On the Metallurgical Background of Amorphous-Nanocrystalline Transformation

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SUMMARY

The nanometer-sized grain dimension is unexclusive criterion for the achievement of exceptional magnetic softness. The ultra-soft magnetic properties during amorphous phase devitrification can be developed only, if the crystallization takes place via primary reaction. This reaction is inherited from the decomposition mechanism of hypo-eutectic Fe-B glasses. In the present contribution it will be shown, how the sufficient separation of the two-step crystallization stages is attained by suitable alloying in the FINEMET glassy precursor. The micromechanism of the effect of nucleating element (Cu) will also be discussed on the basis of the types of quenched-in defects proposed by Egami.

Keywords: amorphous-nanocrystalline transformation, nucleation mechanism, crystallization mechanism.

1. INDRODUCTION

The reason of great technical significance of the nanocrystalline soft magnetic alloys is their exceptional magnetic softness combined with high saturation magnetization (M_s), as it is illustrated in Fig.1.[1-3]. However, the formation of 10-20 nanometer-sized grain structure leads not necessarily to the evolution of exchange softening predicted by the Herzer criterion[4,5]. Nanocrystalline grain structure can be developed via all kind of reaction (primary, eutectic or polymorphous) in several systems when the temperature of reaction approaches to $T/T_m = 0.5$[6]. (T is the temperature of crystallization, T_m is the melting temperature of the parent alloy) On the contrary, magnetic softness is developed only via primary reaction, provided that the formation of magnetically hard, highly anisotropy intermetallic compounds (borides) can be efficiently suppressed[7].

Phenomenological, the formation of ultrafine grain structure is the result of competition between the rate of nucleation and the grain growth during the amorphous phase devitrification.

Itself the magnetic softness is complex category as it appears as technical demand. For example, the optimization (minimalization of coercive force H_c, power loss or to reach the lowest magnetostriction) cannot be simultaneously fulfilled during the same type of heat treatment in a given alloy. Hence, the procedure directed to the optimization of a given property usually means long-time heat treatments called as "property tailoring", involving complex diffusion processes.

The large scale productibility of precursor glass is also pronounced technical requirement, postulating sufficient glass forming ability. It is found however, that glass forming ability of this multicomponent precursor is lower, than that, for the chemically less complicated FeSiB ternary alloy.
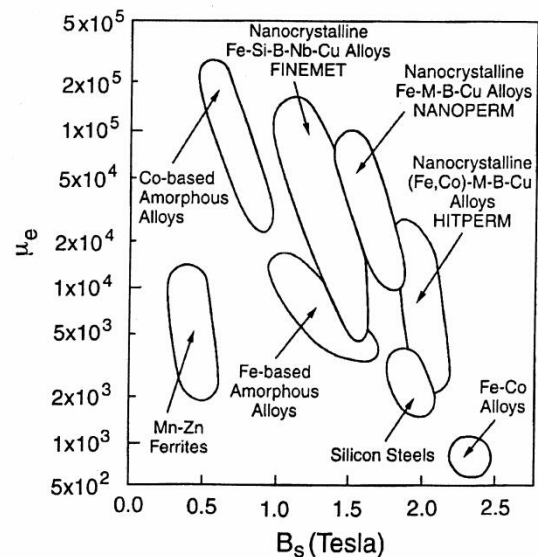
Fig.1. Relation between permeability, μ_e (1 kHz) and saturation polarization for soft magnetic materials (adapted from Ref.[3])

This finding contradicts to the early prediction of glass forming ability GFA ("confusion principle"). The aim of this contribution is to reveal to some aspects of relations between the Glass forming Ability (GFA) and the devitrification mechanism in this type of glassy precursor, showing also the exact role of the each components in the property evolution during the nanocrystalline grain formation and finally, a proposal will be made for the interpretation of nucleation mechanism in which the applied nucleating element(Cu) has an outstanding role. The following topics will be treated:

2. Some aspects of phase selections during the glass formation and glass to-nanocrystalline transformations (comparison of Fe-B and Fe-C system)

3. The significance of primary crystallization in the evolution of magnetic softening
4. The mechanism of nucleation: the role of nucleating element
5. Conclusions

2. SOME ASPECTS OF PHASE SELECTIONS DURING GLASS FORMATION AND GLASS TO NANOCRYSTALLINE TRANSFORMATIONS IN Fe-B(Si,C) SYSTEMS (ANALOGIES BETWEEN GFA AND MARTENSITIC TRANSFORMATION, AND THE RELATED CRYSTALLIZATION SEQUENCES IN Fe-C AND Fe-B SYSTEMS)

During the glass formation the glass transition temperature T_g is approached from supercooled liquid state (from high temperature regime) On the contrary, devitrification takes place by heating the glass (T_g is approached from the glassy state, which can be regarded as hyper cooled liquid.) Special compositional requirements have to be fulfilled in both transformations in order to achieve special phase selections leading either to glassy state or leading to selected crystallization stages among the competing crystalline phases. The change of composition and concentration act on the (GFA) and have a dominant influence on the sequence and reactions during the amorphous state decomposition. In order to reveal the mutual dependence of the related phenomena, the GFA will be compared in the Fe-B and Fe-C systems.

Several criterion exist directed to the judgement of GFA (thermodynamic, kinetics and structural criteria)[8]. According to the thermodynamic criterion, the probability of glassy phase formation depends on the slope of composition-dependent T_o curve, which, for an alloy of composition c, is the temperature at which solid and liquid each of composition c have the same free energy. So it is the maximum solid-liquid interface temperature at which the partition coefficient k_o related to the stability region of solid solution as it is illustrated in Figs.2. a and b. In the case of Fig.2. a, appreciable solid solubility exists (common point T_o and stability area of the crystalline solid α phase). In this case the formation of crystalline solid solution via solute trapping is preferred. On the contrary, if T_o varies steeply without common point with the region of α-solid solution, the glass formation is thermodynamically feasible [9].

The outlined alternatives are in agreement with the prediction of structural and kinetic criteria, i.e. the existence of deep eutectics, which is often applied for the explanation of GFA in Transition Metal Metalloid (TM-M) liquids around the eutectic concentration. Though the different GFA of Fe-C and Fe-B system cannot be understood solely on the basis of this criteria. [10,11]. The GFA is high in Fe-B because of the absence of extended solubility of B in **γ-Fe** (T_o varies steeply) and, GFA is poor in Fe-C, because of the extended solubility region of C in **γ-Fe**. (crystalline phase is stable at high temperature so it forms preferentially via few elementary diffusion step of C in the supercooled liquid).

There are strong phenomenological and kinetic similarities between glass transition and martensitic transformation in carbon steels when the nature of phase selections and the micromechanism of both transformations are compared.

The common features are:

-Both of the transformations occur during the rapid cooling of the parent phases. In addition, the supersaturation effect plays an important role in the characteristics and concentration dependence of these transformations.
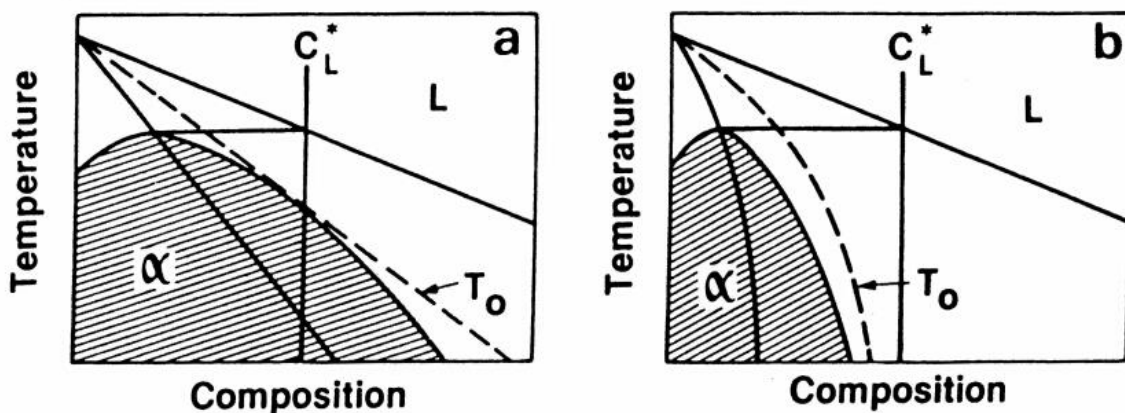
Fig.2. Different variation of T_0 with composition. In (a) and (b) shaded regions show possible solid compositions which can form from liquid of composition C^*_L at various interface temperatures.(adapted from Ref. [9])

-Owing to the high kinetic undercooling (rapid heat extraction) the diffusive transformations are suppressed in both processes.
-Both processes are athermal, taking place within a definite temperature range. The resulting microstructure and physical properties are sensitive function of the applied cooling rate.
-The transformations can be observed within a wide range of metalloid content.
-Shear phenomena plays an important role in the formation of resulting microstructure, though the dimension of highly deformed (sheared) regions is only 1-2 nanometer in glass (which is the typical dimension of medium range order)
-The necessary critical cooling rate for the avoidance the diffusive phase transformation increases rapidly in the hypo-eutectic (hypo-eutectoid) concentration range.
-The existence of primary reactions as the first step during the decomposition of the glass or prior to the co-operative grain growth in austenite decomposition directly indicates the decreasing GFA or the decreasing martensite formation tendencies in the appropriate systems.

3. THE SIGNIFICANCE OF PRIMARY CRYSTALLIZATION IN THE EVOLUTION OF MAGNETIC SOFTENING

As a consequence of large undercooling, the compositional range over which the eutectic (co-operative) crystal growth can occur is often large, as it has been observed during the decomposition of several TM-M glassy systems[12]. In order to ensure the formation of primary **α-Fe** the two step crystallization is inevitable. The formation of α-**Fe** grains via primary reaction is inherited from the hypo-eutectic Fe-B alloys according to the basic scheme[13]

I. : $am_1 ->$ **bcc Fe** $+ am_2$
II. $am_2 -> Fe_3B$
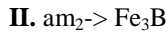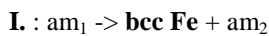
Reaction **II.** should be avoided in order to ensure the magnetic softness. The perfect separation of crystallization stages is possible at very low Boron content only, at which the GFA is extremely poor.

For example, the GFA in the case hypo-eutectic $Fe_{85}B_{15}$ is still satisfactory. Fig 3. shows that (according to the hypo-eutectic concentration) crystallization takes place in two step. Unfortunately the crystallization steps partially overlapped, so the alloy (at this concentration) is not suitable for the fulfilment of complete peak separation. Consequently, additional modification have to apply in the composition using various additives. The purpose of additives is the complete the separation of crystallization steps simultaneously ensuring the
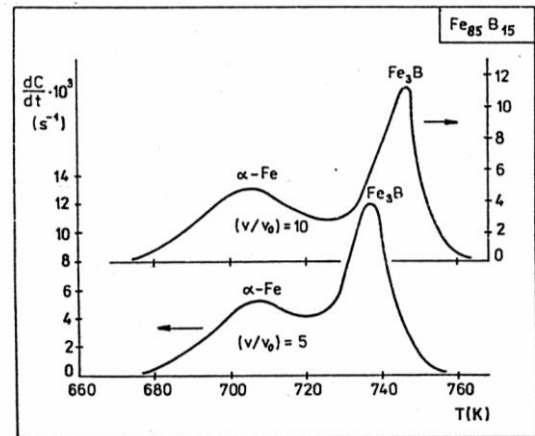
Fig.3. DSC traces obtained by heating $Fe_{85}B_{15}$ hypo-eutectic glasses. There is a slight overlapping between the two crystallization exotherms at this concentration. In addition, the degree of overlapping also depends on the cooling rate applied during the liquid quench.

sufficient GFA. The glass forming ability can be increased significantly by Si addition, approaching the overall metalloid content around to 20 at. % [14]. There is a significant peak overlap without Nb and Cu addition however [7]. The simultaneous suppression of the temperature of primary crystallization, and the increase of crystallization temperature of reaction **II.** (compound precipitation) is possible by the addition of Cu or Nb to the FeSiB basic alloy. The resulting sufficient peak separation enables us to carry out long time heat treatments, causing final concentration distribution between the nanograins and the connecting intergranual amorphous shell [7], as the Fig. 4. shows.

In this Fig. the DSC traces are plotted for $FeCu_1Nb_xSi_{13.5}B_9$ precursor alloys versus the Nb content in order to demonstrate the increasing peak separation corresponding to the precipitation of α - Fe (T_1) and T_2 (crystallization of intermetallic compound). It is clear that there is only a very narrow gap between the two peaks without Cu and Nb additions. If 1 at. % Cu is added, T_1 is lowered, showing clearly the influence of nucleating element. Simultaneously, the T_2 is gradually increases by further addition of Nb, but the peak separation is nearly unchanged as the Nb content increases. It is interesting to note, that with the increasing Nb concentration T_1 also shifts to higher temperatures (slight increase) so the stability of glassy state is the same as in the ternary glass, the only difference is the efficient peak separation due to the additives.
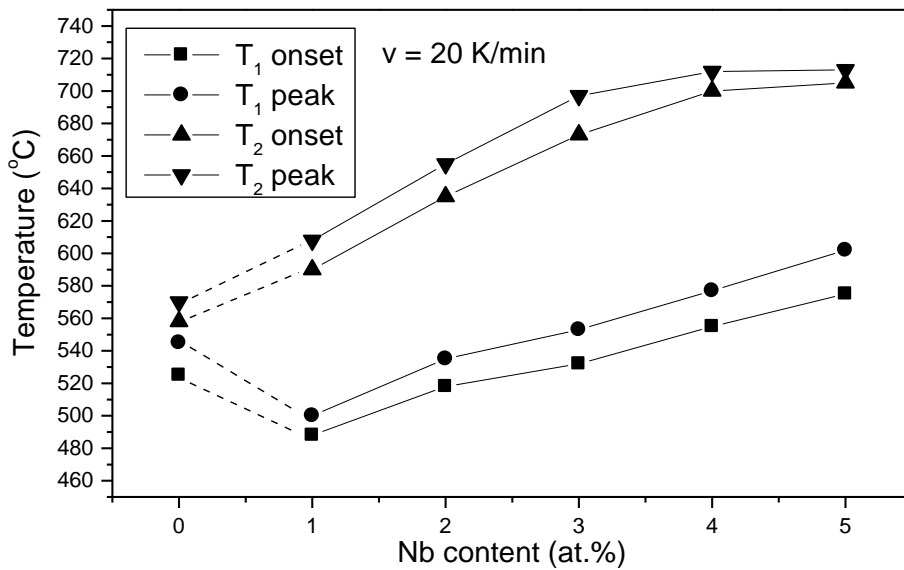
Fig.4. The increasing DSC peak separation due to the addition of Cu and NB in Feb precursor as a function of NB content [15].

4. THE MECHANISM OF NUCLEATION (THE ROLE OF NUCLEATING ELEMENT)

The central problem in the interpretation of nucleation mechanism is, how the nucleating element act producing homogeneously distributed nucleation sites for the α-Fe precipitation. In fact, the essence of the role of nucleating element is the depression of crystallization temperature of reaction I. (bcc-Fe formation) satisfying the separation of reactions. The problem is, that Cu-rich clusters can be found separately from the nanograins as the growth proceeds, so the copper is enriched beyond the nanograins after the nanograin nucleation. It means, that no kind of "epitaxial" mechanism can be imagine in the nucleation process [16]. It is general experience, that the nucleation itself starts well below the observed crystallization temperature [17]. The original interpretation of nucleation mechanism is based on the segregation tendency of Cu in Fe. The nucleation model proposed in [18,19] is based on the observation of nuclei at the very early stage of crystallization. They found, that Cu clusters with nearly fcc symmetry form very early during the heat treatments. The essence of their arguments is the existence of quenched-in clusters which can be found even in as-quenched precursors. All of the cited interpretations are ex-post-facto arguments however, giving no real proposal on the nucleation mechanism.

The starting point of our argument is the co-existence of p-type and n-type defects (compressed and stretched regions) in the as-quenched precursor glass, which are denser or less compact than the average density of the liquid-quenched glass, as it was proposed by [21]. The local composition and bonding state in the "defects" are inherited from the hypo-eutectic Fe-B glass. The mutual annihilation of defects has started already during the irreversible structural relaxation, well below the observed crystallization temperature.[22].The defects can be specified structurally also as "phase reminiscences", which are formed during the liquid quench. The stressed (dense) centres are the reminiscence to the **fcc-Fe** phase. They are responsible for the nucleation step of primary crystallization (reaction **I.**) The activation energy of this nucleation is influenced primarily by the stabilisation or destabilisation tendencies of these centres caused by the alloying elements being present in the melt (and in the resulting glass) ensuring the sufficient GFA. The mechanism of this interaction is governed by two tendencies:

-preferential solubility of alloying elements either in **fcc** or in **bcc-Fe,**

-affinity between Boron and the metallic additives (similarly to the nature of interaction between Carbon and metallic additives in steels)

Based on these tendencies we are in the position to describe the mechanism of nucleation enhanced by the Cu nucleating element. The essence is the enhancement of the collapsing of fcc centres, i.e. causing their local transformation to α-Fe nuclei with **bcc** structure. As the Cu has preferential solubility in **fcc-Fe**, it will be enriched in the γ-like clusters. This tendency is obvious from the equilibrium Fe-Cu phase diagram, shown in Fig.5. The extended solubility of Cu both in δ and γ phase is 5-6 at. % in a wide temperature range. The γ phase
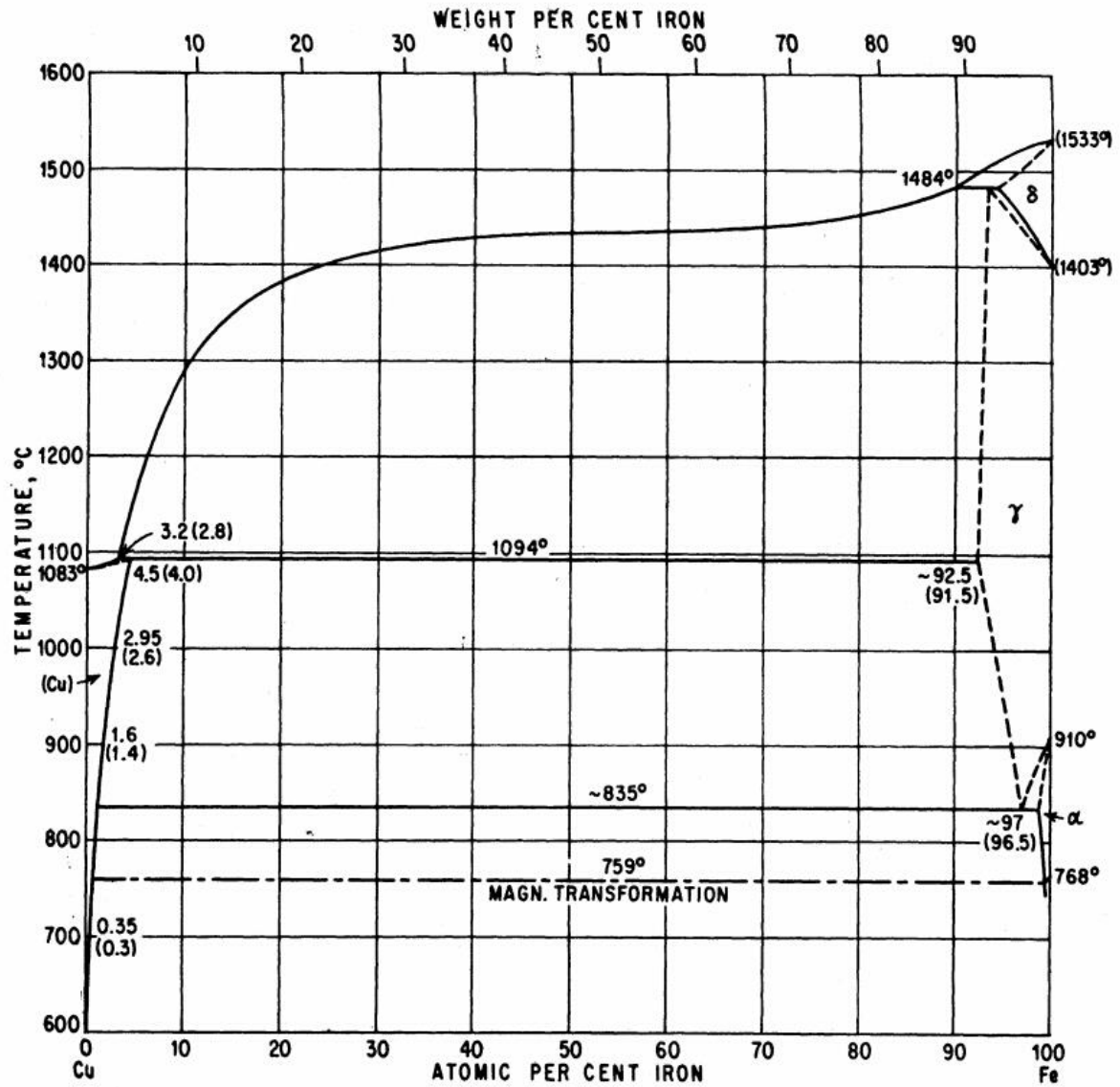
Fig. 337. Cu-Fe

Fig.5. Cu-Fe binary phase diagram, showing the extended solubility of Cu in Fe-rich side in γ-phase[20]

is stabilised by Cu addition beyond 835°C. This solid solution decompose at this temperature via eutectoidal transformation. Consequently, the local chemical composition and the 'dense' character of the quenched-in, fcc like (compressed) centres is dominated by the Cu enrichment, together with the simultaneous suppression of dissolved boron-content in these environments. The basic crystallization reactions are the same in the glass devitrification or in phase transformations between crystalline phases [12]. One can suppose on this basis, that the nuclei formation is essentially eutectoidal, during which Cu rich clusters together with neighbouring **bcc-Fe** rich crystalline embryos are formed in agreement with the observation [18,19]. However, a local dilatation is required, for the formation of crystalline **bcc-type** embryos from **fcc-like** centres, which is considered to be responsible for the energetic barriers of α-Fe nuclei. Due to the easy diffusion of Cu in Fe (low activation energy) this rearrangement will be enhanced. As the Cu atoms diffuse out from the entrapped environments, the bcc nucleation sites are easily developed by the collapsing of this centres.

5. CONCLUSION

1.The phase selections and phase competitions do play important role in the suppression of crystalline phase formation during production of glassy precursors. During the formation of nanocrystalline composite, only the suppression of co-operative crystal growth is needed.

2. The primary crystallization of α–Fe(Si) from the glassy precursor is inherited from the hypo-eutectic crystallization mechanism found in the binary Fe-B glassy system. The sufficient GFA and the separation of crystallization stages have to be ensured simultaneously by the addition of Si, Nb and Cu nucleating element to the hypo-eutectic Fe-B alloy.

3. The mechanism of nucleation can be interpreted as a local eutectoidal reaction, using the basic concept of quenched-in defect types proposed by Egami. The basis of nucleation enhancement is the entrapped of Cu-atoms in the fcc (dense) centres. These centres do collapse easily after the Cu segregation, which takes place already at low temperatures due to the low activation energy of Cu diffusion in Fe.

Acknowledgements

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