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Effect of hydrogen on the magnetic behavior of CoFeCrSiB amorphous alloys

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Abstract Alloying with Fe caused a non-monotonic change in the soft magnetic properties of $Co_{71-X}Fe_XCr_7Si_8B_{14}$ alloys. Hydrogenation caused a progressive deterioration in the soft magnetic properties. The differences in the response of the alloys is possibly due to a non-systematic variation in the inter-atomic exchange interactions which modulates the dipole moment, and due to introduction of internal stresses on hydrogen charging.

Introduction

Amorphous alloys have been found to possess superior soft magnetic properties compared to their crystalline counterparts. Owing to their structural homogeneity, amorphous alloys also exhibit better corrosion resistance than crystalline materials. Due to these interesting properties, there have been numerous studies on different classes of amorphous alloys. Fe-based amorphous alloys exhibit high saturation induction while Co-based amorphous alloys show high permeability [1]. Iron and cobalt based amorphous alloys have received a lot of attention in the last decade as potential magnetic materials on account of their excellent soft magnetic, mechanical and chemical properties. Co–Fe systems have exceptionally high magnetic moments [2] and they can also be used in the areas of high permeability requisites.

The unique properties of amorphous alloys stem from the lack of long-range atomic order. As these alloys are amorphous, they do not exhibit magnetocrystalline anisotropy, whereas some of the alloys are extremely magnetically soft. Incorporation of hydrogen into these amorphous alloys influences the magnetic properties [3–7]. Although a few investigations have been performed to study the behavior of amorphous alloys on hydrogenation, there is lack of similar work in Co-based amorphous alloys [8, 9]. In the present work systematic studies have been done on the effect of hydrogenation on the magnetic properties of the Co–Fe–Cr–Si–B based amorphous alloy. This was motivated by an assessment of hydrogen related alteration of the magnetic properties in these alloys as well as to find out the suitability of such materials for sensors for hydrogen determination.

Experimental

Amorphous materials of nominal composition of $Co_{71-X}Fe_XCr_7Si_8B_{14}$ ($X = 0, 2, 4, 6, 8$ at%, and designated throughout the text as Fe0, Fe2, Fe4, Fe6, Fe8, respectively) prepared in the form of ribbons by rapid solidification technique were used for the experiments. The samples were prepared in an argon atmosphere. The prepared ribbons were 30 μm thick and 12 mm wide. The amorphous state was confirmed by XRD studies. The full width at half maximum (FWHM) was measured from the broad peak of the amorphous alloys. The magnetostriction values of the alloys are reported to change with Fe content from -0.8×10^{-6} for Fe = 0% to $+ 4.0 \times 10^{-6}$ for Fe = 12% [10]. Of the prepared alloys, the one with 4% Fe demonstrated nearly zero

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magnetostriction, those with lower Fe showed negative magnetostriction and those with higher Fe showed positive magnetostriction. The coercivity was calculated from the hysteresis loop measured in a quasi-dc magnetic field. The initial susceptibility was measured by arranging two balancing pick-up coils in series opposition and placing them in an Helmoltz coil. The applied field was 5 mOe (0.4 A/m) at a frequency of 1 KHz. The output voltage of the balancing coils was measured by a Lock-in amplifier. The susceptibility (χ) was calculated from the output voltage (V) using the relationship

$$V = \chi N_c A_s \omega H \chi_0, \tag{1}$$

where N_c = number of turns of the pick up coil, A_s = cross-sectional area of the sample, ω = frequency of the magnetizing field, H = magnetic field strength, χ_0 = susceptibility of air.

The electrochemical response of the five alloys were studied as a precursor to hydrogen charging. This was conducted in the hydrogen charging solution described below, using a potentiostat. 10 cm long ribbons were used to study the effect of hydrogen charging. The hydrogen charging was done electrochemically under ambient conditions for different durations in a solution of 1 N H_2SO_4 with 10 mg/l of Na_2AsO_2 added as hydrogen recombination poison. The amorphous ribbon and a platinum wire were used as the cathode and the counter electrode, respectively. The charging current density was maintained at 0.1 mA/cm^2 while the charging time was varied up to the time when there was significant deterioration in the soft magnetic property (as measured by a decrease in susceptibility and a corresponding increase in coercivity).

Results and discussion

The electrochemical behavior for the alloys in a solution of 1 N H_2SO_4 with 10 mg/l of Na_2AsO_2 is shown in Fig. 1. With the exception of the alloy having no Fe (Co = 71%), the response of the amorphous alloys were remarkably similar in the sulfuric acid solution. In the Fe containing alloy the electrochemical response in sulfuric acid seems to be dictated by protective layer formation at the higher anodic overpotentials. More relevant to the study is that there seems to be not much difference in the cathodic regime for the different alloys; that is, the hydrogen reduction reaction has similar reaction kinetics, irrespective of the Fe content for these alloys.

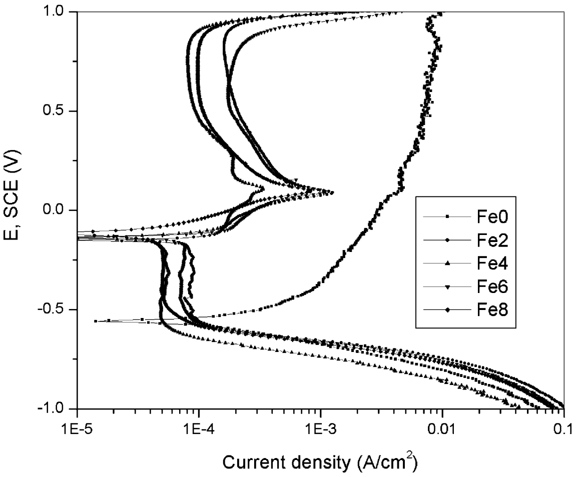

Fig. 1 Electrochemical response of the amorphous alloys in 1 N H_2SO_4 with 10 mg/l of Na_2AsO_2

In their as-received state, the susceptibility varies between 2.43 × 10^4 and 5.2 × 10^4 for the different alloys with no specific trend with respect to the Fe content, as shown in Table 1. The same is true for the as-received coercivity values. Hydrogenation of the samples caused a significant change in their respective hysterisis loops. This is shown for one of the alloys in Fig. 2. It is evident that there was significant change in the coercivity (H_c) of the sample on hydrogenation. The variation in the susceptibility and coercivity of the alloys with hydrogen charging for different times is shown in Figs. 3 and 4, respectively. Prolonged hydrogenation causes a systematic decrease in the susceptibility and increase in the coercivity of the alloys, that is, there is a progressive deterioration in their soft magnetic properties. This deterioration varies in degree depending on the alloy concentration. The deterioration when expressed as percentage change is more for the lower iron content alloys. Changes in coercivity are slower in the higher Fe content alloys.

The non-monotonic variation in magnetic property of the tested alloys with Fe content is possibly due to two reasons. Change in the inter-atomic separation and electron filling brought about by Fe addition to Co in their respective valence shells causes a change in the magnetic moments due to the altered inter-atomic exchange interactions; this is not necessarily a monotonic function of alloy composition. This effect is best substantiated in the saturation magnetization values for the alloys as shown in Fig. 5, which show non-systematic variation with Fe content. Additionally, the degree of disorder of the alloys in

Table 1 Susceptibility and coercivity of the as-received amorphous alloys

Alloy–Fe content	Susceptibility (× 10^4)	Coercivity (A/m)
0	2.68	70
2	5.20	46
4	2.88	44
6	2.45	52
8	2.43	36

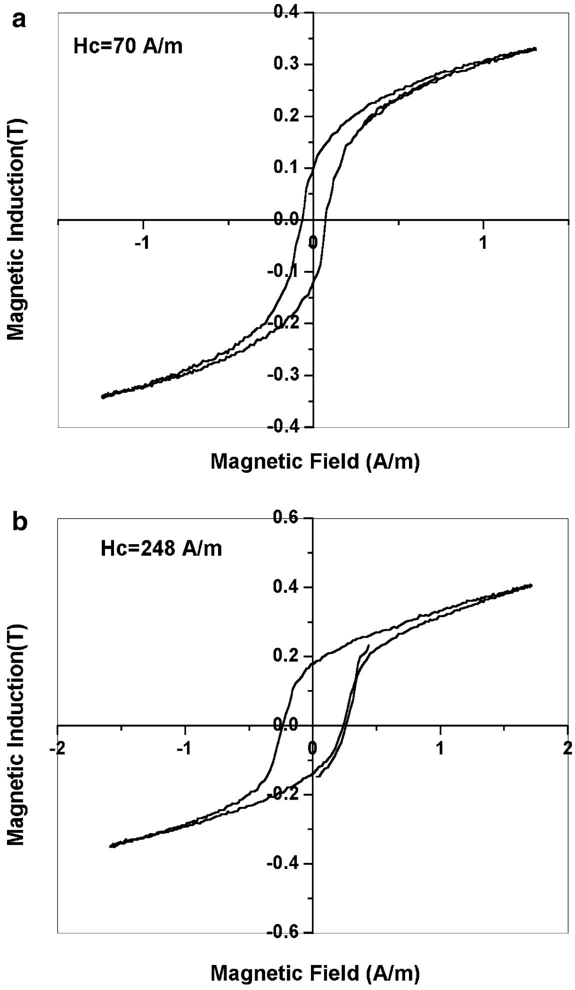

Fig. 2 Change in the low-field magnetic response on hydrogenation. (**a**) As-received alloy (Fe = 0%), (**b**) same alloy after hydrogenation

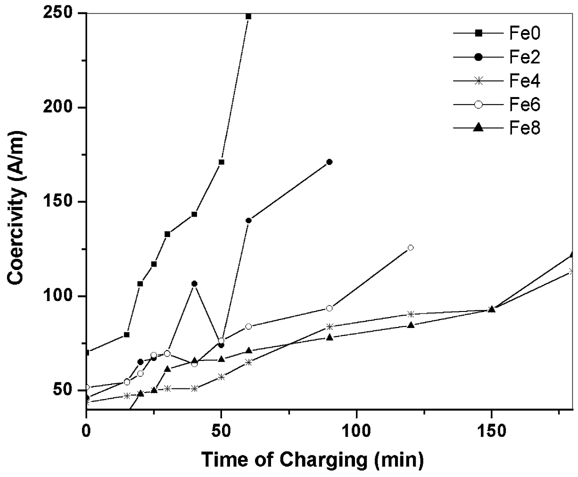

Fig. 4 Dependence of coercivity on the duration of hydrogen charging at a current density of 0.1 mA/cm^2

their amorphous state is different. This can be compared from the FWHM values of the alloys, which are also indicated in Fig. 5. These variations in the topological disordering amongst the alloys is also responsible for the fluctuations in exchange interactions.

The hydrogen effect is due to the following possible reasons. One possibility is the introduction of stresses in the amorphous matrix due to the positive molar volume of hydrogen or reorientation of existing residual stresses [3, 6, 11, 12]. This effect would normally be a function of the sign and magnitude of the magnetostriction constant of the alloy. For instance, the closer the magnetostriction is to zero, the less should be the stress effects of hydrogen provided the stress induced is isotropic. In our studies we have observed that the hydrogen induced changes (change in coercivity, especially) in soft magnetic properties is considerably less in the alloy containing 4% Fe, which has nearly zero magnetostriction. This supports the theory of stress introduction due to hydrogen. Another possible effect is due to the interaction of the hydrogen with the valence shell electrons of the host alloy components

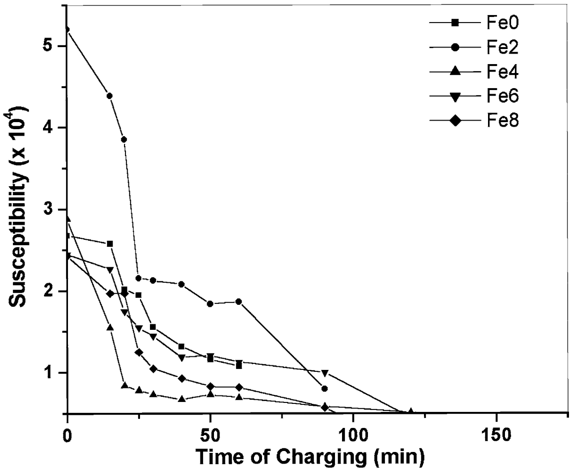

Fig. 3 Dependence of AC susceptibility on the duration of hydrogen charging at a current density of 0.1 mA/cm^2

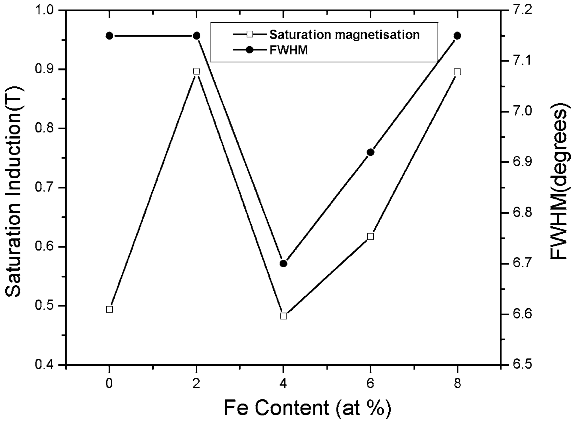

Fig. 5 Variation of saturation magnetization and the FWHM of the alloys with Fe content

specifically Fe and Co, leading to a decrease in the magnetic moment. The difference in the behavior of the alloys could be either due to different amounts of hydrogen absorption dependent on the Fe content, or due to the two effects mentioned earlier where alloy composition determines the corresponding hydrogen interaction even if the same amount of hydrogen is absorbed. It has been indicated that the as-received alloys show non-systematic change in magnetic properties with alloy composition. Therefore, H addition superposes on this altered interaction by donating its own electrons and causing further changes in the inter-atomic interactions and therefore on the dipole moments.

This investigation shows that the hydrogen effect on magnetic properties is not a monotonic function of the alloy composition. The hydrogen effect cannot be attributed to increased hydrogen absorption as is evident from Fig. 1. The amount of hydrogen surface coverage is proportional to the cathodic overpotential and at a current density of 0.1 mA/cm^2, the overpotentials for the different alloys are very similar as they practically overlap. The Hydrogen effect is most likely due to introduction of internal stresses, and due to the changes in the inter-atomic interactions. A detailed study of the change in the inter-atomic interactions with alloy content and with H ingress is required to explain the observed differences, and is being planned.

Conclusions

Alloying with Fe caused a non-monotonic change in the soft magnetic properties of $Co_{71-X}Fe_XCr_7Si_8B_{14}$ alloys. Hydrogenation of the alloys with different hydrogen content caused a progressive decrease in the magnetic properties. The different alloys did not show very different hydrogen evolution characteristics although there was some difference in their electrochemical response in the anodic regimes. The differences in the magnetic behavior of the different alloys is possibly due to a non-systematic variation in the inter-atomic interactions which modulates the dipole moment, on hydrogen charging, and due to introduction of internal stresses.

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