The study of Curie point shifts in Fe(Ni)-based glasses induced by hydrogen absorption and low temperature storage

K Bán¹, J Kováč² and L Novák³
¹Department of Vehicle Manufacturing and Repairing, BUTE, Budapest H-1111, Bertalan Lajos utca 2. Hungary
²Inst. of Exp. Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovakia
³Department of Physics, Technical University of Košice, Park Komenského 2, 042 00 Košice, Slovakia
E-mail: ban@kgtt.bme.hu

Abstract. In this contribution, the influence of hydrogen absorption and low temperature treatments (77K) on the evolution of amorphous Curie temperature shift ($\Delta T_{C_{am}}$) is investigated in some of FeNi and Fe-based glasses. $T_C$ shifts of both types of alloys are surprisingly stable at higher temperatures and behave as a structural imprint in the investigated samples. The origin of these structural imprints is analyzed on the basis of Bethe-Slater conception, supposing the existence of quenched-in phase reminiscences in glassy alloys, being inherited from the super-cooled melt.

1. Introduction

During the past decade several observations have been reported on the influence of hydrogen (H) absorption and low temperature treatments (at temperature of liquid N$_2$, 77K) on various physical properties of glassy alloys [1-4]. Structural and magnetic (mainly stress sensitive) properties are mostly involved in these investigations [5]. The systems in question are not H-storage materials, so the majority of the H-induced changes are reversible [3, 4]. In contrast to the H-induced structural imprints, the effects arising from the “heat treatments” at low temperature (such as liquid N$_2$) are surprisingly stable and sustained over several cycles of heating runs as it is deduced from the amorphous Curie temperature ($T_C^{am}$) measurements [2]. These property changes occur at lower than room temperatures, though they resemble to typical relaxation changes during the high temperature structural relaxation. From the structural point of view the mentioned phenomena has common feature: no long range atomic motion is included. In the present paper, some experimental findings obtained during both types of treatment related to the shift of $T_C^{am}$ will be compared. The results are discussed as the stress induced structural changes at cluster level taking into consideration Bethe-Slater (BS) relation [6].
2. Experimental

The FeNi and Fe-based glassy samples were prepared by traditional planar flow casting or melt spinning technique. The details of hydrogen charging have been described in [3]. Vibration Sample Magnetometer (VSM) was used for the determination of $T_{c_{am}}$. In order to increase the reproducibility of $T_{c_{am}}$ measurements, the samples were subject to stabilization annealing at 250°C for 24 hours prior to the H-saturation or the LN treatment (immersion into liquid $N_2$). The $T_{c_{am}}$ measurements started within 5 minutes after finishing the saturation process, avoiding the possible spontaneous H-desorption, which can be expected in these samples [4]. In order to prove reproducibility three (or two) subsequent runs of the measurement were performed on each sample. In addition, short time in situ isothermal heat treatments were performed in the equipment. Following the individual $T_{c_{am}}$ determination, the cooling of samples was interrupted at 200°C, for 30 min. Then the $T_{c_{am}}$ was determined again, in order to follow the thermal stability of structural imprints caused by the H-absorption and/or the LN treatments.

3. Results and discussion

In Fig. 1 there are four independent series of $T_{c_{am}}$ measurements.

![Figure 1](image.png)

**Figure 1.** The $T_{c_{am}}$ values for heat treated Fe$_{50}$Ni$_{30}$Si$_{10}$B$_{14}$ samples being previously treated or/and charged electrolytically with H.

The first remarkable effect is the obvious $T_{c_{am}}$ depression, resulting either from the LN treatment or from the H-saturation ($\Delta T_{c_{am}} = T_{c_{am}}^{treated} - T_{c_{am}}^{initial}$) in Fig.1b). The role of LN treatment is more pronounced. There is no superposition between the two individual lowering effects when the two treatments were subsequently applied on the same sample. It is also remarkable, that $T_{c_{am}}$ gradually increases during the subsequent runs of the measurement. This increasing tendency can be the consequence of the heat treatment at 200°C supporting qualitatively the existence of inverse relation between equilibrium value of $T_{c_{am}}$ and the temperature of applied isothermal heat treatments. In spite of the high $T_{c_{am}}$ and the associated large “relaxation effect” associated with the measuring process itself, the structural imprints arising from the LN treatment as well as the H-absorption are surprisingly stable, which is in qualitative agreement with the observation reported in [1]. The $T_{c_{am}}$ depression caused by the LN treatment was also typical in the FeNi$_{51}$B$_{16.3}$ glass, as it is depicted in Fig. 2. In this case, the $T_{c_{am}}$ lowering can be detected both in the as quenched and in the pre-annealed samples as well. The effects are even more conspicuous than in the previous alloy. The $T_{c_{am}}$ of FeNi$_{51}$B$_{16.3}$ glass is considerably higher than that for the appropriate binary glassy FeB$_{16.3}$ [7].

The $T_{c_{am}}$ slightly decreased when the samples were pre-annealed (250°C, 24h) but the LN-treatment induced-difference is conserved even during the second run, however, the crystallization onset is approached during the $T_{c_{am}}$ measurements. This large depression and the subsequent rise due to the next run of the measurement („measuring relaxation”, see Fig. 2.) does not support the traditional explanation proposed in [8].
When the measured samples were Fe-based glasses, (see for example Fig. 3., i.e. when the host transition metal is solely Fe,) both the LN treatments and the H-saturation do cause definite rise in the $T_{C_{am}}$. Another interesting feature of cyclic $T_{C_{am}}$ measurements in FeB$_{16}$ was the gradual lowering of $T_{C_{am}}$ values during the repeated runs of the measurement (in contrast to the previous isothermal, stabilization heat treatment at 250°C, 24h). Similar trend was observed in FeB$_{15}$Si$_4$ glasses (these results are not showed here).

![Figure 3](image3.png)

**Figure 3.** The changes of $T_{C_{am}}$ due to liquid N$_2$ treatments (LN) and/or H-saturation (H) in binary FeB$_{16}$ alloy during the repeated measuring runs (similar results were obtained also in FeB$_{15}$Si$_4$ alloys during the same types of experiments).

As only short range atomic rearrangements possible during both treatments (the activation energy is insufficient for the long range diffusion of atoms, except highly mobile hydrogen atoms) the rearrangements occur at local cluster level only.

One can assume that certain, local, frozen-in symmetries in the atomic grouping can supply preferential trapping sites for H-atoms on the analogy of higher solubility of H in the $\gamma$-allotrope of crystalline Fe [9]. The existence of such cluster symmetries (resembling to the FCC symmetries in the $\gamma$-allotrope of Fe), are also manifested indirectly in certain magnetic, electronic properties and are documented on structural basis [10-13]. The change in the steepness of $T_{C_{am}}$ and density as a function of boron content indicates that the structural disorder is different for low and high boron containing alloys [10]. Similar changes were found in FeCrB alloys where a critical range of Cr causes a singularity in the thermopower indicating the existence of a hidden structural change in these hypoeutectic system [11]. As a consequence of the small fraction of these trapping centres, the concentration of dissolved H-atoms is very low in these alloys (max. a few hundred of ppm.). Hence, the preferential site-occupation of H-atoms in such endothermic type of the solution [14] is dominated by the local symmetry of the trapping centres, which are spatially independent. Therefore, their individual activity as H-trapping sites is realistic. As it was proposed in Ref [14], the existence of such local symmetries is inherited from the frozen-in melt structure.

When the glass forming liquid freezes at the temperature $T_g$, a cooling rate dependent cluster equilibrium is developed. The compound-like clusters (in which the strong covalent bonding is dominant) are stable and immobile against any kind of regrouping around and below the room temperature. The small mobility is represented by the quenched-in Fe-allotrope reminiscences which are the mixture of FCC and BCC-like clusters with low metalloid content. A small mobility may exists in the environments of off-stoichiometric clusters in which the local symmetry can fluctuate.
The ratio of the two cluster types depends on the cooling rate and composition in this temperature range. In the present types of Fe(Ni)-based glasses the H-atoms are preferentially incorporated into the centres with FCC-symmetry. The actual magnetic response of these clusters to the local H-incorporation depends on their local Ni-content. When Ni composition $C_{Ni} = 0$ (Fe-based glasses) the H-site occupation of H-atoms and the resulting local expansion contributes to a net increase of the exchange constant, as it is qualitatively illustrated in the Fig. 4. Hence, the $T_C^{am}$ will be increased due to the H-absorption. In contrast, with $C_{Ni} > 0$, the response of local magnetic coupling to the local expansion is dominated by the Ni content (right side of the BS curve in Fig.4). So the H-absorption will cause a net $T_C^{am}$ decrease. The influence of low temperature treatments on the $T_C^{am}$ shift can be described similarly.

4. Conclusions
The influence of H-absorption and “cryogenic treatment” on the Curie temperature shift are compared in some of the Fe(Ni) and Fe-based ferromagnetic glasses.

- It was found, that $T_C^{am}$ decreases due to both treatments in alloys containing Ni as host metal. The imprints, especially those which caused by LN treatments, are stable at high temperatures still close to the crystallization onset.
- The opposite sign (increase) of the $T_C^{am}$ shift was detected in the Fe-based glasses.
- The explanation of these effects is based on the existence of the quenched-in FCC and BCC-like centres. These centres are inherited as phase reminiscences frizzed around the glass transition temperature ($T_g$) causing spatial fluctuation of the strength of magnetic exchange. The response of the quenched-in centres to a given treatment (temperature change or H-dissolution) hence the change of ferromagnetic coupling is influenced by the local composition.

Acknowledgements
This work has been supported by the Hungarian Fund (OTKA) through grant No. T 046239, T 048708 and by the Slovakian Funds VEGA 2/7193, 1/4020/07 and 1/4013/07. L. Novák greatly acknowledges Domus Hungarica for one-month grant.

References
[1] Zaichenko S G, Perov N S, Glezer A M, Ganshina E A, Kachalov V M, Calvo-Dalborg M and Dalborg U 2000 J. Magn. Magn. Mater. 215-216 297-299
[2] Balla S, Kováč J, Novák L and Lovas A 2008 Act. Phys. Pol. A 113 55
[3] Novák L, Lovas A and Kiss L F 2005 J. Appl. Phys. 98 1-5
[4] Novák L, Bán K, Kováč J and Lovas A 2006 J. Magn. Magn. Mater. 304 669-671
[5] Mohanta O, Mitra A and Chattoraj I 2003 J. Magn. Magn. Mater. 266 296-301
[6] Jiles D 1998 Introduction to Magnetism and Magnetic Materials (London: Chapman & Hall)
[7] Hargitai Cs and Lovas A 1977 Proc. of 3rd Int. Conf. on Soft Magn. Materials (Bratislava) p 564
[8] Greer A L and Spaepen F 1981 Structure and Mobility in Molecular and Atomic Glasses (Ann. N. Y. Acad. Sci.) 371 218
[9] Fast J D 1965 Thermodynamics and Phase relations, Interaction of Metals and Gases Vol. 1 (Eindhoven: Philips Technical Library,) p 125
[10] Lovas A, Kísied-Koszó É, Varga L K and Kováč J 1993 Key Eng. Mat. 81-83 607-612
[11] Pál Z and Lovas A 2008 Act. Phys. Pol. A 113 139
[12] Hirata A, Hirotsu Y, Ohkubo T, Hanada T and Bengus V Z 2006 Phys. Rev. B 74 214206
[13] Bakonyi I 2005 Acta Materialia 53 2509-2520
[14] Bán K, Lovas A, Kováč J and L Novák 2006 23th Int. Coll. of Advanced Manufacturing and Repair Techn. in Vehicle Industry (Kollm) p 67