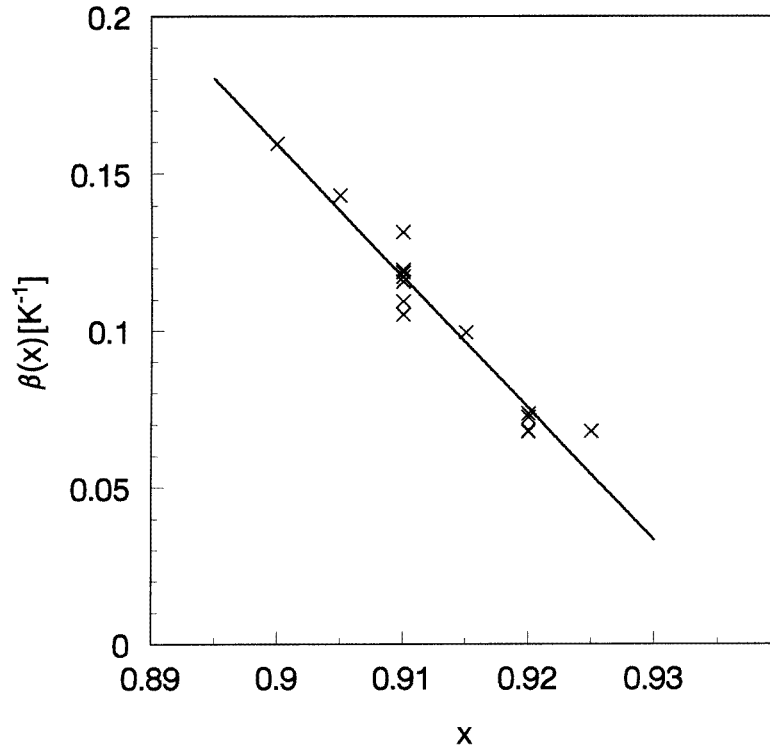
Figure 3. Compositional dependence of parameter $\beta(x)$ for melt-spun Fe_xZr_{1-x} amorphous alloys [7, 13].

defined using equation (1). From figure 1, the volume fraction V_c/V_0 of the Fe-rich cluster can be calculated. Assuming that $\rho(r_c) = \rho_c$, we can show that

$$\frac{V_c}{V_0} = \left[\frac{3}{n+3} \frac{\rho_{00} - \rho_c}{\rho_{00} - \rho_s} \right]^{3/n} \tag{2}$$

where ρ_s is the average density of the sample. The compositional dependence of V_c/V_0 is expected to depend on changes in the densities ρ_{00} and ρ_s. The dependence of ρ_s on the Fe concentration x for melt-spun Fe_xZr_{1-x} alloys [12] has been found to be

$$\rho_s = (6.44 + 1.44x) \text{ g cm}^{-3}. \tag{3}$$

With increasing x we expect an increase in the average density of the Fe-rich clusters. ρ_{00} should therefore have a compositional dependence. The variation of ρ_{00} with x is not expected to be as dramatic as that of ρ_s. However, $\rho_{00}(x) - \rho_c$ could have a significant concentration dependence as $\rho_{00}(x)$ will tend to be slightly larger than ρ_c. The maximum value of ρ_{00} can be deduced from equation (3) for $x = 1$. This gives $\rho_{00} \approx 7.88$ g cm^{-3}. Hence

$$\rho_{00} - \rho_s \approx 1.44(1 - x) \text{ g cm}^{-3}. \tag{4}$$

The compositional dependence of $\rho_{00}(x) - \rho_c$ has yet to be worked out, but $\rho_{00}(x)$ is expected to increase with increasing x. The coercive fields for melt-spun and sputtered Fe-rich alloys [8, 9] at low temperatures (4.2 K $< T <$ 50 K), have been found to vary
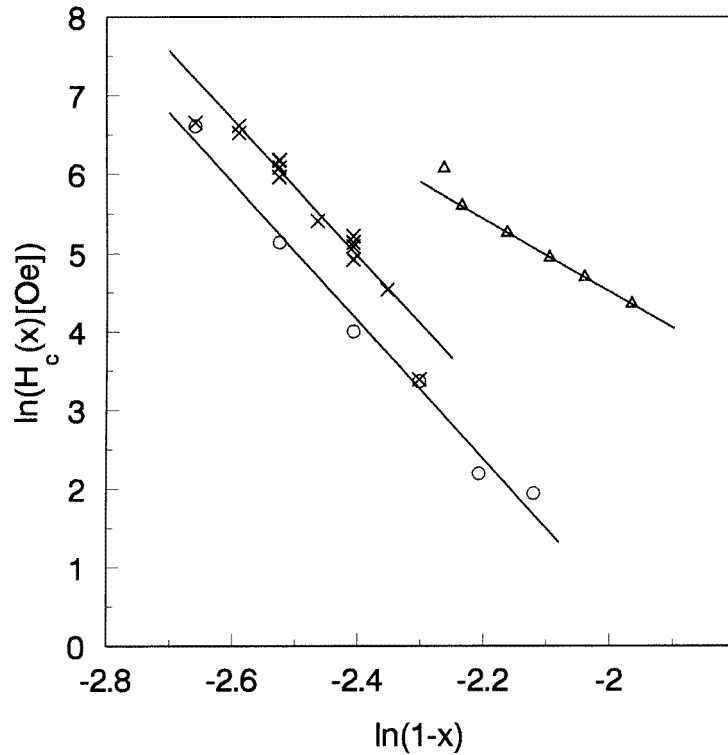
Figure 4. Plots of $\ln H_c(x)$ against $\ln(1 - x)$ for Fe_xZr_{1-x} amorphous alloys: $\times$, melt-spun alloys [8] ($H_c(x)$ data obtained by extrapolating $H_c(x, T)$ data to $T = 0$ K); $\triangle$, sputtered alloys [9] ($H_c(x)$ data obtained by extrapolating $H_c(x, T)$ data to $T = 0$ K); $\bigcirc$, melt-spun alloys [2] ($H_c(x)$ data obtained at 4.2 K).

exponentially with temperature $(H_c(x, T) = H_c(x, 0) \exp[-\beta(x)T])$. Using the Fe density model and assuming that coercive fields change owing to thermal expansion, the parameter $\beta(x)$ in the temperature dependence of coercive field was deduced to be [7]

$$\beta(x) = \frac{(n + 3)\rho_c\alpha_v}{\rho_{00}(x) - \rho_c} \tag{5}$$

where α_v is an expansion coefficient. Thermal expansion is expected to cause a slight expansion of the lattice. This would cause a reduction in the size of Fe-rich clusters similar to the effect of hydrogen doping. The compositional dependence of $\beta(x)$ is consistent with an increase in $\rho_{00}(x)$ with increasing x. Figure 3 shows the compositional dependence of $\beta(x)$ [7, 13]. It appears that a form of

$$\rho_{00}(x) - \rho_c \propto \frac{1}{1 - x} \tag{6}$$

could well reflect the compositional dependence of $\beta(x)$. This implies that we might do well to investigate the variation in V_c/V_0 of the form

$$\frac{V_c}{V_0} \propto [1 - x]^{-6/n}. \tag{7}$$
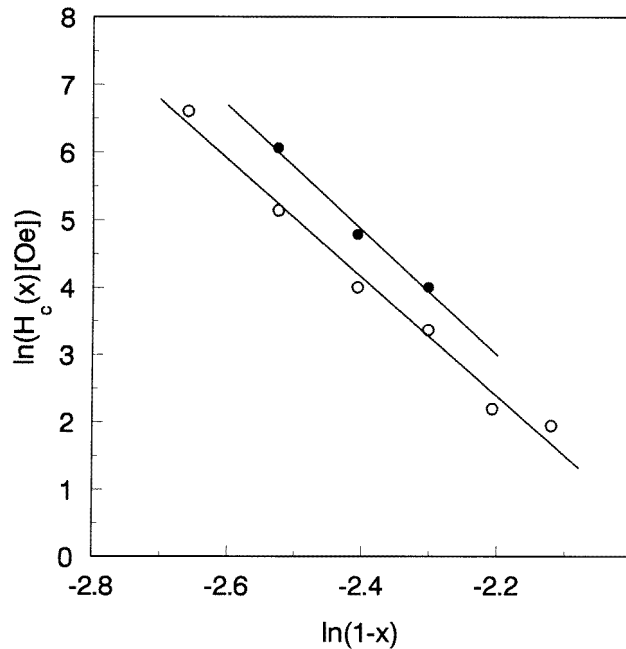
Figure 5. Plots of $\ln H_c(x)$ against $\ln(1-x)$ for melt-spun $Fe_x Zr_{1-x}$ (○) [2] and $Fe_x Hf_{1-x}$ (●) [14] amorphous alloys ($H_c(x)$ data obtained at 4.2 K).

Since coercive fields due to inclusions can be assumed to be proportional to V_c/V_0, we must expect linear plots of $\ln H_c(x)$ against $\ln(1-x)$ with slopes equal to $-6/n$. Figures 4 and 5 show such plots for different alloys. The values of n deduced from such plots for Fe–Zr and Fe–Hf amorphous alloys are displayed in table 1. Similar results involving the coercive field and the Curie temperature $T_C(x)$ were obtained previously [7]. Figure 5 shows plots for Fe–Zr and Fe–Hf alloys from the data obtained by Ryan *et al* [2, 14] for comparison. The values of the index n displayed in table 1 appear to be roughly of the order of unity. The n-values are supposed to provide information about density fluctuations in the alloys [7]. The scatter in n-values might be attributed to slight differences in microstructure and the fact that the Curie point $T_C(x)$ is a more sensitive microstructure parameter than x. In the current work, values of n for melt-spun alloys are almost the same. This implies similarity in characteristics compared with sputtered alloys.

Rough estimates of the volume fraction of Fe-rich clusters in melt-spun alloys can be deduced using equation (2). From equation (3) we may assume that $\rho_{00} \approx 7.88$ g cm^{-3} for $x = 1$ and $\rho_c \approx 7.80$ g cm^{-3} for $x = x_c \approx 0.95$ [8]. Using $n = 0.61$ obtained for melt-spun alloys, we deduce that

$$\frac{V_c}{V_0} \approx \left[\frac{0.046}{1-x}\right]^{4.9}. \tag{8}$$

The estimates of V_c/V_0 against x are plotted in figure 6. The results appear to indicate that total collapse of ferromagnetism in melt-spun Fe–Zr alloys could occur when the volume fraction of Fe-rich clusters exceeds about 60% corresponding to $x = x_c$.
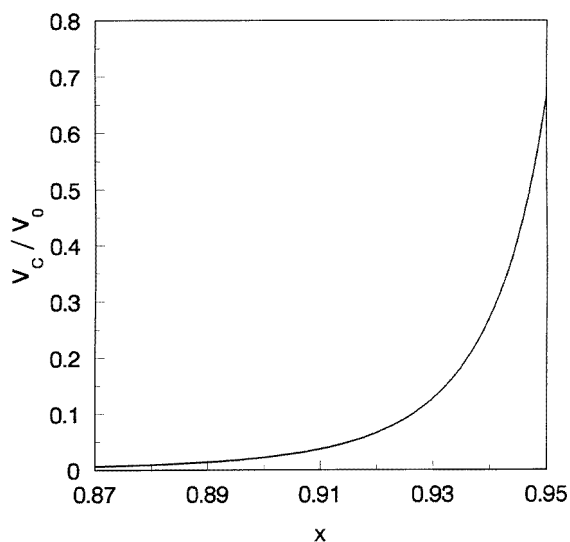
Figure 6. Estimate of compositional dependence of the volume fraction of Fe-rich clusters in melt-spun $Fe_x Zr_{1-x}$ alloys.

Table 1. Values of n for melt-spun and sputtered Fe–Zr amorphous alloys.

| | | n | |
| | | | |
Alloy	Symbol in figures 4 and 5	$\ln H_c(x)$ against $\ln T_C(x)$ [7]	$\ln H_c(x)$ against $\ln(1-x)$ (current work)
Melt-spun Fe–Zr [2]	○	0.61	0.68
Melt-spun Fe–Zr [7]	×	0.91	0.69
Sputtered Fe–Zr [7]	△	0.77	1.30
Melt-spun Fe–Hf [11]	●	—	0.63

4. Hydrogen doping

Hydrogen doping in melt-spun Fe–Zr amorphous alloys is believed to cause not only volume expansion but also modification of the band structure [12, 15]. The presence of Zr seems to enhance hydrogen absorption. There is a tendency for hydrogen atoms to prefer sites near Zr atoms [12]. This effectively acts as a negative pressure on Fe-rich clusters, causing them to shrink in size as illustrated in figure 2. Hence the negative pressure effect can be considered as a predominant cause of decrease in coercive field due to hydrogen doping.

The variation in coercive field with hydrogen doping can be deduced from figure 2 to be

$$\frac{H_c(H)}{H_c(0)} = \left(1 - \frac{\delta r_c}{r_c}\right)^3. \tag{9}$$

Owing to lattice expansion,

$$\int_0^{r_c} (C_0 r^n + \rho_{00}) 4\pi r^2 \, dr = \int_0^{r_c + \delta r_H} (C_H r^n + \rho_{00}) 4\pi r^2 \, dr. \tag{10}$$
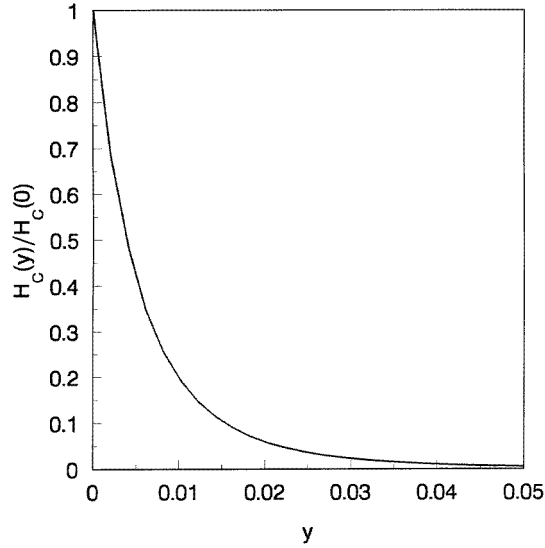
Figure 7. Predicted variation in low-temperature coercive field due to hydrogen doping in $Fe_xZr_{1-x}H_y$ alloys.

C_0 and C_H are defined using $\rho(r_c) = \rho_c$ and $\rho(r_c - \delta r_c) = \rho_c$, respectively. From equation (10) we can deduce that

$$\left(1 - \frac{\delta r_c}{r_c}\right)^n = \frac{1 + (n+3)\,\delta r_H/r_c}{1 + (n+3)\lambda\,\delta r_H/r_c} \tag{11}$$

where $\delta r_H/r_c \ll 1$ and

$$\lambda = \frac{\rho_{00}}{\rho_{00} - \rho_c}. \tag{12}$$

$\delta r_H/r_c$ can be related to the volume strain $\Delta V/V$ of the sample. In the hydrogen-doped alloys $Fe_xZr_{1-x}H_y$, the volume strain has been found to be related to hydrogen absorbed [12, 16, 17] by

$$\frac{\Delta V}{V} \approx 0.32y. \tag{13}$$

From equations (9), (11) and (13), the coercive field of a hydrogen-doped sample can be expressed by

$$\left[\frac{H_c(y)}{H_c(0)}\right]^{n/3} = \frac{1 + 0.11(n+3)y}{1 + 0.11\lambda(n+3)y}. \tag{14}$$

We estimate that $\lambda \approx 100$ using equations (3) and (12). In figure 7 the trend in $H_c(y)/H_c(0)$ is illustrated for $n = 0.61$ and $\lambda = 100$. Clearly, a substantial drop in coercive field is expected to occur at a low level of hydrogen doping. This has been shown to be the case experimentally [5]. Ryan *et al* [14] have also observed that hydrogen-induced expansion of typically 5–10% by volume leads to a fully collinear spin structure.

5. Conclusion

We have obtained an expression describing the compositional dependence of low-temperature coercive fields in Fe-rich Fe–Zr amorphous alloys. The expression seems to fit the experimental data well. We have also investigated the effect of hydrogen doping on coercive field through volume change. This has been shown to be consistent with a dramatic decrease in coercive field in agreement with available experimental results. We propose a more systematic study of the low-temperature coercive field at lower levels of hydrogen doping in order to deduce microstructure information of the alloys.

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