Journal of Optoelectronics and Advanced Materials Vol. 5, No. 1, March 2003, p. 245 - 250

# STRUCTURAL RELAXATION IN $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ AMORPHOUS ALLOY

I. Mihalca*, A. Ercuta[a]

University "Politehnica", Physics Department, 1 P-ta Regina Maria, 1900 Timisoara, Romania
[a]West University, Faculty of Physics, 4 V. Parvan Bul., 1900 Timisoara, Romania

The changes in the Curie temperature and magnetostriction subsequent to structural relaxation by isothermally annealing amorphous ribbons of nominal composition $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ were examined. The alloy is low magnetostrictive in both native and relaxed states, but significant enhancement, from 0.5 ppm to 10.4 ppm, of the saturation magnetostriction coefficient was observed. The relaxation was attributed to free volumes annealing out and short range order changes, both topological and chemical. A value ~ 0.85 eV of the effective activation energy resulted from the analysis of the process kinetics.

(Received January 16, 2003; accepted March 12, 2003)

*Keywords*: Ferromagnetic amorphous alloys, Curie temperature, Magnetostriction, Structure relaxation kinetics, Effective activation energy

## 1. Introduction

The structure relaxation induced by annealing in ferromagnetic amorphous alloys is generally accompanied by changes in some structure-sensitive physical properties as magnetic susceptibility, Curie temperature, coercivity, magnetostriction, electrical resistivity, etc., strongly depending on both annealing temperature and duration [1-3]. The structural processes, which are responsible for these changes, either reversible or irreversible were observed within a large thermal range, from room temperature up to crystallization; the associated activation energy spectrum is continuous [4], usually between 0.5 eV and 2.5 eV [5-8]. The reversible relaxation processes were attributed to the changes in chemical short range order [CSRO] while the irreversible ones, mainly involve topological short range order [TSRO] changes [7,8]. Both magnetostriction constant ($\lambda_S$) and Curie temperature ($T_C$) of the amorphous alloys strongly depend on their chemical composition; the reader may find a synthetic review on the subject in ref. [9]. Inomata et al. [10] show that small additions of elements like Mo, Cr or Nb to Fe-based amorphous alloys lead to a decrease of both $\lambda_S$ and $T_C$. Significant changes, subsequent to structure relaxation, in these physical parameters were also observed [11-16]. Thus, Gibbs [14] reported, via $\lambda_S$ measurements, normal kinetics of thermally activated relaxation in amorphous $Fe_{40}Ni_{40}B_{20}$; he found that the maximum modification in saturation magnetostriction does not depend on the annealing tempetature ($T_a$) within the explored range (250 °C-350 °C). For $\lambda_S$ measurements, Dominguez et al. [15], reported both normal and anomalous (i.e. showing a maximum) kinetics of the structural relaxation by electric current annealing of the $(Co_{0.95}Fe_{0.05})_{70}Si_{12}B_8$ amorphous alloy.

Though the litterature contains several reports (e.g. [17-19]) on comparative studies regarding joint examination of the structure relaxation by different methods, the problem of structural sensitivity as exhibited by the different physical quantities used in measurements, still remains open. The present work examines the extent to which the structural relaxation in amorphous $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ alloy, as induced by isothermal annealing within moderate temperature range (300 °C - 360 °C) is reflected in $T_C$ and $\lambda_S$ changes; the microscopic mechanisms responsible for the relaxation process

* Corresponding author: imihalca@etv.utt.ro

and the associated effective activation energy ($E_A$) were determined from the $T_C$ dependence on the annealing time ($t_a$).

## 2. Experiment

Samples 120 mm long were cut from amorphous ribbons of $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ nominal composition, 2 mm width and 30 μm thicknes, manufactured by the single-roller technique. The amorphous nature of the as-quenched alloy was confirmed by X-ray diffraction, Mössbauer spectroscopy and the crystallization temperature ($T_x$ = 540 ºC) was determined by differential thermal analysis at 15 ºC/min. heating rate.

The experimental setup schematiclly drawn in Fig. 1 was used to examine the magnetic and magnetoelastic behaviour of the samples in different structural states (i.e. as-quenched and annealed, respectively). Performing 12 bit resolution data acquisition on a computer, magnetic hysteresis loops and M(T) records were carried out; in addition, the fundamental magnetization curves were obtained by direct reading the display of two digital voltmeters (0.1 % precision).

From the magnetization vs. temperature records (with the sample reaching technical saturation) the Curie temperature was evaluated numerically using the classical "$M^2$ " method.

The field dependence of the linear magnetostriction examined by means of the Villari effect.

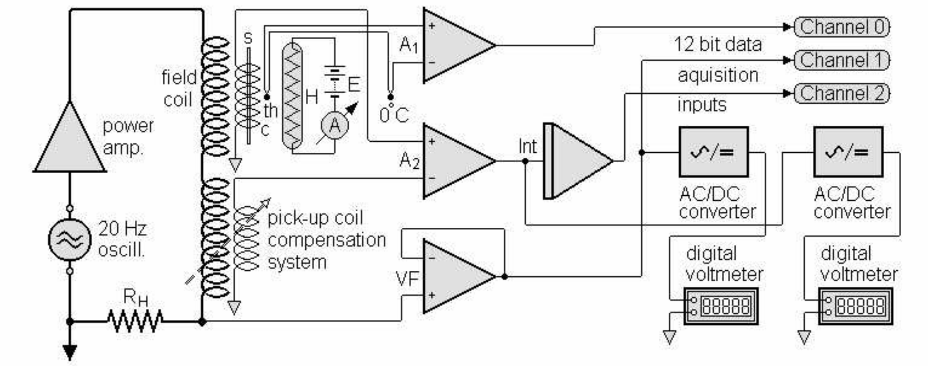


Fig. 1. A schematic drawing of the experimental setup: a very low distortion power generator (oscillator plus power amplifier) was used to produce a 20 Hz sinewave magnetic field, a calibrated resistor ($R_H$=10.0 Ω) provided a voltage drop proportional to the instant magnetic fieldstrength, a K-type thermocouple (th) was used for the temperature measurement and a non-inductive resistor (H), biased by a stabilized voltage supply (E), enabled the sample (s) heating within the pick-up coil (c). $A_1$ and $A_2$ are precision instrumentation amplifiers (AD-521, Analog Devices) of appropriately set gains, Int. is an op-amp (OP-50, PMI) based precision integrator and VF is an op-amp based (LM-108, National Semicond.) voltage follower. The non-linearity of the AC/DC converters was less than 0.2 %. The compensation system for the air flux effect in the pick-up coil mainly includes a trimmable air cored mutual inductance.

Isothermal annealing was carried out on samples taken from the same amorphous ribbon at $T_a$=300 ºC, 320 ºC and 360 ºC, in vacuum, using a cylindrical non-inductive electric furnace.

## 3. Results and discussion

The effect of a relatively small longitudinal tension, one order of magnitude lower than the average internal stress ($\langle\sigma_i\rangle$~30 MPa,) usually observed in the as-quenched amorphous alloys [20], on the magnetic behaviour of the examined composition is illustrated in Fig. 2, where the hysteresis loops of the sample in the as-quenched (Fig. 2a) and annealed (Fig. 2b) states are plotted.

The important enhancement observed in both magnetization swing and magnetoelastic response of the annealed sample clearly suggests domain wall depinning by structure relaxation.

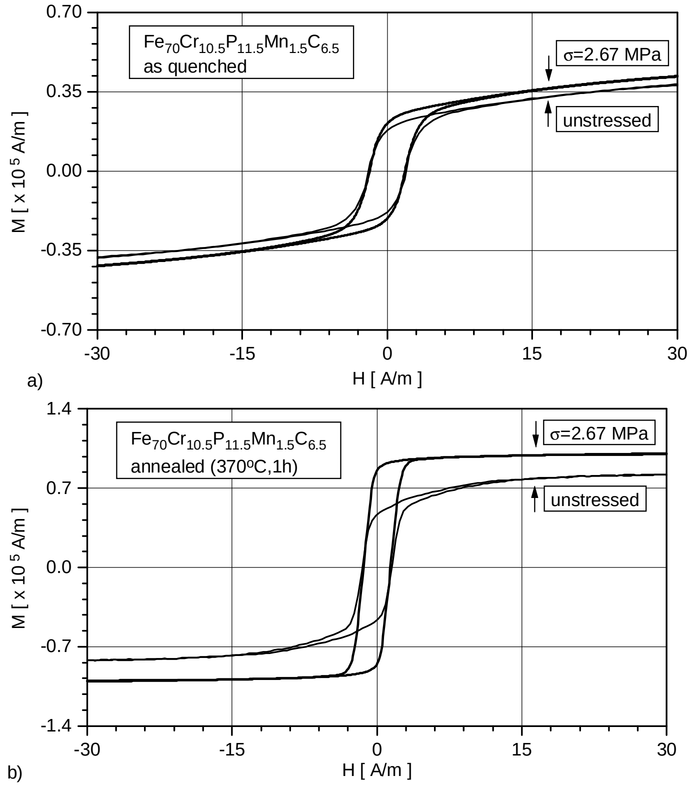


Fig. 2. The effect of the elastic stress (extension) on the magnetic behaviour of the amorphous $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ alloy: a) in the as - quenched state; b) after annealing at 370 $^o$ C for 1 hour.

The structure relaxation kinetics was examinned by $T_C$ changes (from the value $T_{C.O}$ = 56 °C in the as-quenched state) with the isothermal annealing time ($t_a$); in Fig. 3 the variations $\Delta T_C(t_a) = T_C(t_a) - T_{C.O}$ are plotted.

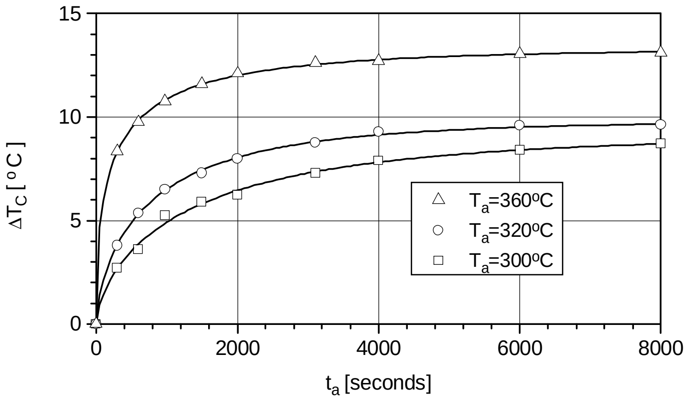


Fig. 3. The Curie temperature evolution wth the isothermal annealing time ($t_a$) with the amorphous $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ alloy.

A normal kinetics may be observed in the explored range of annealing temperatures; the saturation value $\Delta T_{C,max}$ that was reached after $t_a$ exceeding $10^4$ s is an increasing function of $T_a$; a maximum relative $T_C$ change of ~ 4% resulted for $T_A$ = 360 ºC.

The kinetics analysis based on the Kohlrausch-Williams-Watts model [6, 21]

$$\Delta T_C(t_a) = \Delta T_{C,\max}\left[1 - \exp\left(-(t/\tau)^{\beta}\right)\right] \tag{1}$$

where $\tau$ is the effective relaxation time and $\beta$ is a parameter representing the direct measure of the width of the activation energy spectrum. From fitting the experimental data, values of $\beta$ between 0.45 to 0.65 resulted. The effective relaxation time ($\tau$) can be assumed to obey an Arrhenius-type law:

$$\tau^{-1}(T_a) = \nu_{o,\,eff}\exp\left(-E_A/k_B T_a\right) \tag{2}$$

where the parameter $\nu_{o,\,eff}$ is the equivalent of the attempt frequency and $E_A$ is the effective activation energy. From the Arrhenius plot, the values $1.96 \times 10^4$ $s^{-1}$ for $\nu_{o,\,eff}$ and 0.85 eV for $E_A$ resulted.

Dong et al. [5], using single-Debye relaxation function in relaxation kinetics studies via $H_C$ measurements on amorphous $Co_{58}Ni_{10}Fe_5Si_{11}B_{16}$ have obtained $\nu_o = 9.6 \times 10^4$ $s^{-1}$, a value which is comparable as order of magnitude with $\nu_{o,eff}$ found in our experiments. According to Kronmuller et al. [21], the structure relaxation can be attributed to free volumes annealing out and to the accompaning CSRO changes.

The anneal-induced magnetostriction changes were evaluated using a method based on the Villari effect [23]. It consists in measuring the "magnetoelastic susceptibility":

$$\eta = \eta(H,\sigma) = (\partial M/\partial\sigma)_H \tag{3}$$

where H and $\sigma$ are the applied magnetic field and elastic stress, respectively.

The determination of $\eta(H,\sigma)$ was carried out by tracing the fundamental curves at constant tension; in Figs. 4 and 5 some examples are given with the sample in the as-quenched and annealed states, respectively, clearly showing the effect of the structure relaxation by annealing.

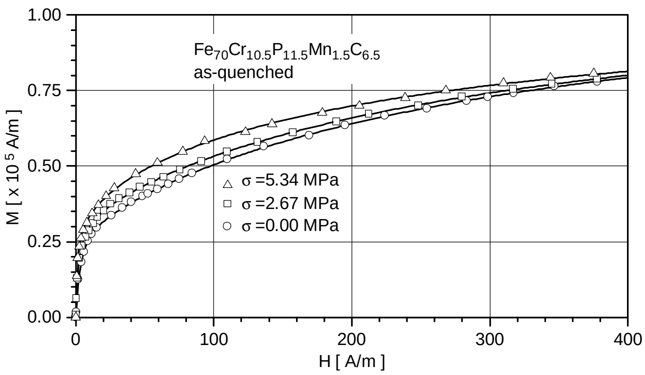


Fig. 4. The effect of longitudinal extension on the magnetization curve (the Villari effect) of the amorphous $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ alloy in the as-quenched state.

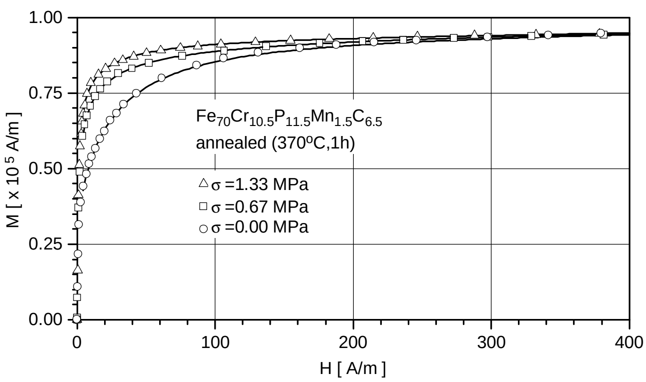


Fig. 5. The effect of longitudinal extension on the magnetization curve (the Villari effect) of the amorphous $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ alloy after annealing at 370 $^o$ C for 1 hour.

If the applied stress is sufficiently small that its effect on the magnetization is reversible, simple alculations lead to the field strength dependence of the magnetostriction [24]:

$$\lambda(H) = \mu_0 \lim_{\sigma \to 0} \int_0^H \eta(H, \sigma)\, dH \tag{4}$$

The "vanishing stress conditions" ($\sigma \to 0$) were imposed by the magnetic flux measurement resolution of the magnetization channel ($A_2$ +Int, Fig. 1) and correspond to $\sigma$ = 2.67 MPa and $\sigma$ = 0.67 MPa for the as-quenched and the annealed states, respectively.

In Fig. 6 the field dependence of the magnetostrictive strain is plotted:

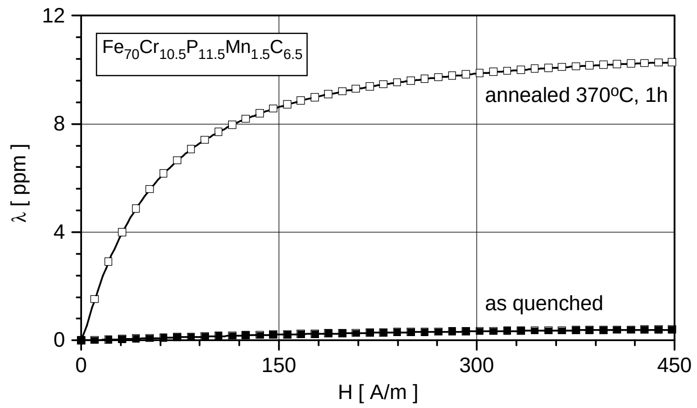


Fig. 6. The field dependence on the linear magnetostriction of the amorphous $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ alloy. a) in the as - quenched state and b) after annealing at 370 °C for 1 hour.

A significant increase, from 0.5 ppm to 10.4 ppm, of $\lambda_S$ was detected. For completeness' sake, in Table 1 values of the relative changes $\Delta\lambda_S/\lambda_S$ in some amorphous alloys are summarized.

Table 1. Relative $\lambda_S$ change as an effect of isothermal annealing in some amorphous alloys.

| Alloy | $\Delta\lambda_S/\lambda_S$ | Annealing conditions | Reference |
|---|---|---|---|
| $Fe_{40}Ni_{40}B_{20}$ ($\lambda_{S,\text{ as quenched}} = 13 \cdot 10^{-6}$) | ~1.3 | isothermal, $T_a$=350ºC, $t_a$=10 min. | [14] |
| $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ ($\lambda_{S,\text{ as quenched}} = 0.2 \cdot 10^{-6}$) | ~20 | isothermal, $T_a$=370ºC, $t_a$=60 min. | this paper |
| $Co_{66.5}Fe_{3.5}Si_{12}B_{18}$ ($\lambda_{S,\text{ as quenched}} = -0.6 \cdot 10^{-6}$) | ~50 | isothermal, $T_a$=340ºC, $t_a$=60 min. | [15] |

One may note that the low magnetostrictive compositions exhibit larger changes as an effect of anneal-induced structure relaxation.

## 4. Conclusions

The structure relaxation activated by isothermal annealing in the amorphous $Fe_{70}Cr_{10.5}P_{11.5}Mn_{1.5}C_{6.5}$ alloy was investigated by Curie temperature and magnetostriction measurements. The examined composition exhibits moderate $T_C$ and low magnetostriction in both native and relaxed states; however, the two measured physical parameters proved to be sensitive to the relaxation process. The observed changes in $T_C$ allowed the annealing kinetics study, leading to of the identification mechanism of relaxation microscopic (free volumes annealing out and CSRO changes) and associated activation energy determination ($E_A$ = 0.85 eV).

## References


[1] T. Egami, Ann. N. Y. Acad. Sci. **371**, 238 (1981).
[2] H. Kronmuller, N. Moser, F. Rettenmeier, I.E.E.E. Trans. Magn. **20** (5), 1388 (1984).
[3] A. L. Greer, J. A. Leake, J. Non-Cryst. Solids **33**, 29 (1979).
[4] M. R. J. Gibbs, J. E. Evetts, J. A. Leake, J. Mat. Sci. **18**, 278 (1983).
[5] X. Z. Dong, W. Fernenghel, H. Kronmuller, Appl. Phys. **A28**, 103 (1982).
[6] P. Kruger, L. Lempen, H. Neuhauser, Key Eng. Mat. **81-83**, 555 (1993).
[7] H. Q. Guo, W. Fernengel, A. Hoffmann, H. Kronmuller, I.E.E.E. Trans. Magn. **20**(5), 1394 (1984).
[8] A. van den Beukel, J. Non-Cryst. Solids **83**, 134 (1986).
[9] K. Handrich, S. Kobe, Amorphe Ferro- und Ferrimagnetika, (Akademie-Verlag Berlin, 1980).
[10] K. Inomata, T. Sava, M. Hasegawa, J. Appl. Phys. **57**, 3582 (1985).
[11] K. Inomata, M. Hasegawa, T. Kobayashi, T. Sawa, J. Appl. Phys. **54** (11), 6553 (1983).
[12] J. M. Barandiaran, A. Hernando, V. Madurga, O. V. Nielsen, M. Vasquez, M. Vasquez-Lopez, Phys. Rev. B **35**, 5066 (1987).
[13] V. Madurga, J. M. Barandiaran, M. Vasquez, O. V. Nielsen, A. Hernando, J. Appl. Phys. **61**, 3228 (1987).
[14] M. R. J. Gibbs, Proc. 5$^{th}$ Conf. Physics of Magn. Mater., J. W. Gutowski, M. Gutowski, H. K. Lakowicz, H. Szymczak Eds., (World Scientific, Singapore, 1990), p. 242.
[15] L. Dominguez, J. M. Blanco, K. Kulakowski, J. Gonzales, J. Magn. Magn. Mater. **140-144**, 347 (1995).
[16] J. Swierczek, J. Zbroszczyk, S. Szymura, B. Wisloky, I.E.E.E. Trans. Magn. **30**(2), 545 (1996).
[17] N. Morito, T. Egami, I.E.E.E.Trans. Magn. **19** (5), 1901 (1983).
[18] P. Flanders, N. Morito, T. Egami, I.E.E.E.Trans. Magn. **19** (5), 1907 (1983).
[19] T. Komatsu, K. Fujita, K. Matusita, K. Nakajima, S. Okamoto, J. Appl. Phys. **68**(5), 2091 (1990).
[20] R. M. Malkinski, J. Magn. Magn. Mater. **140-144**, 267 (1995).
[21] G. W. Scherer in "Materials Science and Technology", R. W. Cahn, P. Haasen and J. Kramer, Eds. (Weinheim, N. Y., Basel, Cambridge, Vol. No. **9)**, p.141.
[22] H. Kronmuller, H. Q. Guo, W. Fernenghel, A. Hoffman, N. Moser, Cryst. Latt. Deff. and Amorph. Mater. **11**,135 (1985).
[23] E. Villari, Ann. Phys. Chem. **126**, 82 (1865).
[24] M. L. Spano, K. B. Hathaway, H. T. Savage, J. Appl. Phys. **53**, 2668 (1982).