NEW EFFECTS IN AMORPHOUS CURIE-TEMPERATURE RELAXATION

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SUMMARY

In this article we present new effects in the amorphous Curie-point wandering due to long time isothermal heat treatments of the sample at different temperatures. In all early papers an inverse relation between the Curie temperature and the temperature of isothermal annealing is observed. We found, that this inverse relation is not fulfilled in the case of $Fe_{40}Ni_{40}\ Si_6\ B_{14}$ *amorphous alloys up to* 350^0C *(low temperature regime), and appears only when the temperature of annealing approaches the temperature of glass transition* (T_g)*. The results are interpreted on the basis of Chemical Short Range Order (CRSO) fluctuation (phase reminiscence effects) in the glass.*

Keywords: *amorphous; Curie-temperature; isothermal heat treatment; structural relaxation*

1. INTRODUCTION

Structural relaxation in glassy alloys is widely investigated in the past two decades [1-3]. It takes place in glassy state due to the heat treatments carried out at temperatures lower, than the glass transition (T_g), resulting in short range atomic rearrangements without the appearance of long range atomic diffusion. Many physical properties change during structural relaxation. Some of them are irreversible, others are (at least partially) reversible. Volume contraction, and most of enthalpy change are irreversible. It is a general belief, that the Curie temperature of the amorphous alloys (T_C^{am}) changes mostly in irreversible, but partially in reversible manner during structural relaxation, depending on the chemical composition and on the temperature of annealing (causing different degree of irreversible change). It is a general finding, that T_C changes monotonically with the time of the isothermal heat treatment and do show saturation value, which is either inverse or proportional to the temperature of heat treatment (T_a) [1,4]. During the reversible T_C change the relation between T_C^{am} and T_a is also inverse [5]. In spite of the numerous investigations, the composition dependence of the inverse or proportional relation between saturation value of T_C and T_a is not fully understood. Therefore, a critical reinvestigation of this problem has begun in order to clarity the role of chemical nature of the components, as well as the concentration relations in the appearance of the proportional or the inverse correlation. This paper is the first part of this comprehensive investigation. The alloy system $Fe_{40-x/2}Ni_{40-x/2}Cr_xSi_6B_{14}$ has been chosen for this purpose, in which the Fe and Ni is gradually replaced by Cr, simultaneously keeping the metalloid content constant (20 at. %). In the present paper the first results obtained on $Fe_{40}Ni_{40}Si_6B_{14}$ alloy are presented.

2. EXPERIMENTAL

The samples were prepared by the melt spinning method. The glassy state of the as quenched ribbons was confirmed by X-ray diffraction and the crystallisation temperature measured by Differential Scanning Calorimeter (DSC). The composition of the samples was chemically analysed by atomic absorption. All the data are collected in Table 1. The isothermal heat treatments were carried out in a simple box-furnace in atmospheric ambience. Thermomagnetic measurements have been performed with a home-made testing system based on AC susceptibility measurements and by a Vibrating Sample Magnetometer (VSM) using 20K/min and 5K/min heating rate respectively.

Sample	$T_{cryst.}$ [°C]	T_C^{am} [°C]
$Fe_{40}Ni_{40}Si_6B_{14}$	475.5	346.3
$Fe_{37}Ni_{37}Cr_6Si_6B_{14}$		225.5
$Fe_{36}Ni_{36}Cr_8Si_6B_{14}$	453.3	133.9
$Fe_{35}Ni_{35}Cr_{10}Si_6B_{14}$	445.5	39.4
$Fe_{34}Ni_{34}Cr_{12}Si_6B_{14}$	461	30

Table 1. List of crystallisation onset ($T_{cryst.}$) and the Curie-temperature (T_C^{am}) of the amorphous alloys in as-quenched state.

3. RESULTS AND DISCUSSION

In very early papers [1,4,6] monotonic increase of T_C during isothermal heat treatments and inverse relation between the saturation value of T_C^{am} and T_a were found in alloys with very different composition. Applying stabilisation heat treatments T_C^{am} reaches an equilibrium value, which is characteristic to the given T_a. This Curie temperature is called as "fictive" T_a. Continuing the heat treatment at different T_a the well known "crossover" effect can be often observed, which is interpreted as the existence of two (or more) relaxation times caused by independent atomic mechanisms during the relaxation process. Such crossover-like phenomena (the existence of definite minimum in T_C versus the time of heat treatment) was found when the T_C was measured on the samples $Fe_{40}Ni_{40}Si_6B_{14}$ after different time of isothermal heat treatments as Fig.1 shows. The measurements were carried out in low field (3 mT). Each T_C is estimated from the heating run. As the value of T_C is around 350^0C in this alloy, the $T_a=250^0$C (lowest temperature) is well below the Curie temperature of the as-quenched sample.

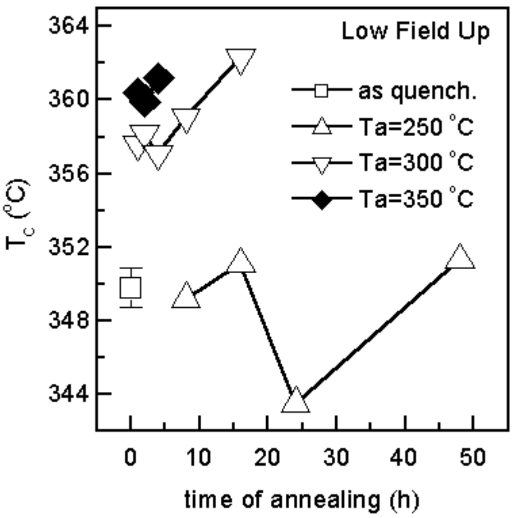

Fig. 1. The effect of isothermal heat treatment on T_C of amorphous $Fe_{40}Ni_{40}Si_6B_{14}$ (applying low field, T_C is estimated from the heating run.).

Except the definite minimum around 24h of heat treatment, there is no detectable change in T_C during this low temperature heat treatments. At longer annealing time (t_a), T_C raises again. At the first glance, this minimum looks like a fluctuation, but similar fluctuation can also be detected in several mechanical properties during similar run of low temperature heat treatments carried out on the same glassy alloy. The samples are already brittle at this heat treatment period, simultaneously the hardness and tensile strength of the samples increases [7]. It means, that low temperature relaxation processes have already started in this temperature range, (sub-sub T_g processes). The run of the curves obtained in higher temperature range (at 300^0C and 350^0C respectively) is similar in character. The only difference is, that the mentioned minimum appears already after shorter time according to the higher mobility of atoms taking part in the rearrangements. Another remarkable finding is the absence of inverse relation between the T_a and the saturation value of T_C^{am}, in this temperature range, opposite to several earlier observations. Similar trend is obtained, when the T_C is estimated from the cooling run. (The samples were overheated up to 400^0C in each measuring run and the T_C was also determined from the cooling run in order to check the magnitude of the additional heat treatment effects associated with the measuring process itself (it means an additional heating of the sample beyond the observed T_C by 50^0C in continuous heating mode). As the T_C^{am} is high and the atomic mobility increases suddenly in this temperature range, an appreciable structural relaxation is taking place during this time-period, which is reflected in the difference between the values of T_C(up) and T_C(down) estimated from the heating and cooling runs, respectively. The values of T_C down are collected in Fig.2. It is clear that T_C (both of the as quenched and the heat treated samples) are shifted considerably to higher temperatures, showing the role of additional heat treatments coupled with the measuring process. Nevertheless, the character of the curves is qualitatively the same as in the Fig.1. This fact hints to the stability of the "CSRO memory " introduced into the sample as a special thermal history - represented by the previous long time heat treatments.

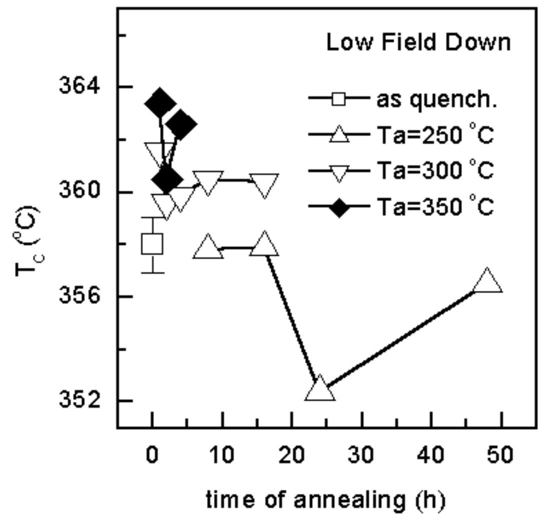

Fig. 2. The effect of isothermal heat treatment on T_C of amorphous $Fe_{40}Ni_{40}Si_6B_{14}$ (applying low field , T_C is estimated from the cooling run.).

The measurements were also repeated using high field (300 mT) applying the same heating rates as before. (see Figs. 3. and 4., in which the T_C obtained from the heating and cooling runs are plotted respectively.) The pronounced minimum of T_C(up) also appears after low-temperature heat treatments as it can be seen in Fig.1. and 2. However, the interpretation of the difference between the high field and low field measurements is not easy, the analysis of the corresponding magnetisation curves is going on.

After higher temperature heat treatments (400^0C) the trend of T_C change begins to turn into opposite as the Fig.5. shows. After a sudden increase (independently on the applied field) the T_C drops steeply showing again a minimum at around 2h of heat treatment time.

It is obvious from the presented results, that neither inverse relation between T_a and T_C nor monotonic $T_C{}^{am}$ increase versus the heat treatments time exist in this alloy in the lower temperature regime up to 350^0C. Approaching the glass transition temperature this tendency seems to be reverse. The non-monotonic nature of T_C change clearly shows that various independent mechanisms are involved in the evolution of T_C during the relaxation heat treatments.

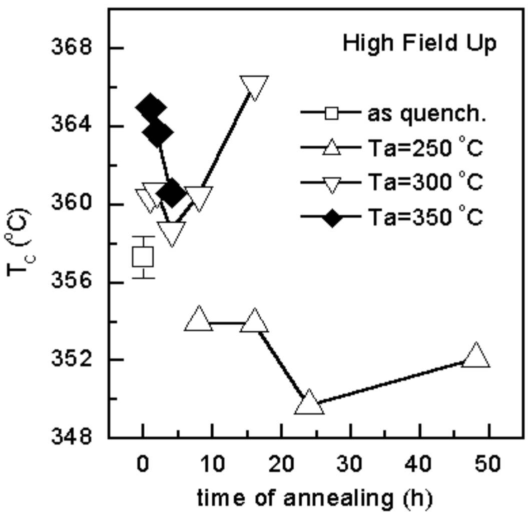

Fig. 3. The effect of isothermal heat treatment on T_C of amorphous $Fe_{40}Ni_{40}Si_6B_{14}$ (applying high field, 300 mT, T_C is estimated from the heating run.).

The definite change of the response to the heat treatments in the higher temperature range (approaching the T_g) shows the significance of the CSRO rearrangement in the high temperature relaxation. The qualitative interpretation of the change in the T_C relaxation mechanism is possible on the analogy of two-level system. The two level can be identified structurally as the coexistence of fcc or bcc like clusters in these alloys. The two cluster types do also correspond to the p and n-type defects proposed by [8]. In order to specify more exactly these clusters which are considered to dominate the glassy structure, the chemical tendencies must be considered, as it is outlined in [9].

The first tendency is dictated by the existence of bcc and fcc crystalline allotropes of Fe, from which the fcc is more dense than the bcc. The fcc is stable at high temperatures (beyond 913 ^{0}C), bcc is stable below this temperature. As it is well known, the fcc-γ field is opened by the Ni addition, i.e. the transformation temperature from fcc to bcc is lowered as the Ni-content increases. The transformation shows a pronounced hysteresis. It means, that fcc to bcc transformation is associated by significant supercooling. As the Ni content is high in the investigated alloy, it is plausible that the coexisting clusters are inherited from the crystalline fcc or bcc phase as a ”packing reminiscence” without crystalline ordering! The competition between these “quenched-in” clusters has started during structural relaxation, as the sample is heated from room temperature.

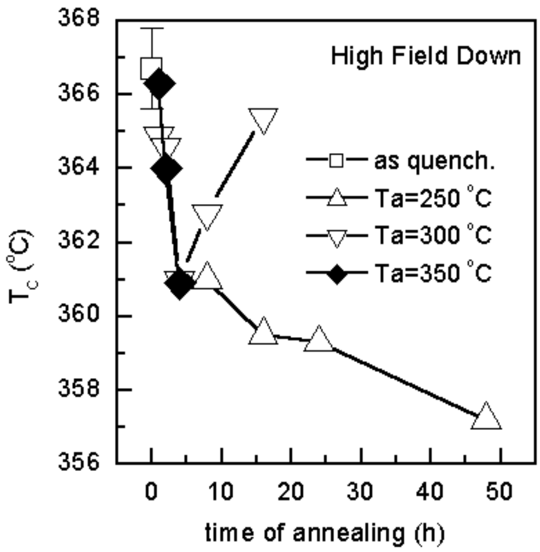

Fig. 4. The effect of isothermal heat treatment on T_C of amorphous $Fe_{40}Ni_{40}Si_6B_{14}$ (applying high field, 300 mT, T_C is estimated from the cooling run.)

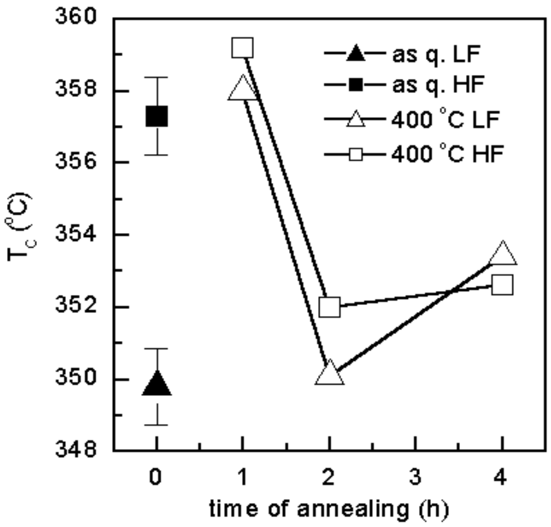

Fig. 5. The effect of isothermal heat treatment at 400^0C on T_C of amorphous $Fe_{40}Ni_{40}Si_6B_{14}$ applying low and high field, T_C is estimated from the heating run.

Raising the temperature, the atoms in bcc environments are activated at first and local reordering takes place with increasing directional character of bonding in the clusters. Hence the exchange interaction between Fe-atoms is strengthened (irreversible part of relaxation, during which the T_C^{am} increases.)

Approaching the T_g (heating to higher temperatures) the bcc to fcc-like rearrangement becomes dominant which results in a weakened ferromagnetic coupling in the sample.

4. CONCLUSIONS

-Contrary to the previous results, neither monotonic change of T_C^{am} versus t_a, nor inverse relation between T_a and T_C^{am} was found during the long time isothermal heat treatments in the low temperature range (up to 350^0C) in the investigated glassy $Fe_{40}Ni_{40}Si_6B_{14}$ alloy.

-The "inverse like" relation between T_a and T_C^{am} appears only, when the T_a approaches the T_g of the investigated glass.

-The relation between the T_C^{am} and T_a is interpreted on the basis of co-existence and competition between the quenched-in bcc and fcc-like clusters being inherited from the appropriate allotropes in the Fe-Ni crystalline alloys.

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BIOGRAPHY

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