

## AGING DEPENDENCE OF MAGNETIC PROPERTIES OF AMORPHOUS Co-Si-B ALLOYS

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In this paper, we report results on the examination of the aging dependence of the magnetic properties of amorphous Co-Si-B ribbons, wires and glass-covered wires. The coercive field,  $H_c$ , and the remanence,  $B_r$ , were investigated by using a stationary – coil magnetometer and a digital flux integrator. Generally, these properties are gradually stabilized to steady state values with respect to time. The aging process was based on chemical etching and oxidation, showing that the magnetic properties are stabilized after introducing the sample into  $H_2SO_4$  solution with  $pH=2$  for 2 hours and consequent oxidation at  $350^\circ C$  in air for 2 hours.

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### 1. Introduction

The dependence of the magnetic properties of the recently developed amorphous magnetic materials, such as ribbons, wires and glass covered wires on the aging process is important in relation to their technological applications [1-5]. It is not very clear how the aging process determines these properties because of the metastable character of their structure. It can be said that the aging process results in gradually stabilized values of magnetic properties. Thus, any aging acceleration process targets to the stabilization of the examined properties to some steady state values.

We have decided to use some rather traditional techniques such as chemical etching and thermal oxidation in order to accelerate the aging process and simulate long periods of time in air or harsh environments. Bearing in mind applications of these materials like transformers, electrical machines and transducers, it is critical to determine the aging dependence of the B-H loop as well as the  $\lambda$ -H loop, in order to design properly the above-mentioned devices.

In this work we report our results on the aging dependence of the B-H loop, measuring the coercive field,  $H_c$ , and remanence,  $B_r$ . We firstly introduce our new B-H loop based on ac-magnetometry and digital integration techniques, able to perform parametric measurements in a wide frequency range. Then, we illustrate our results on aging dependence, concluding that coercivity and remanence are stabilized after introducing the sample into  $H_2SO_4$  solution with  $pH=2$  for 2 hours and consequent oxidation at  $350^\circ C$  in air for 2 hours.

### 2. Experimental set-up

In order to measure the B-H loop and especially the coercivity and the remanence of each magnetic sample we have developed a stationary – coil magnetometer. The reason that we have been chosen to build a stationary – coil magnetometer is that such a device is simple and inexpensive setup in comparison with VCM and VSM [6]. Additionally, the stationary coil – magnetometer offers acceptable levels of precision for the low field magnetic measurements with respect to VCM and VSM. Moreover the stationary – coil magnetometer is able to determine the dependence of B-H loop on the exciting frequency and applied tensile-torsional stress.

The schematic diagram of the experimental set-up used for the determination of the B-H loop is illustrated in Fig. 1. An a.c. current generator (1) is used to generate a sinusoidal current. The current frequency may vary from a few mHz to a few thousands kHz. This current excites a relatively thin four layer and 658 turns solenoid (2) made by winding 1mm enameled Cu wire. The length and the diameter of the solenoid are 16 cm and 12.5 cm, respectively. Therefore the field in the center of the exciting coil is approximately given by:

$$H(t) = \frac{N}{\sqrt{D^2 + L^2}} \cdot I(t) = 324I(t)A/m,$$

where N is the number of turns of the Cu wire, D is the diameter of the solenoid, L its length and I(t) the current passing through the solenoid. This solenoid is in series with a resistance (3) of 1.5  $\Omega$ . The two ends of the resistance are connected to the channel A of a digital oscilloscope (5) in order to measure the output voltage across the resistance  $V_A(t)$ . A 2 cm long, 2 mm in diameter, 2000 turns pick-up coil (4) made from 0.1 mm enameled Cu wire is placed in the center of the exciting solenoid (2). The uncertainty of misplacement of the pick-up coil with respect to the excitation solenoid is  $\pm 0.1$ mm due to the co-axial fixing tubes. The induced output voltage on the pick-up coil is driven to the channel B of the digital oscilloscope (5).

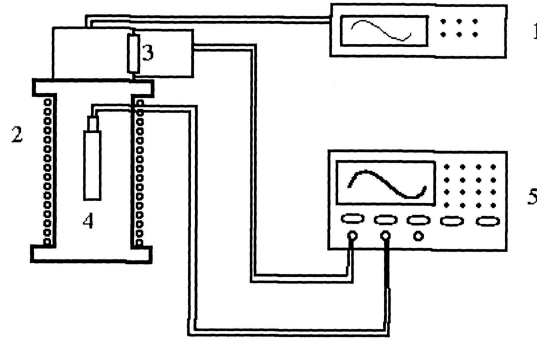


Fig. 1. The experimental set-up. (1) AC current generator, (2) exciting coil, (3) resistance 1.5  $\Omega$ , (4) pick-up coil, (5) digital oscilloscope.

The data collected by the digital oscilloscope are stored to a PC where they are digitally processed. The applied field H(t) is given by:

$$H(t) = \frac{N}{\sqrt{D^2 + L^2}} \cdot \frac{V_A(t)}{R}$$

Data collected on channel B determine the first derivative of the magnetic induction B(t), which is approximately given by:

$$B(t) = -\frac{1}{NA} \int V_B dt,$$

where N and A are the number of turns of the pick-up coil and the cross section of the measured magnetic sample, respectively. The offset value of the digital read-out is determined without magnetic material within the pick-up coil and is subsequently subtracted during the software integrating process. The calibration of the instrument was realized by using polycrystalline Ni wires.

Experimental results on amorphous FeSiB as-cast wire using this set-up are in good agreement with the data reported previously in literature [7, 8]. Furthermore, inter-laboratory comparison tests have been performed using an ac-differential magnetometer from the Institute of Technical Physics, Iasi Romania, and the results being in good agreement with our results.

### 3. Results and discussion

We tested  $\text{Co}_{77}\text{Si}_8\text{B}_{15}$  alloys in the shape of ribbons having width of 0.8 mm and 25  $\mu\text{m}$  thickness, wires with diameters of 110  $\mu\text{m}$  and glass covered wires having 45  $\mu\text{m}$  diameter including glass coat. For calibration we used FeSiB wires 135  $\mu\text{m}$  in diameter.

We tested the sample in the as-cast state, after chemical etching and after oxidation. The aging process taking place within the material was simulated. The chemical etching was carried out by introducing the sample into  $H_2SO_4$  solution with  $pH = 2$  for 10, 30, 60, 120 and 150 minutes. The oxidation process was realized by setting the as-cast and the chemical etched samples at  $350^\circ C$  in an open electric furnace for 10, 30, 60, 120 and 150 minutes. Three samples of each kind were tested several times in order to have a relative small uncertainty on the determination of the coercivity and remanence.

Figs. 2 and 3 illustrate the dependence of the coercive field,  $H_c$ , and the remanence,  $B_r$ , on the aging process. From these results it can be seen that  $H_c$  and  $B_r$  are stabilized after 120 minutes of chemical etching and 120 minutes air oxidation.

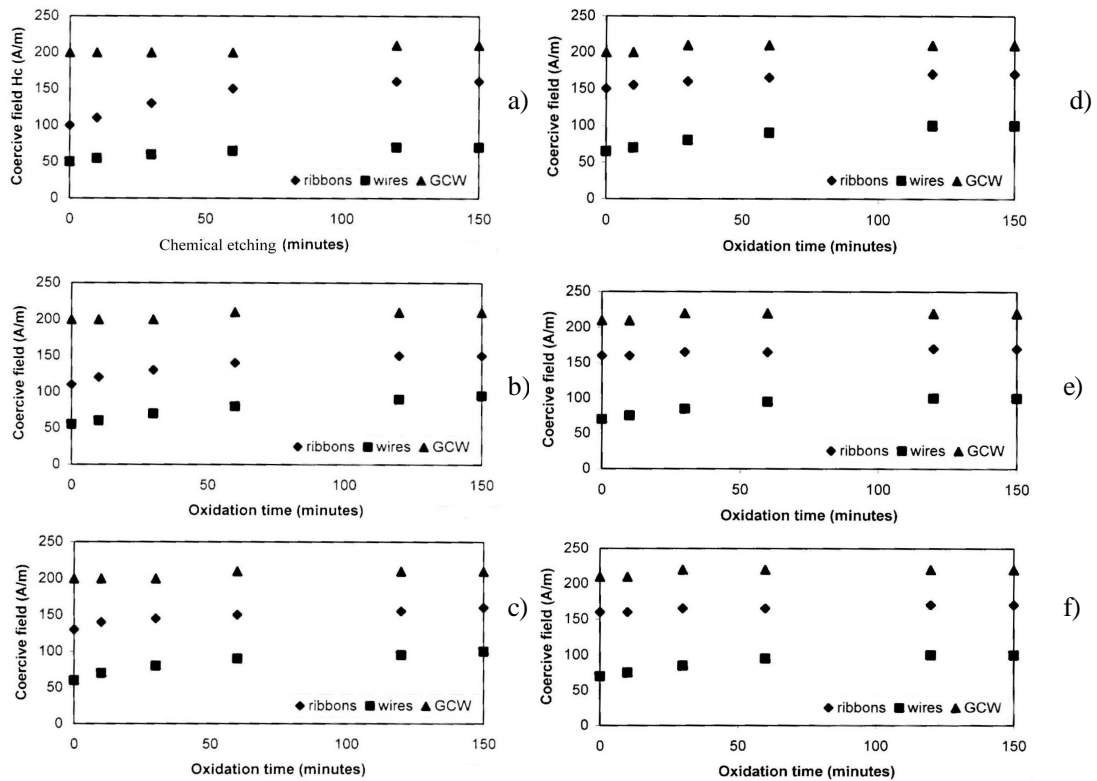
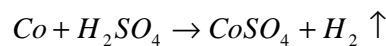
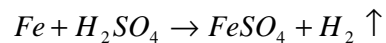
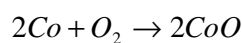
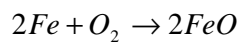


Fig. 2. Dependence of the coercive field,  $H_c$ , of CoSiB ribbons, wires and glass covered wires on aging process: (a) after chemical etching; after oxidation of the chemical etched samples for (b) 10 minutes, (c) 30 minutes, (d) 60 minutes, (e) 120, (f) 150 minutes.

$H_2SO_4$  reacts only with the metallic component from each sample. Therefore the reactions that took place are the following:



In both cases, one of the products resulting after reaction is a salt, which lay on the metal surface. The oxygen from the air inside the electric furnace reacts with the metallic element in a similar way as  $H_2SO_4$ . The products of these reactions are oxides,  $CoO$  and  $FeO$ , which remain on the surface of the sample:



This is in agreement with the increase of the surface DC resistance of the aged samples. In all cases, the quantity of salt and oxide on the sample surface increases in time and is stabilized after a time. The presence of salts and oxides can be observed in Fig. 4. In all cases, after two hours of treatment, the quantity of salt on the surface does not grow anymore. Therefore, the main conclusion of the presented experimental results is that the aging effect on the coercivity and remanence could be determined with respect to the stabilization of  $H_c$  and  $B_r$  after chemical etching in  $H_2SO_4$  solution with  $pH = 2$  for 2 hours and oxidation in air at  $350^\circ C$  for 2 hours.

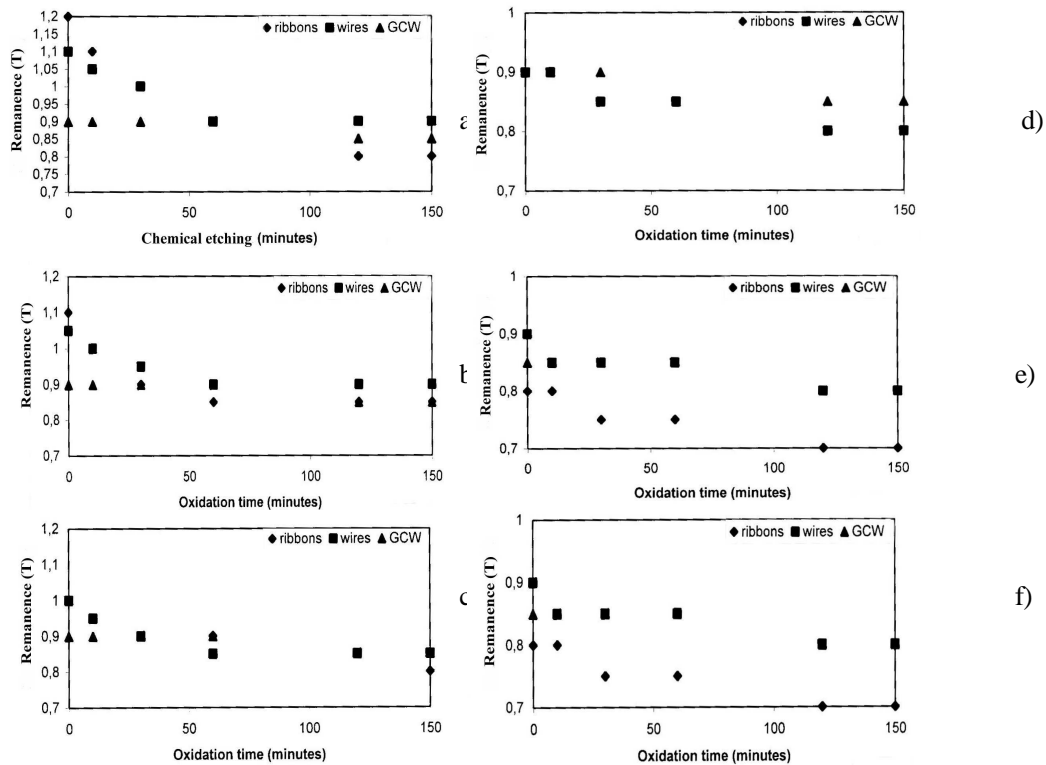


Fig. 3. Dependence of the remanence,  $B_r$ , of CoSiB ribbons, wires and glass covered wires on aging process: (a) after chemical etching; after oxidation of the chemical etched samples for (b) 10 minutes, (c) 30 minutes, (d) 60 minutes, (e) 120, (f) 150 minutes

It is expected that the presence of salts and oxides should generate surface stresses, which affect the amplitudes of coercivity and remanence. Indeed, the increase of  $H_c$  and decrease of  $B_r$  as well as the increase of the surface DC resistance can be explained by that. The reason for such behaviour is that the spots on the surface, where the concentration of the aging products is large, play the role of pinning centres. The larger number of spots laying on the samples surface, the greater is the effect leading to the domain wall motion.

The stress caused by the aging products was observed for both FeSiB and CoSiB samples. In fact, the magnetic moments of the samples tend to re-orientate with respect to the stress direction, which is along the length of the sample. Such orientation of the magnetic moments results in the increase of  $B_r$  of FeSiB samples and the decrease of  $B_r$  of CoSiB samples. This is explained by the different signs of magnetostriction in these two alloys: positive for FeSiB samples and negative for CoSiB samples.

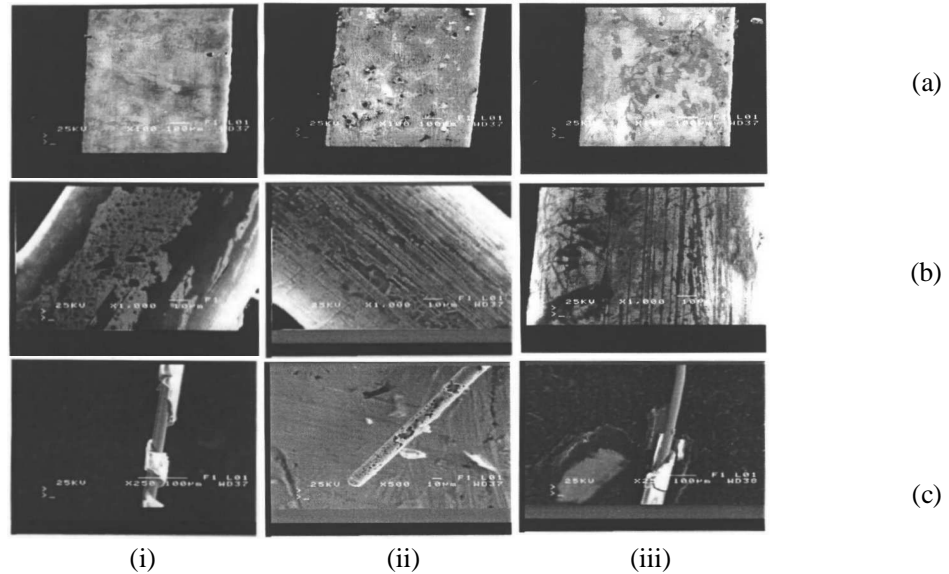


Fig. 4. SEM micrographs of. CoSiB ribbons (a), wires (b), glass covered wires (c) in the as-cast state (i); after chemical etching for 120 minutes (ii) and after chemical etching for 120 minutes and oxidation.

It is known that the coercivity ( $H_c$ ) and the diameter ( $d$ ) of the magnetic domain are connected [9] by the following formula:

$$H_c \cdot d = c$$

where  $c$  is a constant. We consider that the average diameter of the magnetic domains of CoSiB and FeSiB samples is approximately equal to 10 - 15  $\mu\text{m}$ . Therefore using the mathematic formula stated above and the B-H loop measurements, we calculated the size of the magnetic domains of the samples that have suffered aging treatments. The calculation of the change of the size of the magnetic domains in CoSiB wires, ribbons and FeSiB wires is illustrated in Fig. 5.

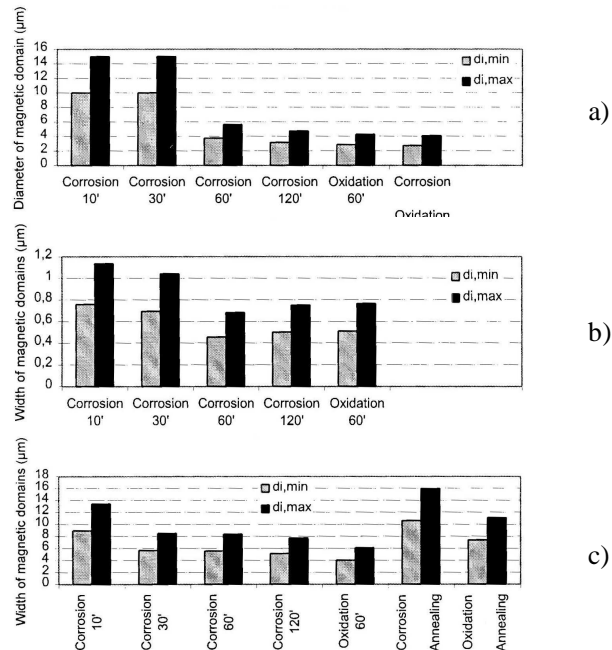


Fig. 5. Calculation of the magnetic domain area for: (a) CoSiB wires, (b) CoSiB ribbons, (c) FeSiB wires.

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