

## FORMATION TENDENCY IN TRANSITION METAL BASED LIQUIDS AND SOME RELATED PROPERTY CHANGES IN GLASSY STATE

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### 1. Thermodynamic and kinetic aspects of cluster formation in the supercooled melts of Fe(TM)-M alloys: relation between glass-forming ability and cluster formation tendency

Thermodynamic description of cluster formation in metallic melts was reported in Ref. [4], It is based on the regular solution model, supposing also the associates formation in glass forming liquids. (eq. 1.)

$$\Delta H = \Delta H^{reg} + \Delta H_{A_i B_j}^{as} \quad (1)$$

The entire mixing enthalpy of alloy formation ( $\Delta H$ , which can be directly determined by calorimetry), consists of two terms:  $\Delta H^{reg}$  which is the consequence of preferential interaction between hetero-atoms A and B, (components) and,  $\Delta H_{A_i B_j}^{as}$ , arising from the additional interaction between the atoms within associates. This term describes the extra stabilization of the melt compared to the prediction of regular solution model.

Accordingly, the cluster formation is responsible for the additional stabilization of the melt, hindering the crystalline nuclei formation. Besides the outlined thermodynamic consideration, the kinetic background should also be taken into account (the overall

temperature dependence of translational and rotational mobility of constituent atoms). The diffusion mobility, which is also necessary to the critical crystalline nuclei formation is increasingly hindered, with increasing supercooling.

The macroscopic characterization of translational mobility is described by the temperature dependence of viscosity  $\eta(T)$  according to [5]:

$$\frac{1}{\eta} = \lambda^2 \cdot \frac{A}{l \cdot k \cdot T \cdot k_0} \quad (2)$$

( $A$ : constant;  $k$ : Boltzmann constant;  $T$ : absolute temperature;  $l$  and  $l$ : molecular level distances; and  $k_0$ : rate constant).

The components distribution between the coexisting clusters play an important role in the actual temperature dependence of atomic level mechanism.

Two basic types of T-dependence is known. In the Arrhenius-relation:

$$\eta = A \cdot e^{\left[ \frac{E}{k_B \cdot T} \right]} \quad (3)$$

( $E$ : activation energy;  $k_B$ : Boltzmann's constant;  $A$  and  $E$ : temperature independent) single activation energy ( $E$ ) is supposed over the whole temperature range of supercooling (SiO<sub>2</sub> liquid) [5]. Such temperature dependence is typical for "strong liquids", in which the bonding type is dominantly covalent. with dominant covalent bonding character. The single activation energy ( $E$ ) over the whole temperature range indicates the constant liquid structure over the whole temperature range (the SiO<sub>2</sub> liquid [5]). Such liquids exhibit high glass forming ability( GFA) (see Fig. 1.)

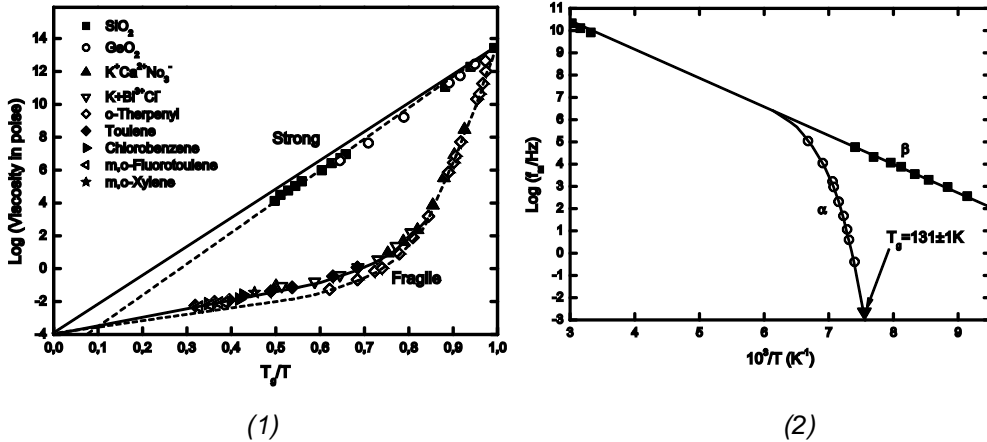
In contrast, Vogel-Fulcher type  $\eta(T)$  dependence is typical in "fragile liquids":

$$\eta = A \cdot e^{\left[ \frac{B}{T - T_0} \right]} \quad (4)$$

The  $B$  is constant within a restricted temperature range only i.e., activation energy is not constant between  $T_{\text{melt}}$  and  $T_g$ ). The viscosity exhibits more pronounced slow-down as  $T$  approaches to  $T_g$ . The GFA is weak in these liquids (see Fig. 1.). Most of glass-forming metallic liquids belong to this category [6]. Two or more bonding types co-exist in these liquids. Consequently, the temperature dependence of atomic displacements is also different. At temperatures close to the melting temperature the frequency range is typically  $10^{13}$ - $10^{14}$  for all kinds of displacements. The change of dielectric relaxation frequency is applied for the monitoring of temperature dependence of displacements, as it is depicted in Fig.2. [7]. In high temperatures, single relaxation peak is visible only, and this peak splits into slow ( $\alpha$ ) and fast ( $\beta$ ) processes as the temperature decreases.

A marked separation of ( $\beta$ ) and ( $\alpha$ ) processes is typical in fragile liquids, showing the increasing difference between the characteristic time-scales of relaxation steps. There are experimental evidence for the spatial separation of two types of processes [8],

which are the clusters itself, in which the time-scale of elementary relaxation steps differ according to the local bonding strength between the constituent atoms.



**Fig. 1** The comparison of  $\eta(T)$  for “strong and “fragile” glass forming liquids (adapted from Ref.[1])

**Fig. 2** Temperature dependence of the peak dielectric relaxation frequency of glass-forming mixture of chlorobenzene/cis-decalin. ( $\alpha$ -process exhibits non-Arrhenius temperature dependence and vanish at  $T_g$  (adapted from Ref.[7] )

## 2. Bonding and relaxation mechanism in metallic, glass-forming melts.

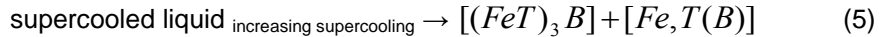
On the analogy of dynamic phenomena in fragile polymer liquids, described in [1,2,7, 8], the concept of fragility (based on the co-existence of various bonding types) is extended to transition metal Fe-(TM)-Metalloid (M) melts.

Besides the dominant metallic behaviour, the partial covalent bonding character is also typical in these liquids, which is inherited from metalloid components (B, Si). Metallic character (electrical and heat conductivity) arises from the d-electron participation in the conduction band.

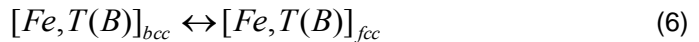
The distribution of metalloid atoms is not random however, but preferential chemical bonding is developed between the TM and M atoms already in the liquid state. (chemical short range order CSRO) [9].

The time-scale of relaxation inside the covalent-like environments increases more rapidly than in the rest of liquid volume. This kind of relaxation assumed to be as  $\alpha$ -like (Fig.2.). As the atomic displacements are slowing down more rapidly the  $\alpha$ -processes vanishes at around the  $T_g$  freeze to solidified skeleton. The essence of cluster formation mechanism is the gradual separation of covalent, and solid-solution-like clusters within the liquid.

The local composition (TM/M ratio) in the compound-like associates is close to that in the Fe<sub>3</sub>B metastable intermetallic compound. The scheme of cluster separation in Fe-B liquid is the following: (5)



The local interatomic bonding is weaker (so the atomic mobility is higher) beyond the compound-like clusters (solid solution-like environments). Such atomic environments are considered as the centers of fast ( $\beta$ ) processes. The driving force for the short range atomic displacements is inherited from the  $\alpha$ - and  $\gamma$ -allotropes of Fe host metal. Such displacements have an outstanding role below the  $T_g$ , according to the scheme:



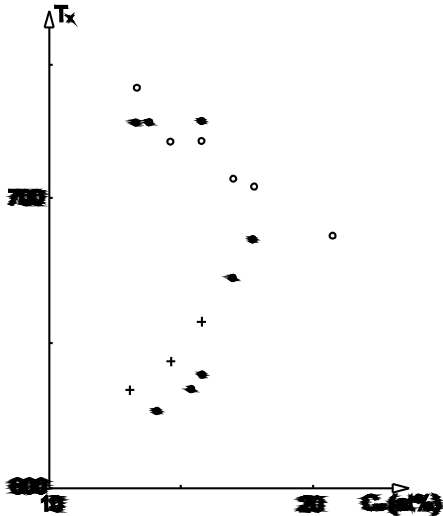
### 3. Alloying effects in the thermal and magnetic properties of Fe(TM)-B glasses as cluster manifestation

The high-resolution electron microscopy (TEM) can supply direct information on the cluster-level organization in the glassy structure [10]. In the physical properties of hypo-eutectic TM-M glasses, several indirect manifestation of cluster structure can be recognized. Thermal and magnetic properties of Fe-B binary glasses, when the concentration of metalloid (B) is changed or, when host metal is partially replaced by another transition elements (constant metalloid content).

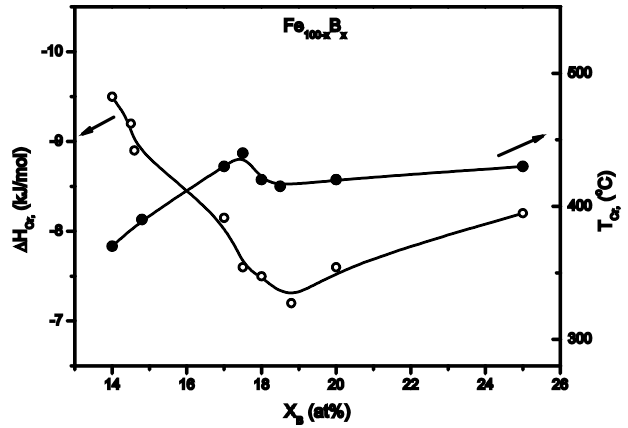
The crystallization mechanism in the hypo-eutectic Fe-B glasses is a good example [9].

- I.  $am\text{-FeB} \rightarrow \alpha\text{-Fe} + am^1\text{-Fe}_{75}\text{B}_{25}$  (composition of the remainder amorphous phase)
- II.  $am^1\text{-Fe}_{75}\text{B}_{25} \rightarrow \text{Fe}_3\text{B}$
- III.  $\text{Fe}_3\text{B} \rightarrow \alpha\text{-Fe} + \text{Fe}_2\text{B}$ .

The difference between the onset of crystallization temperatures for the steps I. and II. increases with lowering of B-content.(Fig.3). After the end of  $\alpha$ -Fe precipitation (I. step) the remainder amorphous phase transforms to a metastable ( $\text{Fe}_3\text{B}$ ) crystalline compound, which is metastable. The  $C_B$ -dependence of crystallization enthalpy provides more detailed information (Fig.4.). The total  $\Delta H_{\text{cryst}}$  rapidly increases in the hypo-eutectic range (with decreasing B-content), indicating, that contribution of am-[Fe,T(B)]-(solid solution-like) cluster has dominant contribution to the accumulation of total, "quenched-in" excess energy.



(3)



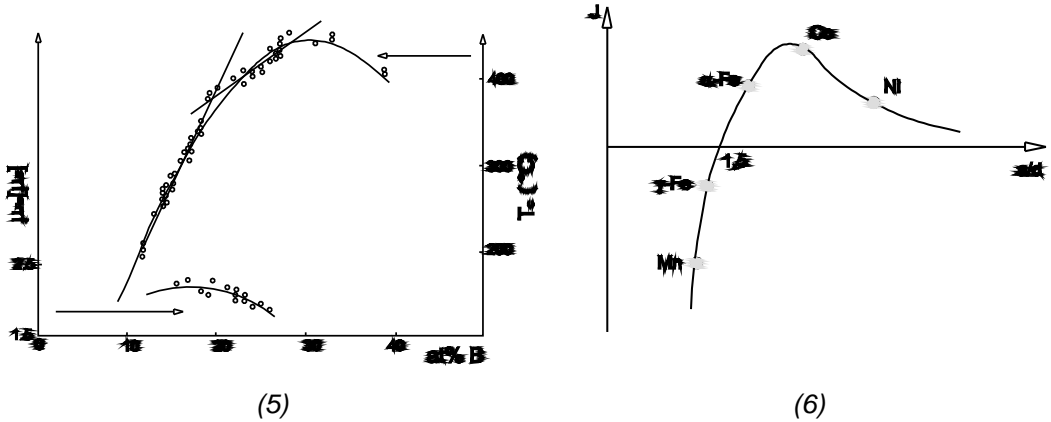
(4)

**Fig. 3** Two-step crystallization in hypo-eutectic Fe-B glasses as a function of B-content  
**Fig. 4** Crystallization enthalpy and temperature versus B-content in binary Fe-B glasses

It is assumed, that localized fcc-centers are entrapped during the liquid quench and contribute to the stored excess energy in the glass, and appears as a fraction of crystallization enthalpy.

#### 4. The extra-ordinary $C_B$ -dependence of amorphous Curie temperature ( $T_c^{am}$ ) and saturation magnetization ( $M$ ) as cluster manifestation

Both the  $T_c^{am}$  and the magnetic moment ( $M$  per Fe atom) decreases in the hypo-eutectic range (decreasing concentration  $C_B$ ). This tendency also confirms the existence of hidden fcc-Fe environments, in which the local ferromagnetic coupling between Fe-atoms is weak [11]. According to the itinerant electron-structure model [12], such concentration dependence of  $T_c^{am}$  is not expected. This contradictory behaviour can be understood on the basis of fluctuating local atomic volume in the hypo-eutectic glass (see Fig. 5.). This fact supports the possible co-existence of anti-ferromagnetic and ferromagnetic couplings between neighbouring Fe atoms due to the local changes in the packing density in the hypo-eutectic region of glassy Fe-B. As the number of “dense centres” (“compressed” cluster-types) increases with decreasing B-content, a continuous slow-down of the  $T_c^{am}$  and the  $\mu_{Fe}$  is observed. The breakdown of ferromagnetic couplings is in agreement with the Bethe–Slater-expectation. [13].

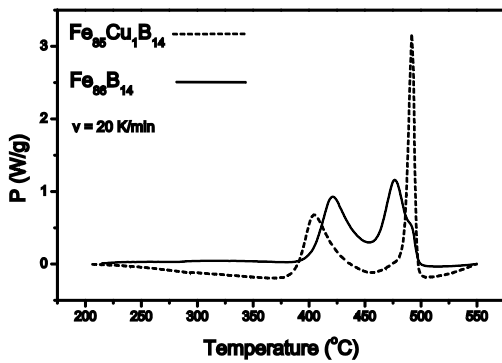


**Fig. 5** The concentration dependence of amorphous Curie temperature ( $T_C^{am}$ ) and  $mFe$  in glassy Fe-B alloys

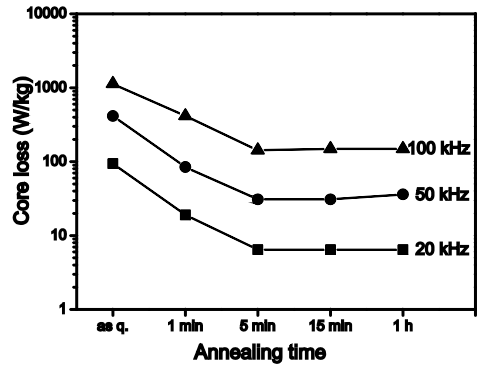
**Fig. 6** The Bethe–Slater-curve representing the variation of the exchange integral  $J$  with interatomic spacing  $a$  and radius  $d$  of the unfilled  $d$  shell, [13]

## 5. Cluster manifestation in the mechanism of amorphous-nanocrystalline transformation (Finemet alloys)

The excellent magnetic softness in nano-crystalline alloys is attributed to the coincidence between the magnetic correlation length and the grain diameters, leading to the average out of crystal anisotropy within the scale of magnetic correlation length in these alloys (which is typically of 100nm). Though, not all types of amorphous-nanocrystalline transformation result in excellent magnetic softness. The ultra-soft magnetic properties are developed only in those systems, in which nanocrystalline assemble is developed via primary crystallization [14]. Nucleation mechanism, as well as nucleating element have an outstanding significance in this process. The mechanism of Cu-enhanced nucleation in  $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$  precursor alloy is interpreted also as cluster phenomenon. The previously outlined two-step crystallization mechanism in hypoeutectic Fe-B glass, is regarded as the master-type of transformation. The addition of nucleating element has two-fold significance in this two-step crystallization mechanism, as shown in Fig. 7. The Cu addition plays an active role in the pronounced peak-separation belonging to the  $\alpha$ -Fe and  $Fe_3B$  formation [15]. The suppression of  $Fe_3B$  crystalline phase formation is highly desirable to avoid magnetic hardening.



**Fig.7** DSC-thermogram for the decomposition of hypo-eutectic  $FeB_{15}$ ,  $FeB_{14}$  and  $FeB_{14}Cu_1$  glasses [15]



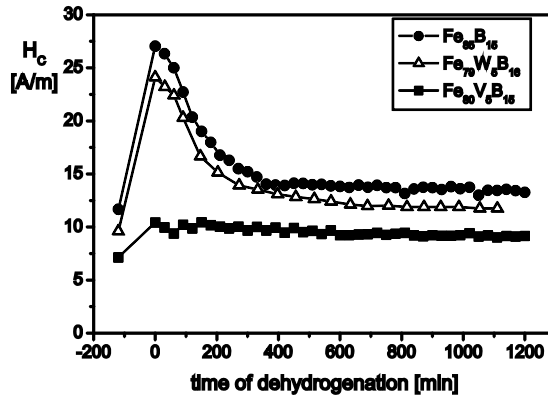
**Fig.8** The change of magnetic loss at different frequencies versus the time of heat treatments at 520 °C [14]

The temperature of  $\alpha$ -Fe nucleation is lowered by the Cu addition, i.e. Cu addition acts as “catalytic” centers for the  $\alpha$ -Fe precipitation. *The mechanism is the following:* The essence of phenomenon is the  $\gamma$ -trapping, which is enhanced by the Cu solute atoms. The solute atoms induced  $\gamma$ -trapping is well known phenomenon in the metallurgy of steels [16]. The solubility of Cu in the Austenite phase ( $\gamma$ , fcc) is significant. In contrast, in ferrite (bcc) (especially around room temperature) it is negligible. Below 850 °C, the  $\gamma$ -Fe (Cu) solid solution decomposes into bcc-Fe ( $\alpha$ -Fe) and fcc-Cu, via eutectoid reaction. Hence, the basic phenomenon of  $\alpha$ -Fe (nano-grain) nucleation is the collapse of  $\gamma$  (fcc-like) clusters via eutectoid mechanism.

## 6. The nature and origin of H-trapping sites in Fe-based glasses

As was discussed above,  $\gamma$ -type environments are entrapped during rapid solidification. Such clusters are potential, preferential trapping sites for the H-atoms. These “ $\gamma$ -reminiscences” contribute to the overall H-content during the saturation period.

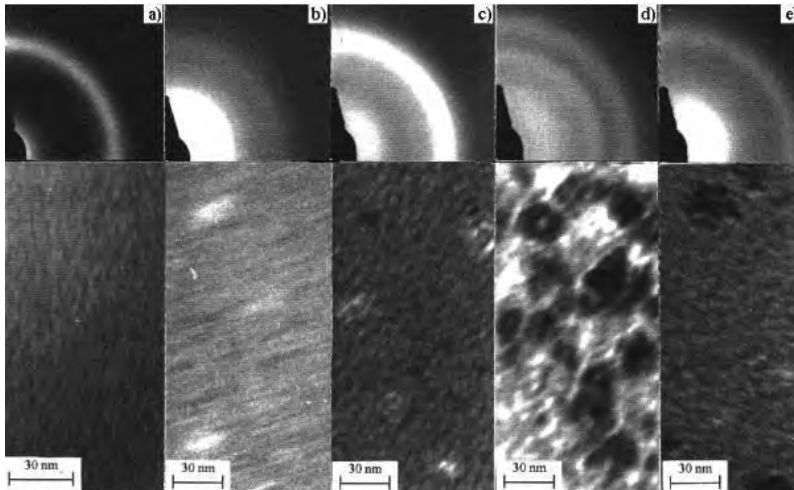
As the bonding between the H-atoms and the surrounding Fe-atoms is weak, spontaneous desorption starts, when the hydrogen saturation is finished (electrolytic H-saturation). The presence of dissolved H atoms and also the time-scale of desorption can be monitored by coercivity measurement, which is known as stress-sensitive magnetic property. Such spontaneous desorption is monitored in Fig.9, indicating also the reversibility of the H-induced stress-level increase.



**Fig.9** The change of coercivity ( $H_c$ ) during hydrogen desorption in Fe85B15 and FeW5B15 and FeV5B15 sample

### 7. H-induced micro-phase separation during exotherm absorption

When the net solution process is exothermal  $\Delta H_{\text{sol}} < 0$ ), micro-phase separation may occur in the glassy matrix [17] which is detectable by electron diffraction. The contrast arises from the neighbouring clusters with different chemical composition. The reason of this H-induced cluster formation is the different chemical affinity of components to hydrogen. The Ni-Zr and the ternary Ni61-XZr33Cux glassy systems are spectacular examples for the H-induced micro-phase separation. The appropriate binary hydride-formation enthalpies are -163kJ/mol, +17kJ/mol and +21 kJ/mol for Zr, Ni and Cu respectively.



**Fig.10** Increasing degree of clusterization (microphase separation) in amorphous state is illustrated, observed during cyclic H-saturation. Enrichment of Cu is detected by SAED (Selected Area Electron Diffraction) [17]



## 8. SUMMARY

Not solely the absence of long range periodicity, but also the CSRO as well as the “medium range order” (cluster formation) is also inherited from the supercooled glass-forming liquids prior to the total freezing at the  $T_g$ .

Intensive cluster formation occurs in the metallic (weak)-glass-former melts. Two cluster-types are developed in the transition metal–metalloid melts: the compound-like clusters ( $\alpha$ -type) represents long-lived structures, with lower atomic mobility inside, and solid-solution-( $\beta$ ) like, in which the atomic mobility is higher.

The driving force within the  $\beta$ -like re-arrangements arise mainly from the competition between fcc-bcc type of local symmetries.

The nucleation phenomenon, leading to nanocrystalline grain-structure, is also explained as the consequence of annihilation of the entrapped  $\gamma$ -centers.

Another type of cluster formation is the consequence of chemical reaction (H-absorption).

This may result in redistribution of metallic components in glassy state due to the preferential interaction of H-atoms with the individual components. (H-induced micro-phase separation).

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### **Summary**

#### **Formation tendency in transition metal based liquids and some related property changes in glassy state**

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The cluster formation tendency in supercooled liquids and the glass forming ability (GFA) are usually discussed independently in the literature [1, 2, 3]. In the present paper we try to connect these phenomena in order to reveal their common origin. In the first part of paper the thermodynamic background of cluster formation will be treated. Subsequently the manifestation in thermal and magnetic properties are discussed. The mechanism of amorphous-nanocrystalline transformation is also explained as cluster phenomena. Finally, some results in the field of H-induced magnetic and structural changes will be reported.