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Characterization of hydrogen in metallic glasses by the use of Hall effect measurements

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Abstract

Hall effect measurements were conducted in samples of melt spun amorphous metallic alloy ribbons with and without previous hydrogen charging. This allowed the determination of Hall coefficient, carrier mobility, carrier density and electrical conductivity. Based on these parameters, two developments were possible, the detection of amorphous hydride in a metallic glass and an alternative procedure to determine the hydrogen concentration, mobility and diffusivity in samples of this material. The values of hydrogen diffusivity determined by the proposed approach compare with those obtained by electrochemical methods. It was shown that the Hall effect measurements represent a viable and useful alternative method to characterize the hydrogen behavior in metallic glasses, being simple, precise and accurate.

Keywords: Amorphous materials; Hydrogen storage materials; Hall effect; Magnetic measurements

1. Introduction

The increasing interest in the characterization of hydrogen behavior in metals and metallic alloys is due to the well known, but not yet solved, problem of hydrogen embrittlement [1] and the modern possibilities of using hydrogen as an energy carrier in electric fuel cells systems [2]. The detection and the characterization of hydrogen properties in the structure of solid materials is a difficult issue as a consequence of its small atomic mass and number which imply that, quantitative determinations cannot be done by traditional analytic methods. These include X-ray dispersive energy and wavelength dispersive spectroscopies, Auger electron spectroscopy and Rutherford backscattering. Secondary ion mass spectroscopy (SIMS) may be used; however, this is a surface analysis method very sensitive to the sputtering mechanisms for which there is limited data availability in the literature. Recently several nuclear techniques became reliable as alternative methodologies for the quantitative hydrogen determination. An example is the elastic recoil detection analysis method (ERDA) which is used for the quantitative analysis and localization of hydrogen and its isotopes [3]. The above-mentioned methods have the inconvenience of requiring sophisticated and voluminous equipments, and laborious experimental procedures. The hydrogen permeation electrochemical test is nowadays a well established and widely used technique to determine the diffusivity, solubility and permeability of hydrogen in metallic materials.

Hall effect measurement is a well known method to characterize semiconductor materials [4]. It is less usually applied to metals due to their high conductivity that implies very small Hall voltage values and, as a consequence, poor signal to noise ratios if the experimental apparatus is not specially designed for that purpose.

In the present work the conventional Hall effect formulation, which applies to semiconductors, is modified to account for the presence of protons as current carriers in metals charged with hydrogen. In fact, in most metallic materials hydrogen is dissolved in solid solution as a proton, thus participating as a fermion in the degenerated conduction gas responsible for the electric current. The

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objective of this work is to verify the applicability of Hall effect measurements as an alternative method to current electrochemical procedures in the characterization of the hydrogen properties in amorphous metallic alloys.

2. Experimental techniques

Samples of melt spun ribbons of the amorphous metallic alloys $Fe_{40}Ni_{38}Mo_4B_{18}$ and $Ni_{81}P_{19}$, with thicknesses equal to 25 and 55 μm, respectively, and width of 25.4 mm, were used in the present work. Gaseous hydrogen charging of the samples was performed during 240 min at 90 °C and at a pressure of 2 atm, except for the $Fe_{40}Ni_{38}Mo_4B_{18}$ amorphous alloy, for which an intermediary charging time of 80 min was also used.

The Hall effect measurements were conducted at 0 °C following the Van der Pauw technique as described in the F76 ASTM standard [5]. Since the Hall voltages involved in the measurements were in the range of a few nV, the electric currents required for the experiment were obtained from a high capacity battery in order to reduce the noise associated with electronic current sources. With the same purpose, the magnetic fields necessary for the measurements were obtained from 0.5 T magnetic field density permanent magnets of NdFeB. The experimental procedure consisted of measuring the Hall voltage in hydrogen charged and uncharged samples. For the purpose of the experiments conducted in this work, the 2.5% ASTM standard criterion of error acceptance in Hall effect measurements was reduced to 1%. To calibrate the experimental apparatus, Hall effect measurements were performed in samples of 99.99% purity crystalline palladium for which the value of the Hall coefficient is available in the literature [6].

3. Results

Table 1 and Fig. 1 present the results of Hall measurements performed, respectively, in samples of hydrogen charged and uncharged $Fe_{40}Ni_{38}Mo_4B_{18}$ and $Ni_{81}P_{19}$ metallic glasses. These measurements include total carrier concentration, n_t, Hall coefficient, R_H, and total carrier mobility, μ_t. The total carrier concentration includes both, the electron and proton (hydrogen atom) concentration, except in the case of the uncharged material where it obviously refers only to the electron concentration.

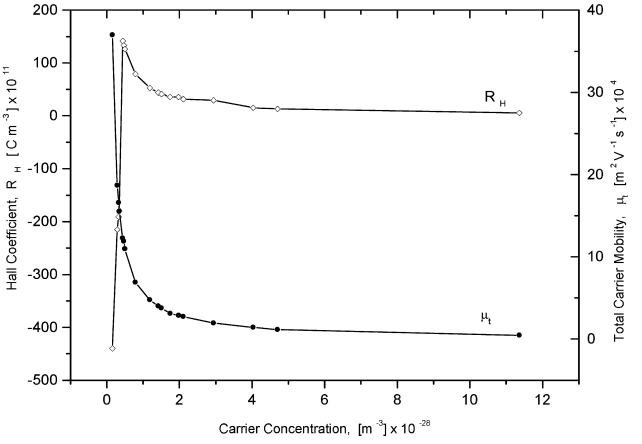

Fig. 1. Hall coefficient, R_H, and total carrier mobility, μ_t, for charged and uncharged samples of $Ni_{81}P_{19}$ metallic glass. The initial point in each curve represents the uncharged material.

4. Discussion

The Hall effect measurements in the $Fe_{40}Ni_{38}Mo_4B_{18}$ melt spun ribbon presented in Table 1 indicate that this technique may be used for the detection of hydrides, as rationalized in the following. The carrier concentration in the uncharged sample, 1.53×10^{26} m^{-3}, increases to 1.60×10^{26} m^{-3} after 80 min of hydrogen charging. This difference in carrier concentration is of the order of 4%, which is greater than the 1% experimental error, indicating that this amount of hydrogen in solid solution in the material is probably below the threshold level for hydride formation. Increasing the charging time to 240 min resulted in a decrease of 20% on the total carrier concentration. This appears to be inconsistent since, in fact, by increasing the hydrogen charging time one increases the amount of hydrogen introduced into the material. Yet, more significant is the fact that each hydrogen atom introduced in the material is ionized into a proton and an electron thus presumably further increasing the total number of charge carriers. Since this is not observed, and considering that the signal of the Hall coefficient changed from negative to

Table 1
Hall effect parameters in *H* charged and uncharged $Fe_{40}Ni_{38}Mo_4B_{18}$ melt spun ribbon

Material condition	Carrier concentration, n_t [m^{-3}]$\times10^{-27}\pm1\%$	Hall coefficient, R_H [C m^{-3}]$\times10^{11}$	Total carrier mobility, μ_t [m^2 $V^{-1}s^{-1}$]$\times10^4$
Uncharged	0.153	−4070.00	224.41
Hydrogen charged for 80 min	0.160	−3909.20	216.26
Hydrogen charged for 240 min	0.122	+5105.94	338.80

positive, this phenomenon must be explained by the transformation of free charge carriers into bound ones by the hydride formation. Indeed, it has been shown, by the use of the electrochemical hydrogen permeation technique, that the $Fe_{40}Ni_{38}Mo_4B_{18}$ metallic glass is a hydride former [7]. The Hall effect method has then proven to be useful as a simple and accurate alternative way of identifying the presence of a hydride phase in metallic glasses, even when this is made difficult by the physical and structural characteristics exhibited by the new phase that can also be amorphous, such as the matrix from which it originated.

Fig. 1 presents the Hall Effect measurements performed for the uncharged $Ni_{81}P_{19}$ metallic glass and, upon hydrogen charging, for a wide range of hydrogen concentrations, i.e., charge carrier concentrations. This is facilitated by the fact that the $Ni_{81}P_{19}$ alloy is a non-hydride former [7]. The determination of the hydrogen diffusion coefficient from this data required the derivation of a new mathematical formulation [8] for the charge carrier mechanisms in this kind of material since the known equations for semiconductor materials did not apply.

The Wiedemann–Franz Law [9] states that, for fermions, at low temperatures the relation between the thermal electronic conductivity, K_{el}, and the electric conductivity, σ, in the material is given by:

$$\frac{K_{el}}{\sigma} = \tau \frac{\pi^2 n k^2 T}{m} \frac{1}{\sigma} = LT \tag{1}$$

where, L is Lorentz's constant, n is the density of free charge carriers, k is Boltzmann's constant, T is the absolute temperature, τ is the charge free-path mean time of the carriers and m is the average mass of the charge carriers given by:

$$m = \frac{(m_p \cdot n_p + m_e \cdot n_e)}{n_t} \tag{2}$$

where $m_p = 1.672 \times 10^{-27}$ kg is the proton mass, $m_e = 9.109 \times 10^{-31}$ kg is the electron mass, n_t is the total carrier density and n_p and n_e are the densities of protons and electrons, respectively. Since the electric conductivity is given by the product of mobility by the charge density and the total density of charge carriers in the hydrogenated material, due to the ionization of hydrogen atoms entering the material, is equal to two times the density of protons plus the density of electrons initially present in the sample, τ may be obtained from Eq. (1). It can be shown that the average collision time of protons, τ_p, and of electrons, τ_e, are determined by the numerical solution of the following equations [8]:

$$\tau \cdot n_t = \tau_e \cdot n_e + \tau_p \cdot F\left(n_p + 2 \cdot \frac{\partial n}{\partial x}\right) \tag{3}$$

$$\frac{\mu_t \cdot n_t}{q} = \tau_e \cdot \frac{n_e}{m_e} + \tau_p \cdot \frac{n_p}{m_p} \cdot F + \frac{kT}{q} \cdot \frac{1}{\varepsilon_L} \cdot F\left(\frac{n_p}{V \cdot m_p} + \frac{n_{ep}}{V \cdot m_e}\right) \tag{4}$$

where μ_t is the total mobility, q is the charge density, V is the volume, n_{ep} is the concentration of electrons displaced with the protons, ε_L is the longitudinal electric field applied, $\partial n / \partial x$ is the concentration gradient in the direction of the electric field and F is a correction factor, based on the Fermi energies of the non-hydrogenated and hydrogenated samples that takes into account the displacement delay of the charge carriers due to the applied electric and magnetic fields. The protons' mobility, μ_p, is then determined by:

$$\mu_p = \tau_p \cdot \frac{q_p}{m_p} \tag{5}$$

The diffusivity of protons, D_p, is obtained by replacing this value into the simplified Nernst–Einstein equation [6]:

$$D_p = \mu_p \cdot \frac{kT}{q_p} \tag{6}$$

Fig. 2 presents a graph of proton diffusivity versus concentration. These values are consistent with the hydrogen diffusion coefficients determined by the electrochemical hydrogen permeation technique [7,8] for amorphous $Ni_{81}P_{19}$ alloy. However, another correction would still be likely to be made to correlate electromigration with diffusion under a chemical potential gradient [8]. Fig. 2 shows that the proton diffusivity increases with the proton concentration for low concentrations, indicating that deep traps are being filled up. Then, it reaches a maximum and decreases with atom fraction augmentation, because more interaction between charge carriers takes place, decreasing τ_p and consequently the mobility. This result is consistent with Kirchheim's [10] Monte Carlo simulations and experimental results on grain boundary diffusion taking into account H–H interactions. The formulation herein proposed, Eqs. (3) and (4), makes this clear by explicitly displaying the dependence of the total mobility and concentration on the charge free-path mean time. It is well

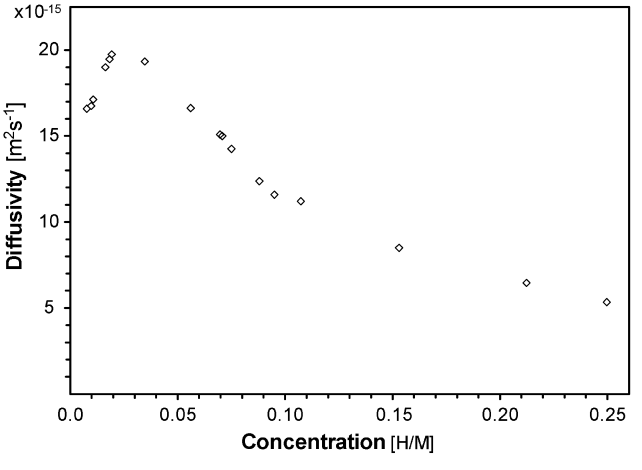

Fig. 2. Hydrogen diffusivity as a function of atom fraction concentration in the $Ni_{81}P_{19}$ melt spun ribbon.

known [11] that in disordered metals and alloys the mean free-path of charge carriers is very short, resulting in scattering events among charge carriers. It means that in the present hydrogen charged amorphous alloys, as the hydrogen concentration is increased, H–H interactions may no longer be neglected.

5. Conclusions

It was shown that the Hall effect technique is a simple, accurate and precise method to characterize the hydrogen properties in metallic glasses. It was possible to detect hydride formation upon hydrogenation of the $Fe_{40}Ni_{38}Mo_4B_{18}$ melt spun ribbon and a new mathematical formulation was used, allowing obtaining consistent values for the hydrogen diffusion coefficient in the $Ni_{81}P_{19}$ amorphous alloy, by measuring Hall effect.

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