

Influence of hydrogen distribution on magnetic properties of amorphous samples

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Abstract. We have studied the effect of the homogeneity of hydrogen distribution on magnetic properties of hydrogen charged amorphous samples (Metglass 2826MB: Fe₄₀Ni₄₀Mo₄B₁₈). The results suggest that, in high magnetostrictive samples, the induced internal stresses and hence the magnetic anisotropy are related to the hydrogen distribution and not to the total quantity of hydrogen inside the sample. To perform this study, the homogeneity of hydrogen distribution in the sample was improved by using a very low rate of hydrogen charging by means of a pulsed electrolytic current. Furthermore, this pulsed electrolytic current allows us to introduce a high quantity of hydrogen without breaking the sample.

PACS. 75.80.+q Magnetomechanical and magnetoelectric effects, magnetostriction – 75.60.-d Domain effects, magnetization curves, and hysteresis – 66.30.-h Diffusion in solids

1 Introduction

The effects of hydrogen charging in amorphous and polycrystalline materials have been widely studied in recent years from both a mechanical and a magnetic point of view [1,2]. In crystals there may be no changes in lattice symmetry on hydrogenation, but there usually is some lattice dilation that can be regarded formally as the effect of a negative pressure [3]. To summarize, the main effect of hydrogen charging seems to be a dilation of the distance between nearest-neighbour atoms.

The change in the magnetic properties of the studied Fe-rich amorphous alloys is, therefore, associated with the internal mechanical stresses induced by the hydrogen in the material. Hydrogen dilates the region where it is present (specially the regions close to the surface of the sample), whereas the remaining volume (in the inner region of the sample) does not change during the process. As the sample must maintain the mechanical equilibrium, the hydrogenated region would be under compressive stresses, whereas the rest of the sample will be under tensile stresses.

In this experiment we used amorphous metallic ribbons obtained by rapid quenching, where the thickness is much smaller than the other two dimensions. After hydrogenation, a considerable perpendicular anisotropy appears in both outer parts of the sample that are under compressive stresses, and then also an in-plane anisotropy appears in the inner part of the sample, which is under

tensile stress [4]. This effect is quasi reversible and the changes in magnetic and mechanical properties disappear when hydrogen is eliminated from the sample [5,6].

In a previous work [4] we have evaluated the internal stresses induced in electrolytic hydrogen charged samples from measurements of the magnetic anisotropy and observations of the domain structure by Bitter technique. From these results, the hydrogenated volume of the sample was evaluated. The maximum volume obtained (current density 100 A/m² and charging time 240 s) was nearly 35% of the total volume. It implies a very inhomogeneous distribution of hydrogen. For a higher hydrogenation time the sample breaks due to the internal stresses induced by this inhomogeneous distribution.

A more homogeneous distribution of hydrogen inside the sample can be obtained by decreasing the electrolytic current intensity thereby reducing the electrolytic hydrogen production. But there is a limit to the decrease of the current density because a minimum voltage is necessary to get the hydrolysis of the bath.

The aim of this work is to find a way to slowly introduce the hydrogen in the sample in order to obtain a more homogeneous distribution and to compare the magnetic changes induced by this hydrogen distribution with the ones observed in previous works [7–9].

2 Experimental

Samples of Metglass 2826MB: Fe₄₀Ni₄₀Mo₄B₁₈ (1.2 mm wide, 50 μm thickness) were hydrogen charged by using

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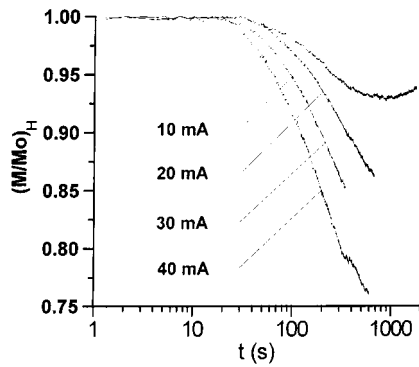


Fig. 1. Behaviour of $(M/M_0)_H$ ratio for different current intensities dc versus hydrogenation time, for a Metglas 2826MB sample.

an electrolytic system similar to that employed by other authors [5], but using platinum as the anode and a current density of 100–300 A/m². The magnetic measurements were performed *in situ* during hydrogenation and dehydrogenation processes. In order to do that the electrolytic system was placed inside the primary coil.

To study the hydrogen charging effect on the magnetic anisotropy of the sample it would be necessary to measure the magnetization work through the magnetization curves. An approximation consists in measuring the $(M/M_0)_H$ ratio versus hydrogenation time. M_0 is the maximum magnetization of the sample for a 23 Hz alternating magnetic field applied with a constant amplitude ($H = 5$ kA/m) not high enough to saturate the sample (before hydrogen charges the sample). M is the maximum magnetization for the same magnetic field H (after hydrogen charges the sample during a time t). Figure 1 shows $(M/M_0)_H$ versus hydrogenation time for different electrolytic current intensities in a 2826MB sample. It is observed that $(M/M_0)_H$ decreases as hydrogenation time increases. For a small electrolytic current (10 mA), $(M/M_0)_H$ ratio decreases first and then begins to recover, but the sample breaks before recovering the $(M/M_0)_H$ initial value.

This behaviour of $(M/M_0)_H$ versus hydrogenation time can not be attributed to a variation in the saturation magnetization, M_s , of the hydrogenated sample. A possible variation of M_s in these curves is negligible in comparison to the variation produced by changes in the induced anisotropy of the sample. The magnetization curves do not show an appreciable variation of the maximum value of magnetization for magnetic fields up to $H = 40$ kA/m [4].

To obtain a very slow rate of hydrogen charging, we have used a time-dependant electrolytic current density. During the interval time t_1 the current amplitude is I_p and the hydrogen comes into the sample. During the interval time t_2 the electrolytic current intensity is zero and then the hydrogen flows from the sample to the bath. Simultaneously, there is a “drive in” diffusive process that allows a more homogeneous distribution of hydrogen into the sample.

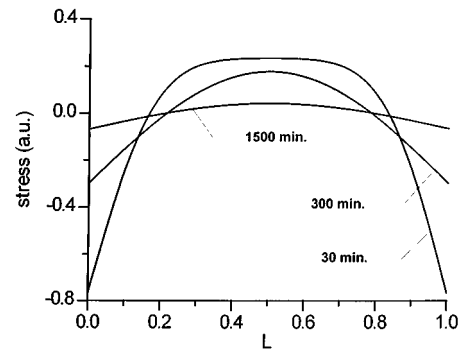


Fig. 2. Distribution of stress on the sample for three different times obtained from the model.

3 Numerical

To estimate the hydrogen distribution in the sample, we have performed an one-dimensional model, considering the geometry of the sample, where the thickness is much smaller than the other two dimensions and according to the symmetry of the experimental set-up. The distribution of concentration at any position x and time t , $\phi(t, x)$, is obtained by solving the Fick's equation, $\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}$, (being D a constant) with the adequate boundary conditions:

$$\begin{aligned} \phi(t, 0) &= \phi(t, L) = \phi_0 \quad \forall t \\ \phi(0, x) &= 0 \quad \forall x \end{aligned}$$

where ϕ_0 is the average hydrogen concentration produced by the pulsed current at both sample surfaces and L is the sample thickness. The solution of Fick's equation is

$$\phi(t, x) = \phi_0 - \frac{4\phi_0}{\pi} \sum_{l=0}^{\infty} \frac{1}{2l+1} e^{-\frac{(2l+1)^2 \pi^2 D t}{L^2}} \sin \frac{(2l+1)\pi x}{L} .$$

By assuming that the volume dilation $\Delta V(x, t)$ of the sample is directly related to its hydrogen concentration, the induced stress $\sigma(x, t)$ of the i layer is directly related to the addition of the concentration difference between this layer and the two neighbours $i-1$ and $i+1$.

$$\sigma(x, t) \approx [(\phi_i - \phi_{i-1}) + (\phi_i - \phi_{i+1})] = \left(\frac{\partial^2 \phi}{\partial x^2} \right)_i h^2$$

h being the layer thickness. Therefore, the induced stress of the i layer is proportional to $\nabla^2 \phi$. Remembering the physical sense of Laplacian, the internal stresses induced by the hydrogen will be $\sigma(x, t) = \langle \phi(t) \rangle - \phi(x, t)$, where $\langle \phi(t) \rangle$ is the average hydrogen concentration in the sample. Figure 2 shows the evolution of $\sigma(x, t)$ by taking t as a parameter. As it can be observed from the shape of these curves, the internal stresses increase up to a maximum value and then there is a progressive decrease down to zero. This effect is also shown in Figure 3 where the r.m.s value of $\sigma(x, t)$ and $\langle \phi(t) \rangle$ are plotted vs. time.

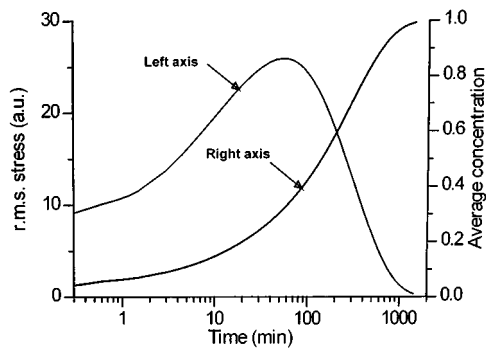


Fig. 3. R.m.s. stress and average concentration *versus* time, obtained from the model.

4 Results

Figure 4 shows the $(M_0/M)_H$ ratio *versus* time for a 2826MB sample, during hydrogen charging by a pulsed electrolytic current ($t_1 = t_2 = 1/40$ s, current density = 240 A/m^2). The magnetic anisotropy ratio, K/K_0 , where K_0 is the anisotropy of the sample before hydrogenation can be related to the magnetization ratio $K/K_0 \approx (M_0/M)_H$. K/K_0 first increases and then decreases, both parts of the curve can be fitted by exponential functions (with exponents 0.132 and -0.302 respectively). In consequence, in spite of the increase of the total quantity of hydrogen inside of the sample, the magnetic anisotropy approaches the initial value. This result can be confirmed by observing the minor hysteresis loops of Figure 5, measured in the same sample at different hydrogenation times, during the above process. Figure 5 shows a minor hysteresis loop of the sample from before hydrogenation up to 150 min of hydrogen charging. At the beginning hydrogen concentration is not homogeneous and then remanence and coercive field increase due to the internal stresses induced by hydrogen, being the non-homogeneity maximum for 60 min of hydrogenation. After enough time (150 min) hydrogen concentration becomes more homogeneous, reducing coercive field and remanence.

These results agree with calculations shown in Figures 2 and 3. In spite of the increasing average hydrogen concentration, the internal stresses (and hence the anisotropy) first grow exponentially up to a maximum value and then they decrease also exponentially but with a higher exponent. From other experimental data, not shown in this work, we have observed that the time to reach the maximum anisotropy is no dependant on the current intensity that also matches with the calculations.

After completing a similar process as the one described in Figure 4, if the pulsed current is switch off, curves like Figure 6 are obtained. During this process the hydrogen is leaving the sample and the $(M_0/M)_H$ behaviour is similar to the first part of Figure 4, because the hydrogen distribution inside the sample becomes less homogeneous and thus the $(M_0/M)_H$ ratio decreases.

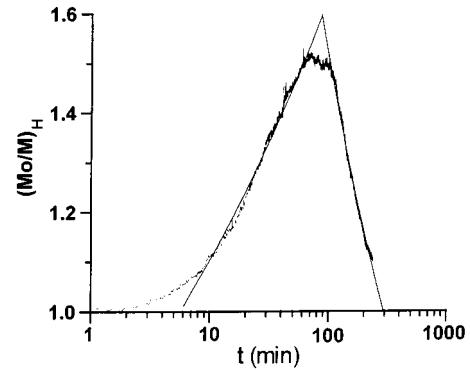


Fig. 4. Experimental evolution of the ratio $(M_0/M)_H$ *versus* time in a Metglas 2826 MB sample by using electrolytic pulsed current.

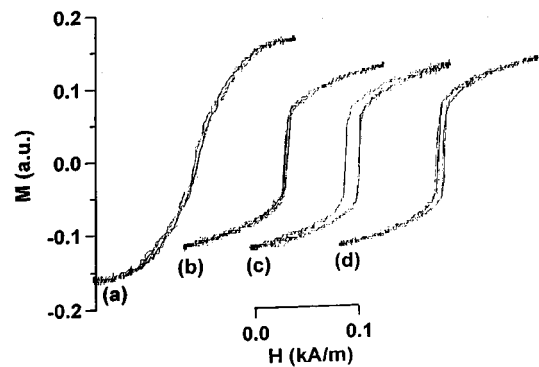


Fig. 5. Minor hysteresis loops of the sample corresponding to process shown in Figure 4: (a) $t = 0$, (b) $t = 30$ min, (c) $t = 60$ min, (d) $t = 150$ min.

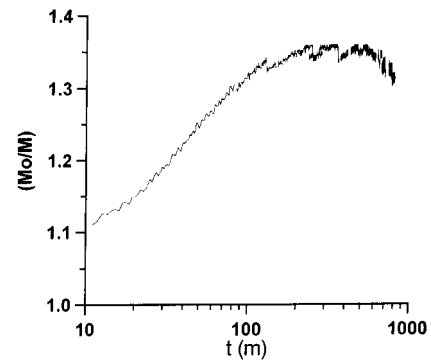


Fig. 6. $(M/M_0)_H$ ratio behaviour *versus* desorption time in a Metglas 2826MB.

5 Conclusions

In this work we have shown the direct relation between the inhomogeneity of hydrogen distribution and the induced internal stresses. It is also shown that by using an electrolytic pulsed current it is possible to obtain a very low rate of hydrogen charging. That way it is possible to obtain a higher hydrogen concentration with a very homogeneous distribution in the sample.

The variety of results published about the hydrogen effect on M_s and on magnetic properties can be explained by considering that the induced anisotropy by hydrogen charging (and so the internal stresses that in some cases drives to the sample breaking) is related to the inhomogeneity of hydrogen distribution but not to the total hydrogen concentration inside of the sample. Similar results in other materials have been obtained by different methods [8].

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