

# Similarities and Differences between the Glass Forming Mechanism in Polymers and Metallic Liquids

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**Abstract:** Survey of categorization of glass forming mechanisms in liquids based on the known principles reported in the literature is given. The metallic glass-forming liquids can be divided into two types – strong (with high glass forming ability) and fragile (with low glass forming ability). While the bulk amorphous alloys formed from strong liquids do not exhibit sensitivity to low temperature relaxation near as well as below room temperature, the glasses formed from fragile liquids contain mobile “hot points” that are active during low temperature or thermo-elastic treatments. Based on this interpretation, the structural imprints induced by treatments at liquid nitrogen (LN) temperature as well as by the absorption of hydrogen (H-absorption) are explained.

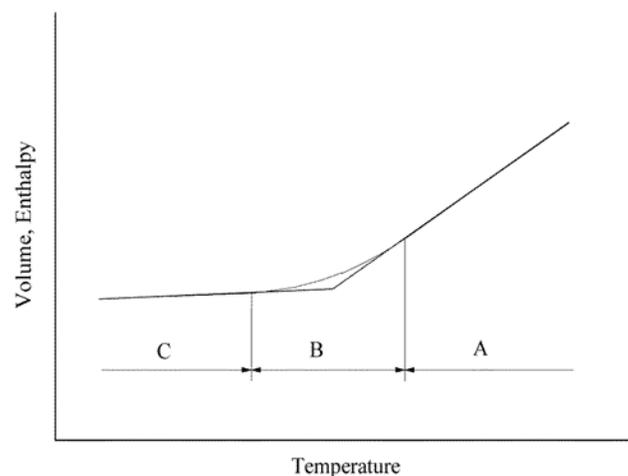
**Keywords:** Glass-forming ability, strong and fragile liquids, relaxation at low and high temperatures, glass transition ( $T_g$ ).

## INTRODUCTION

The liquid-glass transition is a general phenomenon observed in many kinds of condensed matter including inorganic, polymer or even metallic materials. The most common way of glass formation is a sufficiently fast cooling of liquids in order to avoid crystallization. Though the phenomenological background of glass formation is known in the above-mentioned (chemically different) liquids, at molecular level mechanisms leading to glassy state can differ in supercooled liquids and also the factors determining the glass forming ability (GFA) may exhibit a great variety in the different types of liquids.

In this contribution some special features of supercooled (metastable) liquids and the resulting glass transition phenomena will be briefly discussed based on the information available in the literature. Subsequently some specific relaxation phenomena in metallic liquids and glassy state will be treated and related to their glass forming ability (GFA). In order to enhance the comparison of atomic (molecular) level dynamics in supercooled liquids, the schematic illustration of the degree of supercooling in the liquid leading to the glassy state is given in Fig. (1). based on Ref. [1], where the relation between the supercooled liquid and the glass is illustrated. The basic extensive thermodynamic properties such as volume (V) and enthalpy (H) can be seen versus the temperature (heating or cooling runs). In section “A” the system has no history. It means that the values of H or V do not depend on the direction of temperature change, i.e. the system is ergodic except with respect to the crystallization. This can

be understood in terms of basic kinetics, taking into account, that the typical relaxation times (the time-scale of elementary atomic displacements) are in the range of  $10^{-14} < t < 10^{-9}$  s [2] in this temperature interval, i.e. they are shorter by orders than the typical time-scale of observation (experiment). In this respect, the concept of „relaxation” has basic significance, because it already hints to the dynamic characterization of the supercooling. Generally relaxation contains the atomic level displacements leading to the restore of ergodic state after a given perturbation (e.g. a small temperature change). As the relaxation time increases due to the significant slow down of diffusion (at around  $1.2 T_g$ ), the change of H or V can be already noticed during the observation (experiment, section B). In the section C the system is totally frozen.



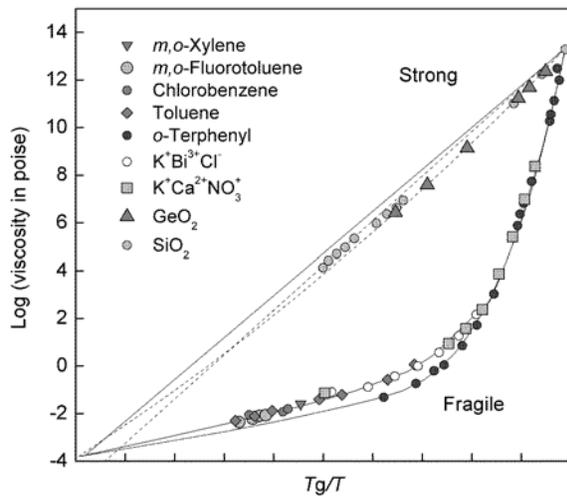
**Fig. (1).** Illustration of the phenomenology of glass formation based on Ref. [1]: In A section: the system is in internal equilibrium, in B relaxation during the experiment, in C is totally frozen.

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## SUBJECT

### Temperature Dependence of Viscosity During the Supercooling

The temperature dependence of viscosity  $\eta(T)$  as macroscopic property can be used for the phenomenological description of dynamic phenomena behind the supercooling. When  $\eta(T)$  is well described by the Arrhenius functionality:  $\eta = A \exp [E/(T-T_0)]$ , where  $A$  is constant, and the activation energy  $E$  is constant over the whole temperature range between the equilibrium melting point and the glass transition temperature  $T_g$ , high GFA is observed (for strong liquids, which are very stable against the crystallization). Typical example is the molten silica glass, in which predominantly tetrahedrally coordinated units are the structural basis of the material both in molten and frozen state. The dominant type of bonding is covalent (see Fig. 2) [3].

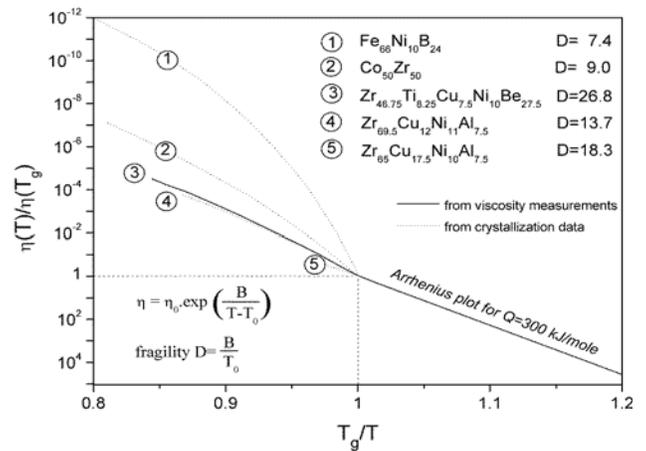


**Fig. (2).** The comparison of  $\eta(T)$  for “strong” and “fragile” glass forming liquids [3].

In contrast,  $\eta(T)$  dependence cannot be described by a single activation in the “fragile” liquids. The Vogel-Tammann-Fulcher type of equation ( $\eta = \eta_0 \exp[B/(T-T_0)]$ ) often holds and gives  $\eta(T)$  change of 2-4 orders of magnitude. As a consequence, the viscosity exhibit more pronounced slow-down close to the  $T_g$  in these liquids. As the resistance to crystallization strongly depends on the  $\eta(T)$ , the GFA in the supercooled melts is categorized according to the outlined approximation. Strong liquids resist to crystallization (high GFA), GFA of „fragile” liquids is low (see Fig. 2).

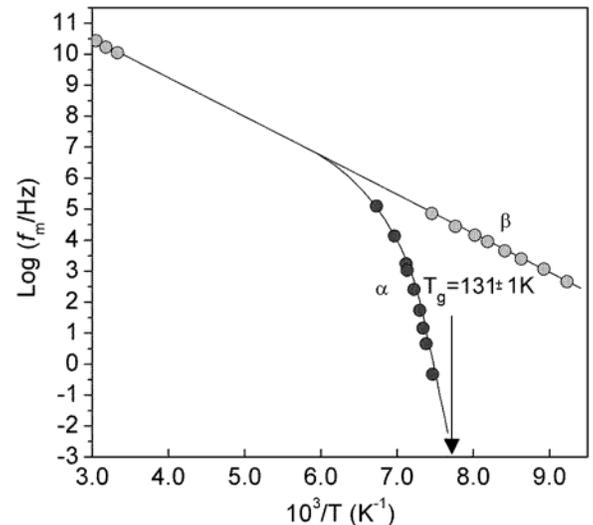
In Ref. [4], the fragility parameter for various glass forming metallic melts was introduced, based on viscosity measurements and crystallization data. In Fig. (3) can be seen that glassy alloys can be formed from both types of liquids: FeNi-based or CoZr melts are “weak” (with low GFA), while certain multi-component liquids belong to the strong liquid types with high GFA (bulk amorphous alloys) [5]. The deviation from Arrhenius-type viscosity dependence (small value of  $D=B/T_0$  fragility parameter) indicates low GFA.

The various forms of atomic motion (which is collectively known as “relaxation”) are responsible for the actual, macroscopic shape of  $\eta(T)$ , i.e. diffusive, rotational motions are the collective background for the actual shape of viscosity. At sufficiently high temperatures (small supercooling, in



**Fig. (3).** The  $\eta(T)$  for metallic melts with varying GFA [4].

the vicinity of melting point) a single relaxation mechanism can be observed only, as it is illustrated in the Fig. (4) [6] (peak of dielectric relaxation frequency). At higher supercooled regime, the peak of dielectric relaxation frequency can split into slow ( $\alpha$ ) and fast ( $\beta$ ) relaxations in which  $\alpha$ -processes exhibit non-Arrhenius temperature dependence and vanish at  $T_g$ . The  $\alpha$ -type relaxation can be discovered in different classes of glass forming liquids and attributed to the structural changes in the liquid [7].



**Fig. (4).** Temperature dependence of the peak dielectric relaxation frequency of the glass-forming mixture of chlorobenzene/cis-decalin. At a high temperature range there is a single relaxation mechanism, lowering the temperature, the peak splits into slow ( $\alpha$ ) and fast ( $\beta$ ), of which  $\alpha$ -processes exhibit non-Arrhenius temperature dependence and vanish at  $T_g$  (adopted from Ref. [6]).

The essence of these structural changes is the beginning of decoupling between various forms of motions, and the decreasing of translation displacement of certain atomic types or molecules [8]. At the same time, the existence of “long lived structures” appears in the supercooled melts, which indicates the spatial separation of the various atomic motion types [9,10].

The fast relaxation ( $\beta$ ) occurs at much higher frequencies than the  $\alpha$ -processes (Fig. 4).

### Bonding and the Elementary Relaxation Steps in Various Glass-Forming Melts

In the liquid state of network glasses there is only one dominant type of bonding - covalent. It is assumed that the single type of bonding is responsible for the single value of activation energy in the  $\eta$  (T) dependence, i.e. the break and the restore of individual Si-O (Ge-O) covalent bonds are the basis of this single activation energy. As a consequence, no abrupt change appears in the viscosity, when the T is lowered. The strong covalent character is also present in certain metallic melts mainly in those, from which the "bulk amorphous alloys" are formed. For the enhancement of crystallization the admixture of 2-3 metalloid types (as glass formers) is often added simultaneously [5]. The metallic conductivity is also maintained partially by the pronounced participation of d-electrons.

In fragile liquids (polymer and metallic liquids) two dominant types of bonding exist. For example within the individual molecules of o-terphenyl covalent bonding exists. The molecules exert largely non-directional, dispersive forces on each other [6] (fragile liquid).

In contrast to polymers or network glasses, the glassy alloys are composed from metallic atoms as well as glass forming (metalloid) elements. However, the distribution of hetero-atoms is not random, and preferential chemical bonding is developed between the transition metallic host atoms and the metalloids, leading to the development of local coordination and symmetry [11], i.e., associations between hetero-atoms are developed in the melt which can be also expressed by thermodynamic considerations introduced by Predel *et al.* [12].

$$\Delta H = \Delta H_{reg} + \Delta H_{ass} A_j B_j$$

The total heat of formation,  $\Delta H$  consists of the heat of formation ( $\Delta H_{reg}$ ) obtained from the regular solution model and the extra stabilization energy ( $\Delta H_{ass}$ ) arising from the atomic interactions within the associates.

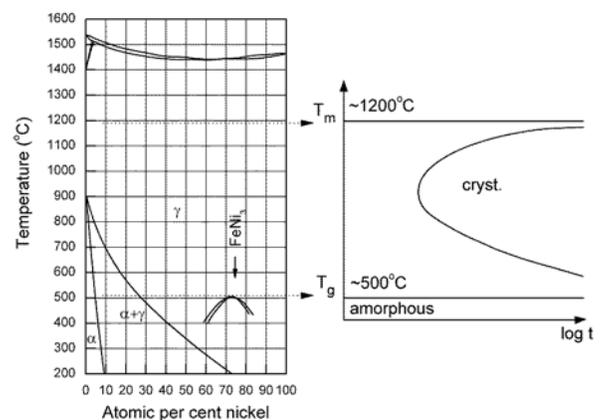
According to this conception the formation of associates contributes by an extra stabilization (extra formation enthalpy) to the whole heat of mixing.

Another special feature of these melts is that bonding between two metal atoms in a supercooled liquid state is stronger than the traditional dispersive forces or even stronger hydrogen bonds.

Due to the spatially varying strength of atomic interactions, the atomic motion in liquid state is performed mostly in the cooperative way. It means, that splitting and recombination of bonds take place simultaneously, i.e., the motions are the superposition of oscillations and translations. [13]. Close to the equilibrium melting point, (when the supercooling is small), the relaxation times arising from various motions cannot be distinguished, so apparently a single relaxation process is observed only. Lowering the temperature, the relaxation peak splits into slow ( $\alpha$ ) and fast ( $\beta$ ) processes,  $\alpha$ -processes exhibit non-Arrhenius temperature dependence and vanish at  $T_g$ . This splitting is quite general in various types of fragile liquids. Hence, this basic phenomenon can serve as an argument for the explanation of several

relaxation phenomena in the metallic glassy state taking place well below the glass transition temperature.

Based on the general structural characteristics of fragile liquids, the dynamic phenomena in Transition Metal(TM)-Metalloid(M) melts can be described as follows: the liquid consists of compound-like associates in which the ratio of (TM/M) is similar to the (stable or metastable) intermetallic compound in solid state. The bonding in these clusters is covalent. The bonding strength itself in these clusters is locally higher than the average (bulk) cohesive force in the melt. It is expected, that such clusters are formed at around 0.8 melting temperature of the alloy, as it is schematically illustrated in Fig. (5). Though these cluster units are relatively stable, they behave dynamically especially at high temperatures (low supercooling) that involves breaking and recombination of bonds. The frequency of this recombination decreases rapidly as the temperature is lowered. One can assume that such elementary steps are the basis of slow ( $\alpha$ ) relaxation in TM-M melts. It is also expected, that the size of these units increases approaching the typical dimension of medium range order [14]. As the frequency of elementary  $\alpha$ -relaxation steps breaks down rapidly with the increasing supercooling, the  $\alpha$ -processes disappear at the  $T_g$ , forming the stable skeleton of the glass. In contrast, relatively weak bonding exists within molecular units beyond the compound-like clusters, with relatively high internal mobility (solid solution-like regions). These molecular-level regions would be the centers of fast ( $\beta$ )-type of relaxation. The form of atomic displacements can be collective in nature. The driving force has a stability difference between the fcc and bcc allotropes, determined by the Fe-host metal. Such transformations resemble corresponding symmetry changes in crystal-line state (see Fig. 5). Hence, these liquids are spatially heterogeneous, including both immobile and mobile regions, being the bases of  $\alpha$  and  $\beta$  processes separated in space [14].



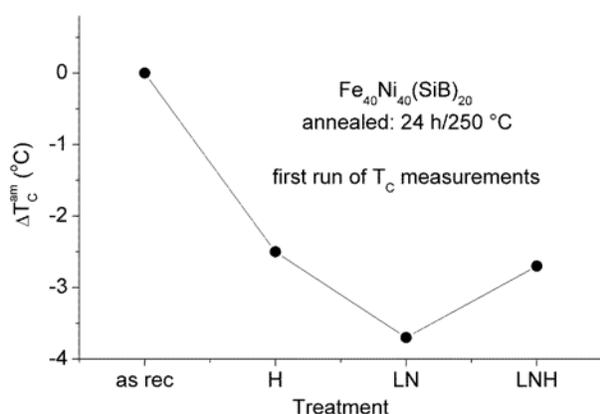
**Fig. (5).** The equilibrium diagram of Fe-Ni system together with the proposed cluster formation in the supercooled melt, together with the schematic TTT diagram for crystal growth in the frozen FeNiSiB glass [12]. The temperature range of  $T_g$  line is approximately 500 °C in this alloy.

### Experimental Indications for the Low Temperature Relaxations in Metallic Glasses Formed from Fragile Liquids (Relaxation Below Room Temperature)

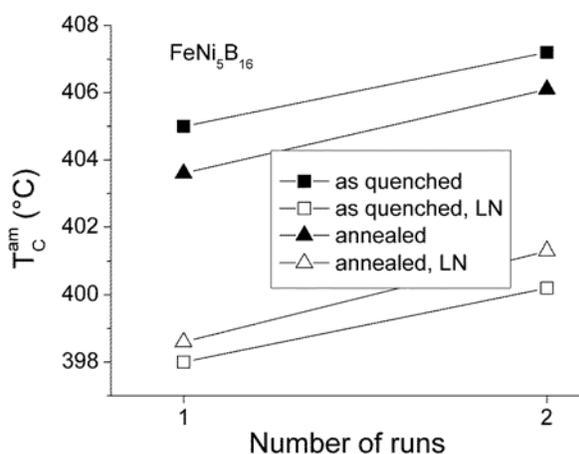
As was mentioned above in contrast to strong liquids from which the network glasses are formed, fragile liquids

contain different types of bonding and their GFA is lower. In these liquids strong bonds are represented by the TM-M contacts resembling covalent (directional) bonding. The other (metallic) types of bonding resemble rather dispersive forces, enabling higher local, or collective atomic mobility, as well as symmetry change within the clusters. Such mobile regions can easily transform *via* small atomic displacements. The origin of activation can be either thermal or induced by a stress field. Local stresses can also be induced by H-sorption. The local high mobility of constituent atoms or atom-groups is the dynamic background for the irreversible or reversible structural relaxations in these glasses well below the  $T_g$  (hot points) [6].

Typical experimental results are summarized in Figs. (6 and 7). The shift of  $T_C^{am}$  is shown in Fig. (6) compared to the “as rec” state (which is previously stabilized by heat treatment at 250 °C).



**Fig. (6).** The shift of amorphous Curie temperature ( $T_C^{am}$ ) of  $Fe_{40}Ni_{40}(SiB)_{20}$  sample caused by various treatments (the samples were previously stabilized at 250 °C, for 24 hours).



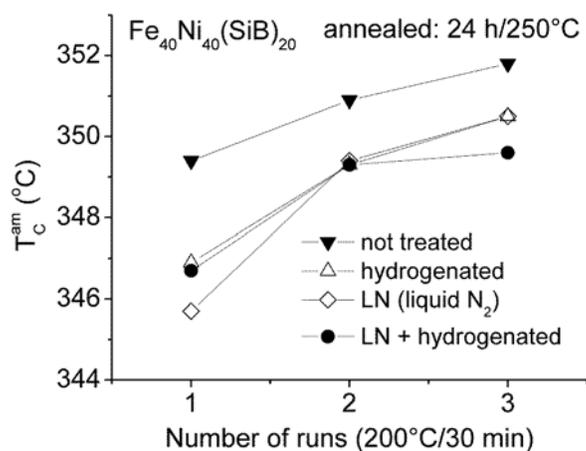
**Fig. (7).**  $T_C^{am}$  of  $Fe_{78}Ni_6B_{16}$  sample in as quenched state and after heat treatment during two subsequent measuring runs. Both kinds of samples were treated at LN temperature.

$T_C^{am}$  depression was detected after H saturation and/or after the low temperature treatment (LN), in  $FeNiSiB$  and  $FeNiB$  glasses. The  $T_C^{am}$  depression is typical in the case of Ni-containing samples. The role of pre-annealing can be deduced from Fig. (7). One can see that the previous annealing can slightly modify the effect of LN treatments. Never-

theless, this kind of treatment causes surprisingly stable structural imprint in the samples in agreement with Ref. [15]. This stability hints to the origin of this imprint. One can expect that this imprint originates predominantly in the high temperature range (around the glass transition) and can be eliminated only by high temperature treatments near the  $T_g$ . This is also supported by the recent observation being reported in Ref. [16], namely, that low temperature (LN) annealing has influence even on crystallization mechanism in these glasses. This influence is strong in fragile liquids (weak glass formers) in which high cooling rate has to be applied to achieve the glassy state (in order to avoid the crystal nuclei formation from the supercooled liquid state). The essence of our argument is, that these low temperature transformations belong to the glass transformation, which is not necessarily completed in every detail at  $T_g$ . In this respect the glass transition resembles the martensitic transformation, which covers a wide temperature range and, will be completed only at lowered temperatures under certain cooling conditions and compositions. This is the case of fragile metallic liquids, or strong melts when very high cooling rate is applied (see further text).

### Comparison of Thermal and H-Absorption Induced Effects

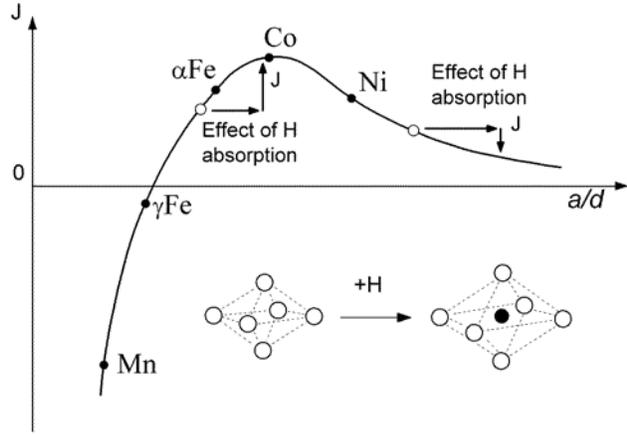
In the Figs. (6 and 7) we focused solely on the  $T_C^{am}$  shift as a specific phenomenon caused by the low temperature treatments. In the Fig. (8) combined effects are summarized, which are observed after saturation of  $FeNiSiB$  samples with hydrogen and/or, previously immersed in LN for 24 hours. After completion of these treatments, the  $T_C^{am}$  were measured during 3 subsequent runs. The following conclusions can be drawn:



**Fig. (8).** The  $T_C^{am}$  values for heat treated  $Fe_{40}Ni_{40}Si_6B_{14}$  samples being previously LN-treated or/and charged electrolytically with H.

1. The  $T_C^{am}$  is lowered due to both of treatments
2. The stability of imprints is surprising: though sample heating up to 350 °C is involved in the cyclic measurements, the imprints cannot be fully suppressed by the repeated heating itself; the H-absorption was performed at room temperature (electrolytic saturation). The activation energy of H-diffusion is lower by several orders than that for the self diffusion of either matrix elements [17], which is also supported by ex-

perimental verification reported in [18]. The complete collapse of imprints is expected on this basis. One can conclude, therefore, that duration of imprints is independent on the residence time of H-atoms in the glassy host. The possible mechanism of H-induced  $T_C^{am}$  lowering can be qualitatively explained on the basis of Fig. (9).



**Fig. (9).** The local H-induced expansion in cluster level and the connected change in the exchange integral ( $J$ ) in the case of pure fcc symmetry Fe-environments (left side of the BS curve) and in Ni containing fcc symmetries (right side of the BS curve).

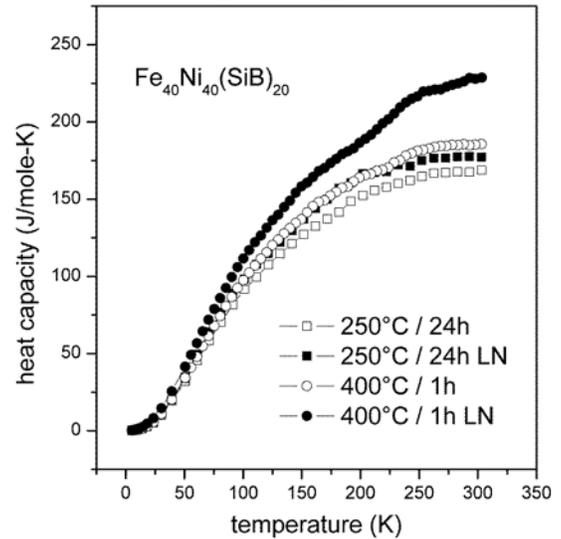
In the spirit of Bethe-Slater conception, the strength of ferromagnetic exchange depends sensitively on the atomic distances, which is expressed by the sign and magnitude of exchange integral (see Fig. 9). The abrupt change in the sign of  $J$  with increasing atomic distance is typical for the Fe, (decreasing packing density during bcc to fcc transformation). The tendency is opposite in the case of Ni (fcc type of crystal structure). As the H site-occupation is preferential in fcc environments [19], and Ni atoms occupy first coordination sphere, the decrease of  $J$  is expected. Hence, the local volume expansion within the fcc-like clusters would be the structural background of magnetic response to the H-absorption. The time-decoupling of H-mobility and the displacements of matrix atoms is the basis of the thermal stability of  $T_C^{am}$  shift.

It was also reported, that LN-induced imprints has also some manifestation in the thermal properties [16].

An additional example is presented in the Fig. (10), supporting this observation. The temperature dependence of specific heat is influenced by low temperature treatment. The  $C_p$  of LN treated sample is higher and, the difference the two samples increases with rising temperature in the temperature range between 4.2 and 300 K.

Based on these observations one can conclude, that LN treatment induced  $T_C^{am}$  shifts are coupled with structural rearrangements in the scale of atomic short range order. Following the previously outlined arguments, one should keep in mind the similarity of glass transition and the martensitic transformation. This similarity allows assumption, that glass transition is not fully completed in this alloy at  $T_g$  (at around 500 °C, see Fig. 5), but a small fraction of “mobile” hot points are entrapped together with the compound-like disordered skeleton. These “mobile” centres are essentially a mix-

ture of fcc/bcc solid solution-like clusters, in which volume-forced symmetry changes may occur when the temperature further decreases.



**Fig. (10).** Heat capacity of  $Fe_{40}Ni_{40}Si_6B_{14}$  glassy samples with and without LN treatments. Previously the samples are subjected to isothermal heat treatments at 250 C.

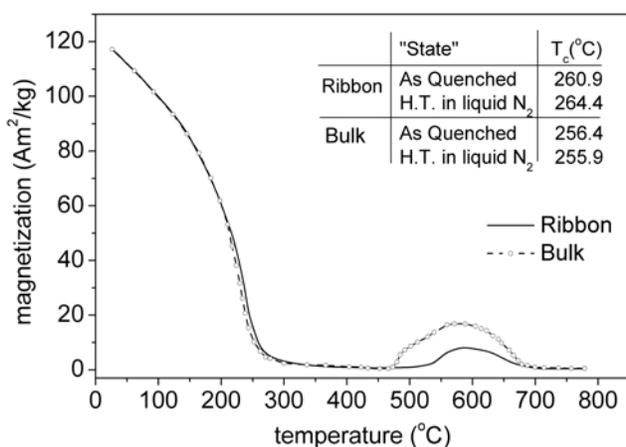
The direction of symmetry change is influenced by the rate of liquid quench, as well as by the sign of temperature change during the relaxation heat treatments. The relation between the stability range (temperature domains) of bcc and fcc environments and the  $T_g$  determine the direction of  $T_C^{am}$  shifts during the “low and “high” temperature relaxations. One can consider, that a given ratio of fcc/bcc environments which are frozen at  $T_g$ , being expressed by

$$\left( \frac{[Fe, Ni(B)]_{bcc}}{[Fe, Ni(B)]_{fcc}} \right)_{T_{anneal} \cdot v_{quench}}$$

can be shifted into the direction of fcc enrichment, due to the thermal contraction, when the sample is further cooled from 300 K to 78 K. However, the bcc symmetries are thermodynamically favoured. Therefore when the sample is heated again the transformation proceeds in opposite way. Accordingly, higher activation energy is consumed to overcome the volume-forced compression, which is developed during the cooling process (extra dilatation increment is assumed during the re-heating)

The bulk amorphous alloys are formed from multi-component, (strong) melts, in which the GFA is high. The metalloid content is usually high; several intermetallic compound phases exist in the equilibrium crystalline state. Due to the high metalloid content, the overall bonding state resembles that in the extended network (oxide) glasses. Though the necessary critical cooling rate for the achievement of glassy state is low, these melts can be cooled by high cooling rates as well. The considerable heat conductivity makes possible the preparation of thin ribbons from these melts. The actual cooling rate in this case is by an order higher than during the formation of bulk samples during die-casting of the same melt (in this case the sample thickness is between 1-1.5mm) [20]. Two interesting facts can be ob-

served in Fig. (11). The LN treatment induced  $T_C^{\text{am}}$  shift is higher at the rapidly cooled (ribbon shape) samples, i.e. when the samples were prepared by high cooling rate, the glassy state is more sensitive to the low temperature treatments, than using bulk sample. This indicates again, that the “quenched in” hot points (mobile regions) - which are active during the low temperature transformation - are entrapped from the supercooled liquid around the  $T_g$ , or even at higher temperatures. Another interesting observation is the shape of thermomagnetic curves around the amorphous phase decomposition which exhibits significant difference in the bulk and ribbon-shaped samples. The possible origin is the different cluster structure in as quenched state, leading to various decomposition mechanism of the amorphous sample.



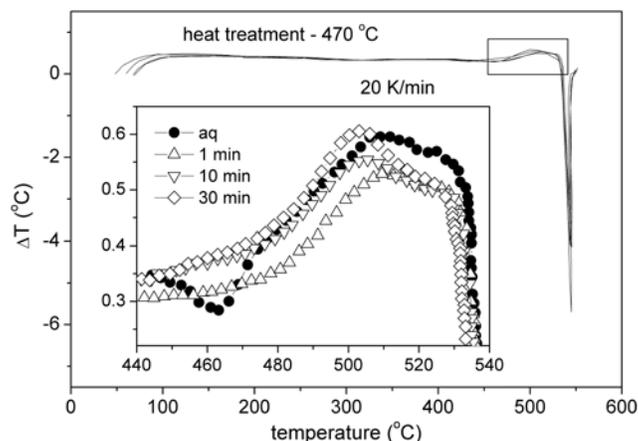
**Fig. (11).** Thermomagnetic curves for the as-quenched ribbon and bulk samples  $\text{Fe}_{70.7}\text{C}_{6.7}\text{P}_{10.4}\text{B}_5\text{Si}_{1.1}\text{Mn}_{0.1}\text{Cr}_2\text{Mo}_2\text{Ga}_2$  alloy. In the inset also the Curie temperature obtained after undercooling in liquid nitrogen is given.

The insensitivity of (slowly quenched) bulk amorphous state manifests itself also in the negligible response to the high temperature heat treatments, which has generally significant benefit to the magnetic softening of amorphous alloys. It was reported [21] that by applying heat treatments below the  $T_g$  (400 °C) only negligible improvement of the soft magnetic properties is achieved. This result also supports the assumption that “hot points” - which are responsible for the low temperature structural or magnetic activity - are not present in the slowly cooled samples. The quenched-in structure is very stable in these bulk samples, and it is not influenced by the heat treatments below  $T_g$ , as it is illustrated in Fig. (12), where the DSC traces are plotted for the sample of  $\text{Fe}_{70.7}\text{C}_{6.7}\text{P}_{10.4}\text{B}_5\text{Si}_{1.1}\text{Mn}_{0.1}\text{Cr}_2\text{Mo}_2\text{Ga}_2$  bulk amorphous alloy in the vicinity of glass transition temperature after various heat treatments.

Fig. (12) shows that detectable changes in the structure occur when the temperature of heat treatment approaches the endothermic part of DSC traces, which indicates again stability of this sample against atomic displacements at low activation energies.

## SUMMARY

The glass forming metallic liquids can be divided into two types - strong and fragile which possess high and low glass forming ability, respectively. In the alloys formed from



**Fig. (12).** The details of DSC traces in the sample of  $\text{Fe}_{70.7}\text{C}_{6.7}\text{P}_{10.4}\text{B}_5\text{Si}_{1.1}\text{Mn}_{0.1}\text{Cr}_2\text{Mo}_2\text{Ga}_2$  bulk amorphous alloy in the vicinity of glass transition temperature after various heat treatments.

fragile liquids by applying high cooling rate, mobile atomic environments (hot points) are entrapped. These environments are sensitive to low temperature treatments at LN and also to the formation of H-induced stresses. The similarities and differences in the properties associated with low temperature relaxation, such as the LN treatments and the H-absorption, were analyzed.

It was found that both the low temperature treatment and the H-absorption bring about stable structural imprints in the glassy state, which cannot be eliminated even at around the  $T_C^{\text{am}}$  ( $\sim 350$  °C) of these glassy alloys. It is therefore expected that hot points are entrapped in the glassy structure even beyond the glass transition temperature.

In this respect, significant difference exists between the alloys formed from liquids with high and low GFA. Alloys formed from the liquids with high GFA (prepared using low cooling rates) are not sensitive to the low temperature treatments.

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