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Ph.D. Thesis

NEW EFFECTS IN MAGNETIC PROPERTIES OF FE-BASED GLASSY ALLOYS INDUCED BY RELAXATION AND H-ABSORPTION

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1. INTRODUCTION

The development of glassy alloys and its applications started several decades ago. The main structural characteristic (absence of long range crystalline order) opens several advantages. For example they have excellent soft magnetic properties (cores, magnetic sensors ect.), and they are precursor alloys of nanocrystalline cores, but good mechanical and corrosive properties may open new possibilities also. The limit of the application in many occasions is the special geometry arising from the production technology. The most usual production technologies now the free jet melt spinning and the planar flow casting techniques. The researches, which concern applications and production technologies, refer to such physical phenomena and questions for which physical and scientifical background have not been composed completely yet. These developments have already been in the focus of research, and there is possibility of the appearance of new phenomena, applications and developments nowadays. In **Table 1**. there are summarised the important applications, the connected properties, technologies and the physical backgrounds of these.

In this thesis several new phenomena in Curie temperature change will be discussed induced by structural relaxation and hydrogen absorption. In spite of the several papers reported in this field [1, 2, 3, 4, 5] the explanation of atomic mechanism either in structural relaxation, or in H-absorption has not been complete yet. The difficulty of these type of examination that structural changes in glassy alloys (only short range rearrangement of atoms appears in the glassy state) can not directly identify by structural examinations. Nevertheless the **resulted changes in the physical properties** are high and **have a great importance in technical applications** (for example changes in soft magnetic and mechanical properties under the process of structural relaxation).

Some results are related with the **effect of low temperature treatment (in liquid N_2 temperature, 77K) on magnetic properties and Curie temperature.** Phenomenologically this is belonging to the structural relaxation also, and it has only a ten years history in the international research.

At this time we have not been yet in possession such theories which to be able to give complete explanation for all phenomena. In contrast to the well developed explanation in the field of crystalline alloys we can give possible theories only. It is necessary to find precise models to connect

the structural changes with the changes of physical properties, only in this case we can explain the experimental results and modify the properties at technical applications.

Table 1. The applications, the connected physical properties and phenomena, the applied technologies and theoretical background of glassy alloys.

Researches in our department:			
Application:	**Properties and physical phenomena**	**Connected technologies**	**Physical and theoretical background**
Inductive parts, transformers, base materials of cores	Soft magnetic properties	Annealing, thermal treatment for nanocryst. struct., alloying	Structural relaxation, crystallization mechanism, alloying effect
Outdoor heating system in concrete host material	Higher resistivity, good corrosion properties, easy handling		Thermal stability → structural relaxation
sensors: thermal switching element for outdoor heating system based on ferromagnetic–paramagnetic transform.	Ferromagnetic–paramagnetic transformation: Curie temperature	Modification of Curie temperature by alloying and annealing	Alloying effect, struct. relaxation, thermal stability of properties → effect of struct. relaxation
Bulk amorphous alloys	Glass forming ability	Casting, annealing	Glass transition, struct. relaxation
Other applications:			
Thermal switches: cooling water, temperature regulation of the motor oil	Ferromagnetic–paramagnetic transformation: Curie temperature	Modification of Curie temperature by alloying and annealing	Alloying effect, struct. relaxation, thermal stability of properties → effect of struct. relaxation
Position sensors: ignition transmitter, tachometer	Barkhausen effect, magnetoinductive phenomenon, soft magnetic properties	Annealing, thermal treatment for nanocryst. struct., alloying	Struct. relaxation, crystallization mechanism, alloying effect
High sensitivity magnetometers	soft magnetic properties	Annealing, alloying	Struct. relaxation, alloying effect

However H-absorption in this type of glassy alloys (non hydride forming systems, ΔH>0) is not significant, the changes in physical properties are obvious. Therefore the indirect effect of H-absorption on magnetic properties was examined versus the desorption time.

In my examinations I try to discover the similarities and connection between the liquid N_2 treatment, H-absorption and structural relaxation.

2. QUESTIONS TREATED PREVIOUSLY IN THE REFERENCES

2.1. Glass transition, glassy states and structural relaxation

The long range crystalline periodicity represents the lowest free energy for the condensed matter around room temperature, which can be reached by crystallization.

Solidification may takes places via glass transition also (T_g is the temperature of glass transition) when the cooling rate of the melt is sufficient high. An excess enthalpy (H), entropy (S) and excess volume (v) will be frozen in this case, as it is illustrated in **Fig. 1**.

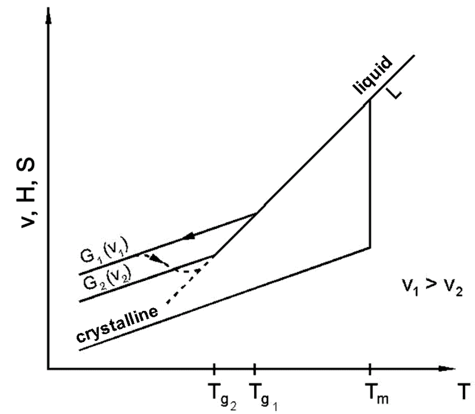

Fig. 1. The schematic changes of thermodynamic parameters (H: enthalpy, S: entropy) and specific volume (v) under the process of glass transition. G_1 and G_2 are two types of glassy states were formed by two quenching rates [on the basis of Ref. 2].

The structural relaxation is a diffusionless short range atomic rearrangement in which the alloy reaches a thermodynamically more stable glassy state for example from G_1 state to G_2. Two types of processes

are involved in structural relaxation. First is topological, the second results chemical short range ordering (TSRO and CSRO). The manifestation in the physical properties of these can be reversible or irreversible.

For the explanation of amorphous state several theory and idea were initiated. In **Table 2.** were given those important ideas which was used for the explanations of changes of magnetic properties and H-absorption as a result of structural relaxation.

Table 2. The main ideas of glassy state

Free volume [6,7]	Those atoms which have an excess volume compared with ideal state.
Flow defect [6,7], Diffusion defect [3],	Flow defect is an atom which has a free volume over the critical value. Both defect taking part in the development of the named property.
Cluster theory [8]	Refer to this theory glassy state has not a homogenous structure. It contains a nanometre sized atomic environments with different structural and chemical properties.

2.2. Effect of structural relaxation on magnetic properties

The effects of structural relaxation on magnetic properties have been discussed by several references. Detailed summary can be found in [9, 2]. Generally the stress and structure sensitive magnetic properties are affected by two phenomena: primary by the heat treatment, secondary by the relaxation of stresses caused by the production. Heat treatment causes the decrease of the free volume (interatomic spacing) therefore on the basis of Bethe–Slater-curve the magnetic coupling changes. In this way considerable decreases the magnetostrictic anisotropy for example or with the decreases of coercive force the permeability increases (magnetic softening of the alloy).

A few basic observations are widely accepted by the references in the field of T_C^{am} changes versus the heat treatment:

– the existence of irreversible and monotonic change of T_C^{am} (usually at the beginning of the heat treatments),
– inverse relation between the equilibrium value of T_C^{am} and the temperature of isothermal annealing (T_a) [10, 11, 12], but this inverse relation is general when the temperature of the isothermal heat treatment is above the 70% of the T_g [9, 1696. o.].

2.2.1. The effect of cryogenic treatment on the amorphous Curie-temperature (T_C^{am})

The effect of cryogenic treatment was observed in the last decade. The samples were immersed into liquid nitrogen (–196°C= 77K). It was found that irreversible changes of the measured physical properties and the structure of the amorphous alloys were occurred during the cryogenic treatment [13]. Initially the possible modification of the mechanical and magnetical properties was examined [14].

According to the experimental findings the examinations were focused on the magnetic properties, because its indicate sensitively the structural modifications (though in indirect way) caused by the cryogenic treatment. The thermomagnetic measurements carried out on Fe- and Co-based amorphous ribbons show the decrease of the T_C^{am} in most cases. The possible reason of the decrease in ferromagnetic coupling as suggested by [15] is the evolution of local concentration fluctuation which promoted by thermoelastic stresses. In this process the content of metalloid atoms (Si, B) increase in the nearest neighbourhood of metal–metal atoms.

It was also investigated that changes of cryogenic treatment how can be affected by previous heat treatments (in which direction and degree) [16]. The examined magnetic properties were the saturation magnetisation and coercive force, which are stress sensitive properties. The saturation magnetisation was changed within the limits of the experimental error (magnetisation depends mainly on concentration). The direction of coercive force was changed depending on annealing time and duration of cryogenic treatment. It was suggested that stress level arising from production was decreased only by previous heat treatments and the stress centres came out of local concentration fluctuation was affected only by the cryogenic treatments. This was confirmed by the neutron diffraction investigation: some shifts of the second and third maxima of structural factor were observed as a result of cryogenic treatment [17].

2.3. H-absorption in amorphous alloys

The explanation of H-absorption in amorphous alloys was worked out by J. H. Harris et al. on the basis of previously developed structural model of the amorphous state. The basis of Harris–Curtin–Tenhover-model [18] is that amorphous matrix can be built up by elementary tetrahedrons without any contradiction. The order that H occupies these interstitial, tetrahedral sites depends on the energy level of these sites. This theory

gives a choice to connect this process to the two types of atomic rearrangements of the structural relaxation: the chemical and topological short range ordering.

We can found a complete summary about the diffusion in amorphous alloys in [2]. The initialization of diffusion defects gave an exact explanation about the diffusivity under the process of structural relaxation [3], because of the value of diffusion coefficient is related to the concentration of diffusion defects. Another advantage that diffusion defects has a connection with atomic processes of structural relaxation, because a flow defect can be explained as a pair of diffusion defect, and under the process of structural relaxation a diffusion defect and a flow defect neutralize each other.

The effect of H-absorption on magnetic properties [19 and 20] gives experimental data. The solution of H causes an increase in the stress level of the amorphous matrix, and we can register a change in the stress sensitive magnetic properties. Therefore it is possible to follow the presence of H in the amorphous matrix with the examination of coercive force (H_C), permeability (μ_r) and anisotropy (K) for example.

The effect of structural relaxation on the H-absorption there are few data can be found in references. Ref. [2] gives a description about the changes of self-diffusion of iron indicated by structural relaxation.

Another question, that the H-absorption capable to modify the local atomic rearrangement, and does it reversible or irreversible. Some answer and detailed data can be found in [21, 22]. They give some evidence about the irreversible effect with the results of X-ray examinations.

2.4. Summary

The structural relaxation has been studied for several decades in many papers and books. The general theories were described but in unusual cases and phenomena there is a lack of the atomic level description. This is the fact at T_C^{am} relaxation of Fe–Ni amorphous systems for example and the description in atomic level insufficient.

The influence of treatment in liquid N_2 was considered as new phenomena and theme in the references. There are some theoretical ideas but most of the questions there are no answers in this time.

In the references it is difficult to find any data about the connection between the H-absorption and structural relaxation. It is exceptionally true at ferromagnetic (soft magnetic) glassy alloys at which H-absorption not considerable but the influence on stress sensitive magnetic properties is high. The effect of low temperature treatment (in liquid N_2) on the H solubility can be suspected have not been examined yet neither at crystalline alloys nor at amorphous alloys.

3. OBJECTS OF INVESTIGATIONS

The first task was the **improvement of previous AC susceptibility testing system** including construction and the control program of the equipment.

The **critical reinvestigation of T_C^{am}-relaxation and effect of H-absorption in FeNi-based and Finemet** type alloys required, because the previous examinations showed a fluctuation of the investigated magnetic properties (T_C, permeability ect.). In these types of alloys which has a great importance in applications the fluctuations depends on the production technologies. The results of the previous examinations has not been in agreement with the expectations which could conclude on the basis of references, therefore a **close exploration of the atomic backgrounds** needed.

The results of the references suggested the **examination of the cryogenic treatment** in Fe-based alloys with high Ni or increasing Si content and in other comparative samples. The explanation of these changes **can help to interpret the unusual phenomena of glassy states and structural relaxation.**

In the references it is possible to find several results in connection with the **mechanism of H dissolution on the evolution of stress-sensitive sensitive magnetic properties** (for example anisotropy, coercive force ect.) **during the widely applied heat treatment.** But the changes **in the Curie-temperature** have not examined yet, though the H-absorption modify the local atomic rearrangements. In this type of soft magnetic alloys there are no chemical interactions between the components and H (hydrides), therefore the absorption kinetic depends on the local atomic symmetry and topology only. This investigation can give an answer that

- **H how can modify (quantity) the topology of amorphous alloys**,
- this modification in **what degree resemble to the process of structural relaxation** and
- these similarities how can relate to the modification of H-absorption capability after the process of structural relaxation.

4. SAMPLES AND MEASURING METHODS

4.1. Alloys and examinations

Most of the samples were made in the Institute of Solid State Physics and Optics of Hungarian Academy of Sciences but there are some industrial materials (Finemet) also used. The production sizes had a great variation. The thickness of the ribbons were typically 20–50 μm, the widths were 0,5–15 mm. Wider ribbons were necessary only for the electrolytic H saturation. The next table (**Table 3**.) contains the experimental samples and the examinations which were carried out on these.

Table 3. The experimental samples and the examinations

Composition of alloy	Examination
$Fe_{40}Ni_{40}Si_6B_{14}$	annealing and determination of T_C^{am}
$Fe_{37}Ni_{37}Cr_6Si_6B_{14}$	annealing and determination of T_C^{am}
$Fe_{36}Ni_{36}Cr_8Si_6B_{14}$	annealing and determination of T_C^{am}
$Fe_{35}Ni_{35}Cr_{10}Si_6B_{14}$	annealing and determination of T_C^{am}
$Fe_{34}Ni_{34}Cr_{12}Si_6B_{14}$	annealing and determination of T_C^{am}
$Fe_{(85-x)}B_{15}Si_x$	annealing, treatment in liq. N_2, determination of T_C^{am}
$Fe_{73,5}Si_{13,5}Nb_3B_9Cu_1$ (Finemet)	annealing, electrolytic H saturation, determination of K, H_C, D
$Fe_{40}Ni_{40}Si_6B_{14}$	annealing, treatment in liquid N_2 and determination of T_C^{am}, μ and H_C, examination of production effect with T_C^{am} measurements
$Fe_{20}Ni_{60}Si_6B_{14}$	annealing, treatment in liquid N_2 and determination of T_C^{am} and H_C
$Fe_{72,5}Cr_{11,5}B_{16}$	annealing, electrolytic H saturation, determin. of T_C^{am}
$Fe_{75,3}Cr_{9,2}B_{15.5}$	electrolytic H saturation, determination of T_C^{am}
$Fe_{86,2}B_{13,8}$	treatment in liquid N_2, electrolytic H saturation, determination of T_C^{am}

4.2. Experimental methods and equipments

The thermomagnetic curves and the T_C^{am} were determined by two types of experiment. The first was an AC susceptibility measurement system (excitation with altering current) with 20K/min heating rate. The samples were heated in a platinum sample holder and the sign indicated by sample magnetisation was in situ detected. The second was a vibrating sample magnetometer (VSM) with 10K/min or 5K/min heating rates. The detected signal was indicated by vibration of the sample between two electromagnets. The indirect heating of the samples was based on the electrical resistance loss of a heating coil. Both experiments have a computer controlled measuring method. According to my experience the error of repeated T_C^{am} measurements in all temperature region was not greater than ±0,75°C.

There is an addition effect during detection of thermomagnetic curve, that **it is not possible to separate the effect of measurement from the measured T_C^{am} data**. In order to determine T_C^{am} we had to heat the sample above the T_C^{am} and this meant an additional heat treatment. The degree of additional heat treatment effect depends on the value of measured T_C^{am}, previous heat treatments and composition also. To evaluate the liability of the samples to this effect I calculated the difference between T_C^{am} measured during the cooling and heating runs ($\Delta T_C^{am}=T_C^{am}(down)-T_C^{am}(up)$). At the H-saturated samples the basic difficulty is the separatism of H-induced relaxation effect from measurement effect (arising from the sample heating). The minimisation of this effect required low T_C^{am} of the sample.

The isothermal annealings were carried out in a simple box-furnace in atmospheric ambience. In other cases the isothermal heat treatments were carried out (in situ) in the VSM equipment, if measurement cycles connected with annealings had been necessary. The low temperature treatment carried out by immersion of the samples into liquid N_2 (-196 °C, 77 K).

The electrolytic H charge was carried out in a computer controlled experiment. The quantitative determination of hydrogen content of the sample during desorption cycle was measured in a pressure chamber, which works on the basis of precise pressure-change measurements [23, S9].

Differential Scanning Calorimeter (DSC) was used for the determination of thermal stability ($T_{cryst.}$) of samples to avoid the partially crystallisation of the samples during the heat treatments and thermomagnetic measurements.

The magnetic properties, as anisotropy (K), permeability (μ), demagnetizing factor (D), saturation magnetization (J_s) and coercive force (H_C) were determined in a magnetometer. In combined measurements (when T_C^{am} and H_C determination were combined with in situ heat treatments) the coercive force measured in the VSM equipment.

The composition of the samples in some cases was chemically analysed by atomic absorption.

5. EXPERIMENTAL RESULTS

5.1. Improvement of AC susceptibility measurement system

The examination from the new point of view of structural relaxation required new measurement methods. Therefore it was necessary to carry out some investigation on the previous experiment. The improvement contained the next steps:

- a new segment of the control program was developed and inserted in the previous one, therefore it became possible to define and automatically run an optional measuring and annealing program in a controlled way (possible heating and cooling rates are ±1–±255 K/min); the previous system could carry out only a heating and cooling runs with a discrete heating rate [S5];
- for the stability of the temperature determination an electronic cold junction was developed;
- the measuring head was redesigned: the fixing of the thermocouples except the possibility of short circuit of the thermocouples, the ceramic body protect the sample holder against mechanical effects and fluctuations of temperature measurement caused by inert gas flow, it was resolved the long time cooling of the head and the new construction makes the later reparation easier;
- it was decreased the fluctuation of the temperature measurement from 1°C to 0,1°C and increased the precision from ±2°C to ±1°C.

At this time an improved version of the measuring head is in operation.

5.2. New effects in structural relaxation

5.2.1. Examination of Curie-point relaxation in FeNiCrSiB glassy alloys

The examination of $Fe_{40-x/2}Ni_{40-x/2}Cr_xSi_6B_{14}$ glassy system had a practical purpose: with Cr addition it was used as a temperature switch element (T_C^{am} switch) in resistance heating system [24]. With the effect of heat treatments on T_C^{am} I examined the stability of the switching temperature.

The data of T_C^{am} measurements at $Fe_{37}Ni_{37}Cr_6Si_6B_{14}$ glassy alloy (**Fig. 2**.), well characterise the results of other samples without any important differention.

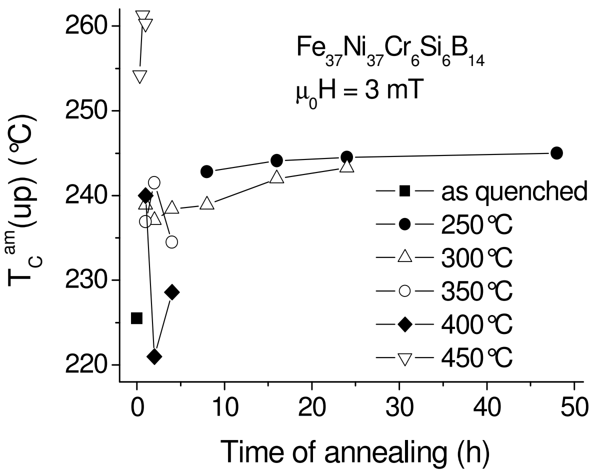

Fig. 2. Effect of isothermal heat treatments on T_C^{am}(up) at $Fe_{37}Ni_{37}Cr_6Si_6B_{14}$ glassy alloy. T_C^{am}(up) estimated from the heating run, measured in low magnetic field [S4].

Contrast to the earlier experiments of references it is obvious from the Fig. that **neither monotonic changes, nor inverse relation of saturation T_C^{am} versus temperature of isothermal heat treatment (T_a)** occurred. The alloying with Cr resulted higher effect of relaxation but as the T_C^{am} became lower the relaxation resulted by measurement decreased. The appearance of minimum hints to two types and independent processes in time which cause reverse shift of the T_C^{am} [S2, S4].

5.2.2. Effect of complex thermal history on the shift of Curie-point in FeNi-based glassy alloys

I examined the effect of thermal history in $Fe_{40}Ni_{40}Si_6B_{14}$ and $Fe_{20}Ni_{60}Si_6B_{14}$ glassy alloys. The system was proposed by the fact that Fe–Ni crystalline system forms two phases. According to the analogy of two phases it is possible that in glassy state two types of clusters forms with different magnetic coupling. The other fact that the relaxation behaviour of the first alloy previously had been examined (see 5.2.1.) and T_C^{am} of the second alloy not so high for relaxation with measurements itself supposed to be negligible.

The next figure (**Fig. 3**) shows the schematic process of the heat treatments and measurements carried out in the alloys.

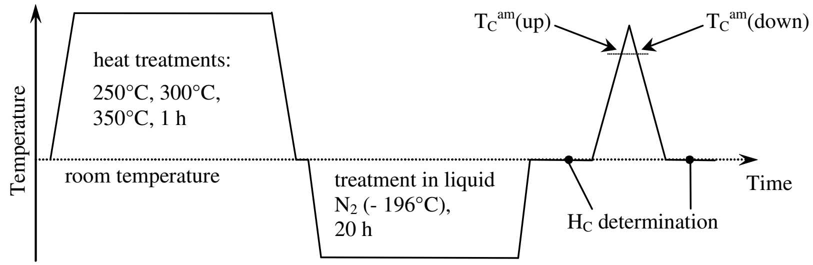

Fig. 3. The processes of heat treatments and measurements [S6].

The results of complex treatments are collected in **Fig. 4.** The decrease of the T_C^{am} was experienced but it is remarkable, that the rate of T_C^{am} relaxation caused by the determination itself increased due to the previous cryogenic treatments.

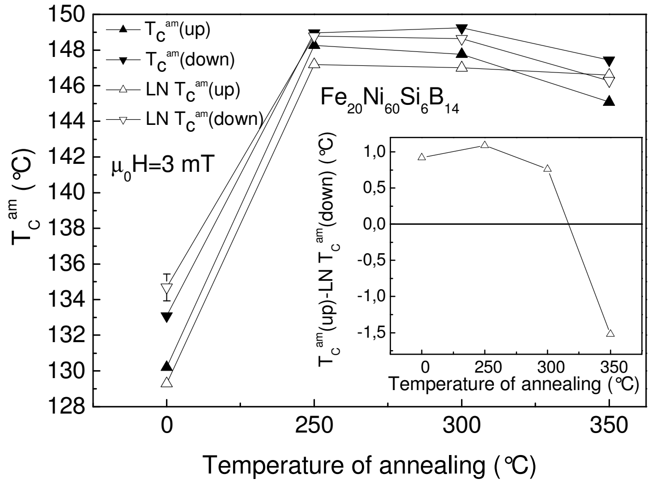

Fig. 4. The changes of T_C^{am} in $Fe_{20}Ni_{60}Si_6B_{14}$ glassy alloys as a result of heat treatment for 1 hour. A parallel set of samples (signed with LN) after the heat treatment was immersed into liquid N_2 (-196°C) for 20 hours. In the inset the difference of T_C^{am} between the LN and not treated sample is plotted [S6].

In the other magnetic properties also appeared the effect of treatment in liquid nitrogen. The coercive force for example increased in the examined alloys (**Fig. 5.**), in spite of the previous heat treatment at 350°C which previously experienced as a temperature limit at the T_C^{am} measurements also. The changes of magnetic properties hint to hidden structural changes under the room temperature.

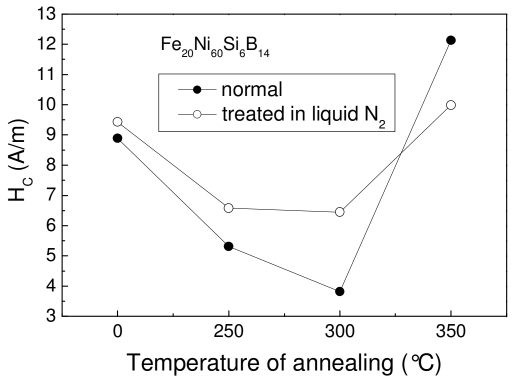

Fig. 5. The changes of coercive force (H_C) at heat treated samples in different temperatures. The parallel set of samples treated in liquid N_2 between the heat treatment and measurement [S6].

5.2.3. Curie-point relaxation processes in Fe(SiB) amorphous systems

In this series of investigation I tried to discover the role of metalloid content in the T_C^{am} shift caused by cryogenic treatment in Fe(SiB) amorphous systems. It was found, that the direction of the changes (decrease or increase the T_C^{am}) depends on the ratio of the two metalloid elements. More than 2 at.% Si content and the previous heat treatment increased the effect of cryogenic treatment (higher changes of T_C^{am}) and caused the depression of the T_C^{am} as I experienced at FeNi amorphous alloys. At the as quenched samples this depression appeared only above 2 at.%, below this the cryogenic treatment caused only the increase of the measured T_C^{am}. Fig. 6. shows the general tendency that the effect of cryogenic treatment higher at that samples which had higher cooling rate at the production process. The possible cause of this phenomenon is the less relaxated structure which was formed by the higher cooling rate. This result confirms a general observation that the samples with higher cooling rate have lower T_C^{am} [2, p. 277.]. The changes caused by cryogenic treatment turned into the opposite direction as an effect of the previous heat treatments: at the as quenched samples increase, while at the annealed samples decrease change of the T_C^{am} was observed. It was concluded that **the direction of T_C^{am} shift due to cryogenic treatment is composition dependent,** in addition is also **influenced by the thermal history and the quenching rate** applied during the sample preparation.

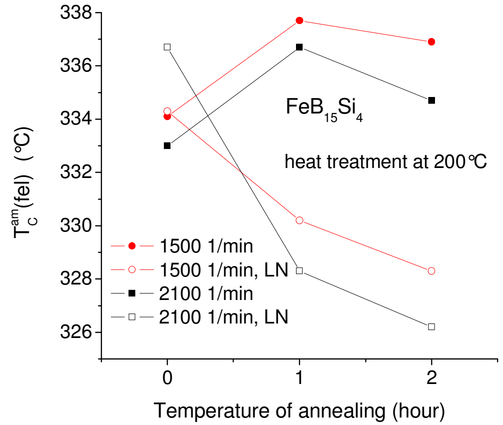

Fig. 6. Evaluation of T_C^{am} at $Fe_{81}B_{15}Si_4$ amorphous alloy versus cooling rate from the melt and time of previous heat treatment. Between the annealing and measurement a set of sample immersed into liquid N_2 (signed as LN) for four days [S7].

5.2.4. Interpretation: cluster structure in the glassy state inherited from the two-phase nature of Fe-Ni alloy system

The interpretation of experimental result is based phenomenologically on the polycluster concept of glassy alloys introduced by Bakai [8]. The cluster structure in glassy state is inherited from the supercooled glass forming melt supposing the existence of compound like environments and cluster assemblies of fcc/bcc symmetries which are capable transform without long range diffusion as the melt freeze around the T_g. The magnetic properties are determined by these symmetries, for example the T_C^{am} is depend on the packing density of the clusters.

The location of the examined alloys ($Fe_{40}Ni_{40}Si_6B_{14}$ and $Fe_{20}Ni_{60}Si_6B_{14}$) in the Fe–Ni crystalline phase diagram (**Fig. 7.**) point out that in room temperature and crystalline sate the system is composed by two phases. Due to this two-phase tendency and the well known sluggish nature of $\alpha \leftrightarrow \gamma$ transformation the formation of two types of clusters were supposed. One of these bcc like (low dense packed) environments with higher magnetic coupling, the other is fcc like (dense packed) environment with low magnetic coupling. The possible formation of the two types of clusters was demonstrated by the comparison of the TTT diagram of supercooled melt with the Fe–Ni biner phase diagram (see **Fig. 7.**). The glass formation occurs in the temperature range of $\alpha \leftrightarrow \gamma$ transformation.

In addition this range is become wider than other systems due to the sluggish transformation. The reversible and irreversible T_C^{am} change in glassy state is a manifestation of a local atomic transformation inherited from $\alpha \leftrightarrow \gamma$ transformation of crystalline state.

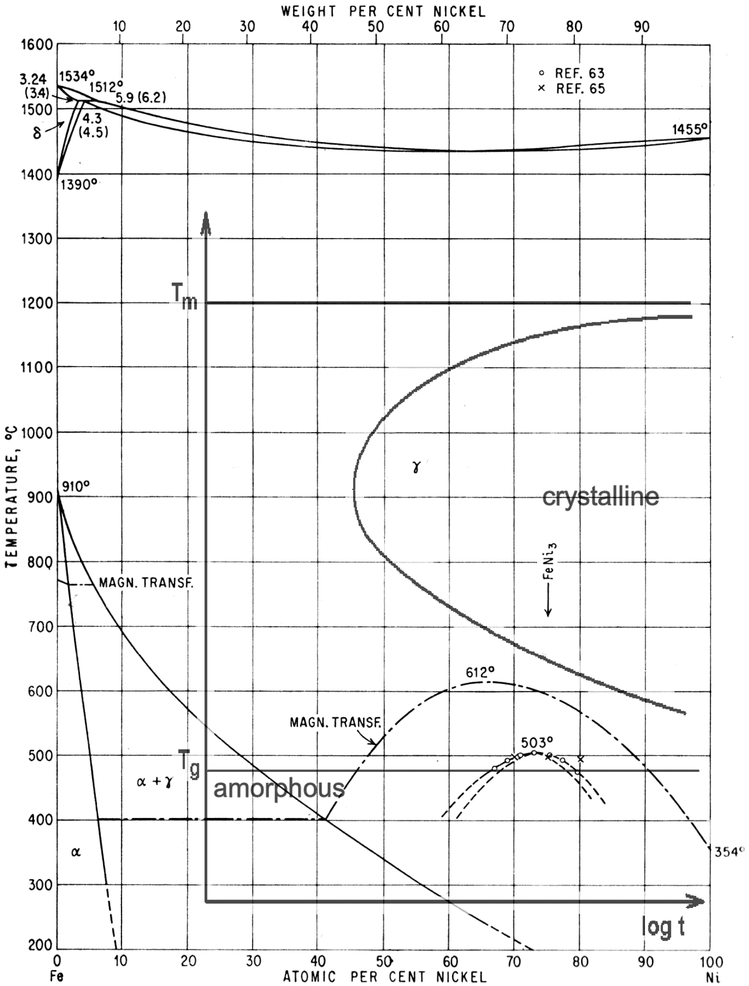

Fig. 7. Fe–Ni equilibrium phase diagram and schematic TTT diagram of supercooled melt of $Fe_{40}Ni_{40}Si_6B_{14}$ alloy [S12 and S13].

The possible explanation of cryogenic treatment that due to high Ni content the $\alpha \leftrightarrow \gamma$ like transformation become slower and the end point of the transformation shifts under the room temperature. During the cryogenic treatment the transformation completes which causes a structural imprint. Similar process occurs at steels in martenzitic transformation. In some types of steels the martenzitic transformation completes only under the room temperature. **Fig. 8.** schematically summarizes the main points of the explanation.

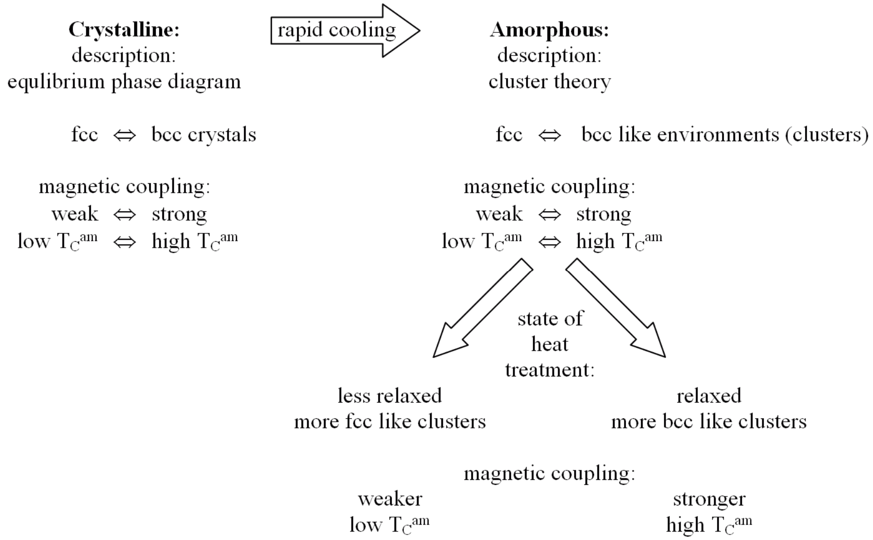

Fig. 8. Inheritance of properties from the equilibrium state to the amorphous state [S13].

To control the explanation some test measurements was carried out on $Fe_{40}Ni_{40}Si_6B_{14}$ alloys. The results confirmed that less relaxed samples (high cooling rate, thin ribbon) had lower ferromagnetic coupling than more relaxed samples (lower cooling rate, thick ribbon): the T_C^{am} of thin ribbons lower than T_C^{am} of thick ribbons as plotted in **Fig. 9.**

As in equilibrium state the bcc structure stable at lower temperatures and fcc at higher temperatures, supposed that this behaviour inherits to the glassy state. Therefore the heat treatments cause the relaxation of frozen in fcc environments, the free volume decreases and the environments changes into bcc like clusters. This fact is a possible explanation of the behaviour (less sensitiveness and opposite direction of changes to cryogenic treatment) of samples heat treated above 300°C because above this temperature fcc environments which are reactive to cryogenic treatments disappears.

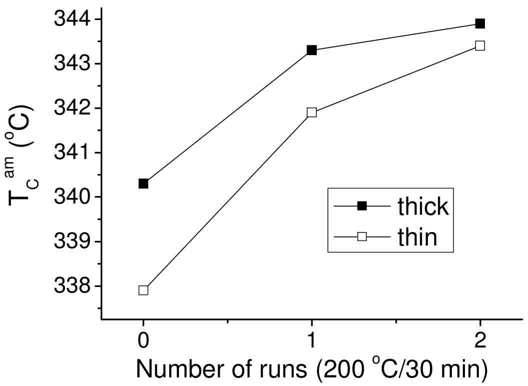

Fig. 9. Evaluation of T_C^{am} of $Fe_{40}Ni_{40}Si_6B_{14}$ amorphous ribbons versus the annealing cycles. Thick ribbons was made by lower cooling rate and thin ribbons by higher cooling rate from the melt [S13].

In conclusion as **a result of cryogenic treatment the ratio of fcc/bcc environments is slightly changes**, the low depression of specific volume increases the ratio of fcc clusters which **causes the decrease of the T_C^{am}**.

5.3. Hydrogen absorption

5.3.1. Stress sensitive magnetic property changes during H-absorption and -desorption process

In this examination the stress sensitive magnetic properties of an industrial precursor alloy (for production of nanocrystalline soft magnetic material), Finemet ($Fe_{73,5}Si_{13,5}Nb_3B_9Cu_1$), was examined. The effect of H-desorption was measured in as quenched and isothermal heat treated samples.

The examination of anisotropy (K), coercive force (H_C) and demagnetising factor (D), from which only the experimental results of anisotropy was plotted in **Fig. 10.**, pointed out that H-absorption at as quenched state caused the highest changes. Therefore the quenched in stress centres plays an important role in evaluation of magnetic properties. As a stress centres disappear during the annealing the effect of H-absorption also decreases. The H-absorption caused property changes generally reversible changes and the evaluation of this properties has the same time scale as the H-desorption occurs, therefore the change in stress level caused by H-absorption connected with the presence of dissolved H atoms.

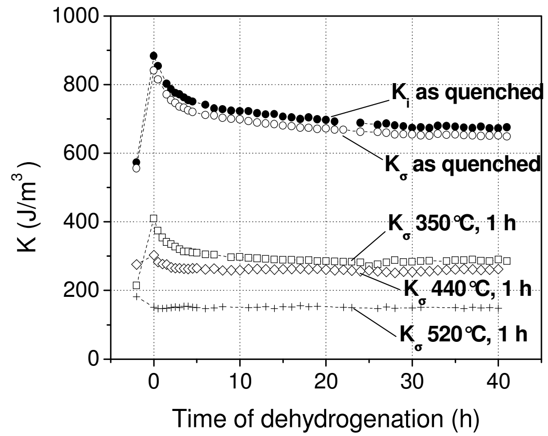

Fig. 10. Changes of anisotropy (K) versus H-desorption process in samples with different structural states caused heat treatment in appropriate temperatures (relaxed: 350°C, partially nanocrystalline: 440°C, nanocrystalline: 520°C) [S8].

5.3.2. The effect of H-absorption to the amorphous Curie-temperature

The H-absorption induced T_C^{am} shift was positive in Fe-based alloys in all cases and this effect generally was reversible. Similar character and degree of T_C^{am} change was observed due to the annealing, coupled with the T_C^{am} measurements.

There is a difficulty with T_C^{am} determination that it is not possible to separate the absorption effect manifested in T_C^{am} and relaxation which occurs during the measurement. A possible solution of the problem to chose alloys with low T_C^{am} and in this case the relaxation effect of measurement and annealing out of changes caused by H-absorption becomes lower. When the effect of relaxation during the measurement is high the sign of ΔT_C^{am} turns into opposite as it is shown in **Fig. 11.**

It was the effect of measurement that at independent samples the value of T_C^{am} measured from the heating and cooling run turned into opposite. The explanation is that in this temperature the velocity of H-desorption higher than the relaxation effect of measurement: the decreasing effect of H-desorption dominant against the T_C^{am} increasing effect of relaxation caused by the measurement. It was evidence by the results of repeated measurements carried out in the same samples: the direction of T_C^{am} measured from the heating and cooling run turned into the appropriate direction generally experienced at T_C^{am} measurements.

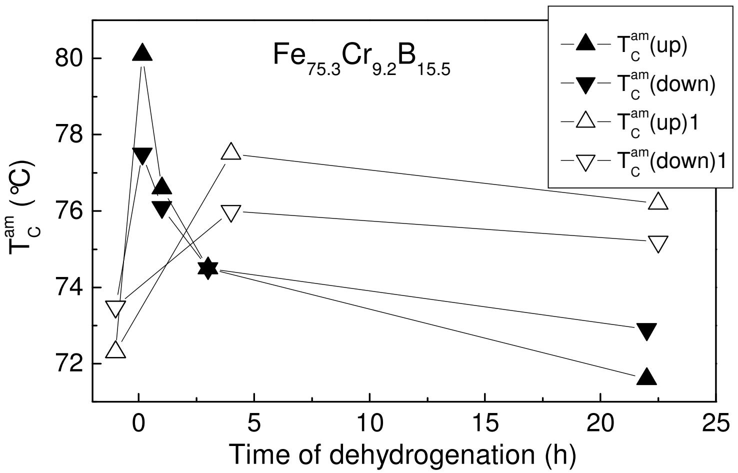

Fig. 11. The evolution of T_C^{am} (T_C^{am}(up): measured from the heating run, T_C^{am}(down): from the cooling run) in $Fe_{75,3}Cr_{9,2}B_{15,5}$ samples during the H-charging, and the subsequent spontaneous discharging. The solid triangle signs repeated measurements on the same sample, the open triangles signs a set of measurements carried out on independent samples [S11].

5.3.3. The influence of cryogenic treatment on the H solubility

The investigation of cryogenic treatments predicted that some modification occurs in the amorphous structure during the treatment. The following examination was proposed by this theory: the structural modification should affect the solubility of hydrogen (on the basis of Curtin–Tenhover-model).

In this investigation the H solubility of samples treated in liquid N_2 with not treated ones was compared. For the comparison to other samples T_C^{am} measurement was carried out on the same alloy but a little bit different concentration ($Fe_{85}B_{15}$).

The results (**Fig. 12.**) pointed out that previous cryogenic treatments caused three times lower solubility of H which hints to a hidden structural changes supposed earlier.

The T_C^{am} measurements manifested that at this samples cryogenic treatments influenced T_C^{am} in the same direction as at previously measured alloys, consequently T_C^{am} decreased in this case also.

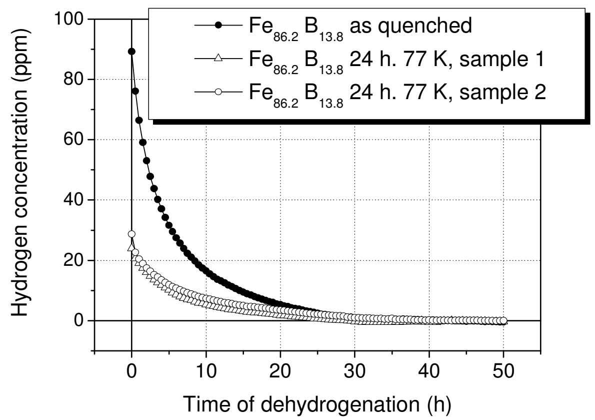

Fig. 12. The change of H-concentration versus dehydrogenation time in $Fe_{86,2}B_{13,8}$ samples for as-quenched and N_2-treated states (24 hours, 77 K) [S9].

5.3.4. The interpretation of H-absorption induced phenomena based on the cluster structure of glassy state

The structural interpretation of T_C^{am} increase in Fe-based amorphous alloys during structural relaxation was given by Lovas et al. [25]. The base of the theory is the existence of two types of Fe rich atomic environments in the biner Fe–B glassy system (mainly in hypoeutectic region). One of these is fcc like (dense packed) clusters which decrease the intensity of ferromagnetic coupling. This is the reason of the low T_C^{am} at hypoeutectic Fe–B amorphous alloys. During the heat treatments the changes of local symmetry from fcc to bcc like environments occurs which increase the intensity of ferromagnetic coupling. It is known that H solubility in bcc allotrope of Fe lower than in fcc. Therefore the lower concentration of fcc like centres in glassy alloy involve lower H solubility. In the examination of cryogenic treatment the decrease of T_C^{am} was detected which contradicts to earlier explanations: the depression of T_C^{am} means dominant existence of fcc like clusters, but for lower H solubility hints to higher concentration of bcc like clusters.

On the other hand the site occupancy of atoms by H (mainly fcc environments) increases the local atomic distances. On the basis of Betehe–Slater-curve this fact results the increase of ferromagnetic coupling and the increase of T_C^{am}.

At Fe–Cr–B alloys the properties of H solubility was inherited form Fe–B systems.

5.4. Summary

As a result of magnetic measurements a new model was proposed for the cluster level building up of Fe(Ni)-based glasses which supposed the existence of two type of cluster with low and high ferromagnetic coupling. This theory is a possible interpretation for the phenomena of structural relaxation which has not been detailed interpretation yet in the references and for new effects of cryogenic treatment and H-absorption. On the basis of this theory the similarities are obvious: the three types of treatment changed the ratio of local atomic symmetries (high and low packing density) in different way and caused the modification of magnetic properties.

Though the model pointed out some disciples for the direction of the changes, but contains several contradictions. Therefore for the complete interpretation further research activity is needed in this field.

6. THESIS

1. The AC susceptibility measurement system was improved. It was completed for the suitable registration of structural relaxation process in the glassy alloys. The improvement was contained:
   - a new segment of the control program which was inserted into the previous one, therefore it became possible to define and automatically run an optional measuring and annealing program in a controlled way (possible heating and cooling rates are ±1–±255 K/min); the previous system could carry out only a heating and cooling run with a discrete heating rates [S5];
   - decrease of the fluctuation of the temperature measurement from 1°C to 0,1°C and increase of the precision from ±2°C to ±1°C.
2. Contrast to the general experiences during Curie-point relaxation, the universality (validity) of inverse relation between saturation Curie temperature (T_C^{am}) and appropriate annealing temperature of isothermal heat treatment (T_a) was questioned. In the investigation:
   - neither monotonic time dependence of T_C^{am} but a minimum (or maximum) which depended on the temperature of isothermal annealing and composition,

   - nor inverse relation between T_C^{am} and T_a but a breakpoint which position also depended on the composition and temperature of isothermal annealing (thermal history)

   could be detected in the investigated FeNi-based glassy systems ($Fe_{40}Ni_{40}Si_6B_{14}$ and $Fe_{40-x/2}Ni_{40-x/2}Cr_xSi_6B_{14}$) [S2, S4].
3. The role of low temperature (77K) cryo-treatments on the stress sensitive magnetic properties as well as on T_C^{am} were observed and explained based on the quenched-in cluster structure in these iron-based glasses ($Fe_{85}B_{15}$, $Fe_{85-x}B_{15}Si_x$, $Fe_{40}Ni_{40}Si_6B_{14}$, $Fe_{20}Ni_{60}Si_6B_{14}$). On the basis of experimental results the transition was not completed in the close range of glass transition temperature, but continued far below the room temperature without any long range diffusion. The analogy of temperature dependence of martenzitic transformation in Fe–C crystalline system was supposed. From the investigated structure sensitive magnetic properties:
   - the Curie temperature increased or decreased, which depending on composition, as an effect of previous treatment in liquid nitrogen [S6, S7, S9],
   - the coercive force and permeability increased in the examined alloys [S7].
4. It was found that previous cryogenic treatments (77 K, 24 hours) caused a significant decrease of H solubility (three times lower) in $Fe_{86}B_{14}$ amorphous alloy [S9].
5. The presence and value of dissolved hydrogen is indirectly manifested in changes of stress sensitive magnetic properties at the investigated alloy. The increase of coercive force and anisotropy was resulted by the increase of stress level caused by H solution. These changes were mainly reversible, because the connection with presence of dissolved H was obvious. At $Fe_{85}B_{15}$ and FINEMET alloys the stress level indicated by dissolved H decreased as a function of H desorption (in the same time scale): monotonic depression of anisotropy and coercive force was also found in the same time scale [S8, S9].
6. On the basis of investigations an analogy and coherence were possible found between the effect of H absorption and structural relaxation. At the examination of $Fe_{72,5}Cr_{11,5}B_{16}$ and $Fe_{75,3}Cr_{9,2}B_{15,5}$ alloys the structure sensitive Curie temperature increased versus the H dissolution and the depression of it occurred in the same time scale as H desorption [S11].

7. For the results of T_C^{am} relaxation and effect of treatment in liquid nitrogen examined in FeNi-based amorphous alloys the following interpretation is possible allowed:
   – the packing density of atoms of Fe–Ni crystalline equilibrium system inherits to the cluster structure of amorphous alloy,
   – as a result of rapid quenching formed fcc like, denser and bcc like clusters with lower packing density,
   – the fcc like clusters have lower ferromagnetic coupling therefore lower T_C^{am} also, while bcc like clusters have higher magnetic coupling and higher T_C^{am},
   – the treatment in liquid nitrogen stabilizes the fcc like clusters hence decreases the T_C^{am} of it,
   – the heat treatment (structural relaxation) increases the rate of bcc like clusters therefore the T_C^{am} of the alloys increases [S12, S13].

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